CONGRESSO LATINO-AMERICANO DE CROMATOGRAFIA E TÉCNICAS RELACIONADAS

Campos do Jordão, Brasil

28-31, Outubro 2025

COLACRO XX (2025)

LIVRO DE RESUMOS

BOOK OF ABSTRACTS

COLACRO XX
28 – 31, Out, 2025

Agradecemos a todos os congressistas que enviaram e apresentaram seus trabalhos durante o evento, viabilizando conversas produtivas e intercâmbio de informações que, potencialmente, formarão grandes parcerias futuras em desenvolvimento científico, ampliando a importância de **Cromatografia** e técnicas a ela relacionadas pelo Brasil e outros locais do mundo.

O presente documento engloba os trabalhos aceitos pelo Comitê Científico do COLACRO XX (2025) após avaliação, considerados relevantes para apresentação durante o evento na forma de poster, gerando discussão e interação entre autores e congressistas em geral.

Os autores dos trabalhos são responsáveis pela veracidade e acurácia do conteúdo de seus trabalhos.

We would like to thank all participants who shared their research during the event. Your contributions facilitated productive discussions and the exchange of ideas that may lead to great future partnerships, highlighting the importance of Chromatography and related techniques in Brazil and globally.

This document contains the submissions accepted by the COLACRO XX (2025) Scientific Committee. Each abstract was evaluated and selected for poster presentation, creating opportunities for engagement between authors and the general audience.

The authors are responsible for the truthfulness and accuracy of their respective contributions.

Agradecemos às empresas que participaram do evento com patrocínio e/ou exposição de equipamentos, transformando a Exposição uma área de interação e negócios.

Patrocinador/Expositor DIAMANTE:

analitica

Patrocinadores/Expositores PRATA:

Agilent
Trusted Answers

Waters™

Expositores:

ALLCROM 35 Anos
A Ciência em Benefício de Todos®

BÜCHI

Chromastore

JASCO

LECO
EMPOWERING RESULTS

MERCK

PRÓ-ANÁLISE 30 anos

SCIEX
The power of precision

SHIMADZU
Excellence in Science

TECNAL®
EQUIPAMENTOS CIENTÍFICOS

Agradecemos aos apoiadores do evento que viabilizaram a ida de diversos congressistas de todas as regiões do Brasil, abrilhantando o conteúdo de palestras, posters e discussões científicas, tornando o COLACRO XX (2025) um sucesso.

INCT-ALIM

CNPq

USP

MINISTÉRIO DA AGRICULTURA E PECUÁRIA

GOVERNO FEDERAL

BRASIL

UNIÃO E RECONSTRUÇÃO

CROMA

WARPA

WORKSHOP EM AVANÇOS RECENTES NO PREPARO DE AMOSTRAS

CAMPOS DO JORDÃO E REGIÃO
Convention & Visitors Bureau

A MICRO-QuEChERS AND GC-MS METHOD FOR THE DETERMINATION OF PAHs IN YERBA MATE SAMPLES

Julia Bitencourt da Cunha*, Gabriel França Borges, Paula de Souza Garcia, Maria Luiza Soares Trindade, Sergiane Caldas Barbosa, Ednei Gilberto Primel, Jean Lucas de Oliveira Arias

Universidade Federal do Rio Grande - FURG, Laboratório de Análise de Compostos Orgânicos e Metais - LACOM, Rio Grande, Rio Grande do Sul, Brazil, 96203-900

* Corresponding author: juliabdacunha20@gmail.com

Yerba mate (Ilex paraguariensis) is a plant rich in caffeine, theobromine, vitamins, and antioxidants, with stimulating and diuretic properties. While known for its beneficial properties, the yerba mate also holds significant cultural and economic importance in southern Brazil, Argentina, Paraguay, and Uruguay. The contamination of yerba mate by Polycyclic Aromatic Hydrocarbons (PAHs) is a concern, since these compounds, formed during the plant's drying process, are toxic and potentially carcinogenic. The association between yerba mate consumption and cancer risk has been attributed to the presence of PAHs in the beverage, as reported in several studies, which highlights the need for the continuous evaluation of these compounds in the beverage. Thus, this study aimed at the development of an analytical method using the Micro-QuEChERS for the extraction of PAHs and determination by Gas Chromatography with Mass Spectrometry (GC-MS). The work highlights that the choice of yerba mate as the study matrix is justified by its wide consumption in the Southern region of Brazil and its susceptibility to contamination by PAHs during the drying process. The determination of PAHs was carried out in a Shimadzu GCMS-QP2010 Plus, using a ZB-5MS analytical column, with conditions adapted from the work of Escarrone et al. 2014. Firstly, the QuEChERS method was evaluated in its original, acetate and citrate versions, by means of accuracy and precision. It was observed that the QuEChERS method presents similar performance in the extraction of PAHs from yerba mate samples. Thus, the original version was selected due to its simplicity and lower use of reagents. After selecting the original version, it was properly miniaturized, by reducing the amounts of sample, acetonitrile and the partition salts. Similar behavior was obtained between the regular version and the miniaturized version of the original QuEChERS. Finally, the clean-up step was assessed, by evaluating different sorbents: PSA, chitin, chitosan, activated carbon and reused C18. Although the activated carbon was efficient in the removal of pigments from the extract, it also removed the PAHs, being inappropriate for analytical purposes. Thus, the reused C18 was selected since it provided higher recovery rates and promotes the use of a residue, being an advantage from the sustainability point of view. Finally, the project employs the Micro-QuEChERS method, which is advantageous for being low-cost, using a low volume of solvent, having easy applicability, and being versatile. The validated method will be further applied to the determination of PAHs from samples marketed in the Southern Brazil and from other countries with high consumption of yerba mate.

Acknowledgements: The authors acknowledge the scholarships provided by FURG and CNPq and the financial support provided by CNPq, FAPERGS, CAPES and FINEP.

A NOVEL HIGH-THROUGHPUT METHOD FOR ACRYLAMIDE DETERMINATION IN POTATO CHIPS BY HIGH-PERFORMANCE THIN-LAYER CHROMATOGRAPHY COUPLED TO FLUORESCENCE AND MASS SPECTROMETRY DETECTION

Lina Patiño-Arias[1], Joaquín Fernández-Martínez[1], Beatriz Rodríguez[1], María Salome Mariotti-Celis[2], Karem Henriquez-Aedo[3], Mario Aranda*[1]

[1]Pontificia Universidad Católica de Chile
[2]Universidad Finis Terrae
[3]Universidad del Bio Bio

* Corresponding author: mario.aranda@uc.cl

Acrylamide (AA) is a probable human carcinogen present in several highly consumed starchy foods like potato chips. Due to the lack of important chromophore groups in its chemical structure, it is generally derivatized to be detected by ultraviolet (UV) or fluorescence (FL). The objective of this work was to develop a novel high-throughput high-performance thin-layer chromatography method to determine AA in starchy foods using the fluorescent probe 7-mercapto-4-methylcoumarin (7M4MC). The main derivatization factors for AA and N,N-Dimethylacrylamide (DMAA, internal standard) were optimized using a Face-centered Central Composite Design, establishing the following optimal conditions: temperature (50°C), time (10 min), and catalyst concentration (0.5 mmol/L of 4-dimethylaminopyridine). Chromatography was carried out on silica gel 60 F254 HPTLC plates using a mobile phase composed of dichloromethane, acetic acid, and acetone (94.5: 3.9: 1.6 v/v/v). The analytical method was validated according to the International Conference on Harmonization (ICH) guidelines. Analytical response in the range from 5 to 400 ng/band showed an R2>0.998. Repeatability and intermediate precision showed RSD values lower than 7% and 5%, respectively, mean recovery was 74.43±5.83% (RSD

Acknowledgements: Thanks to FONDECYT N° 1251474 and 1251584; ANID Nº 21210061; Academy Installation Grant Nº 85220091 and FONDEQUIP EQY220018 and EQM210203

A VOLATILE PROFILE OF EDIBLE FILMS BASED ON OKRA MUCILAGE AND STARCH ENRICHED WITH LIQUID SMOKE BY GC-MS

Nayanne Lima dos Santos Ferreira*, Antonia Carlota de Souza Lima, Joaquim Rodrigues de Vasconcelos Neto, Luana Kelly Sampaio Facundo, Amélia Ruth Nascimento Lima, Elisabeth Mariano Batista, Ronaldo Ferreira do Nascimento, Crisiana de Andrade Nobre, Luciana de Siqueira Oliveira

Federal University of Ceará - UFC

* Corresponding author: nayannelimas@gmail.com

The search for sustainable and active packaging has encouraged the development of edible films from biopolymers, such as okra mucilage combined with starch. To add functionality, the incorporation of natural additives like liquid smoke—rich in phenolic compounds with antioxidant and antimicrobial properties—is a promising strategy. This work aimed to characterize the volatile compound profile of edible films based on okra mucilage and corn starch enriched with different concentrations of liquid smoke (0%, 1%, 2%, and 3%) using Gas Chromatography coupled with Mass Spectrometry (GC-MS). The films were produced by the casting method, where a film-forming solution containing starch, okra mucilage, and glycerol was prepared, heated to 60°C, and subsequently incorporated with liquid smoke according to the treatment. The solutions were spread on glass plates and dried at room temperature. The analysis of volatiles was performed by Headspace Solid-Phase Microextraction (HS-SPME) using a DVB/CAR/PDMS fiber. Both the pure liquid smoke and the films were heated to 60°C for volatile release, which were subsequently analyzed by GC-MS on a DB-5 column with a temperature program from 40 to 270°C. The analysis of the liquid smoke revealed a characteristic profile, with compounds such as guaiacol, creosol, syringol, 4-ethylguaiacol, and furfural. In the edible films, the detection of these compounds was directly influenced by the addition of liquid smoke. The control film (0%) showed only traces of phenols, while the films with liquid smoke (1 to 3%) exhibited a more intense and diverse presence of smoking markers. Syringol and phenol were identified in all enriched treatments, while creosol and 4-ethylguaiacol were detected from the 1% concentration. The absence of furfural in the films suggests its volatilization or degradation during processing. The results demonstrate that the polymeric matrix of starch and okra mucilage was effective in retaining the main volatiles from the liquid smoke, with a correlation between the addition of the ingredient and the identified smoked compounds. The incorporation of liquid smoke was efficient in conferring the volatile compounds to the films, indicating their potential for application as active packaging.

Acknowledgements: National Institute of Food Science and Technology (INCT-ALIM); Federal University of Ceara - (UFC).

ACELERANDO A DESCOBERTA DE FÁRMACOS: DETERMINAÇÃO DE PROPRIEDADES ADME DIRETIVAS A PARTIR DE DADOS DE RETENÇÃO POR LC-MS

Larissa Gaiola*, Carlos Alberto Montanari

Grupo de Química Medicinal e Biológica (NEQUIMED – IQSC/USP)

* Corresponding author: larissagaiola@usp.br

A busca por novas substâncias bioativas com propriedades farmacocinéticas otimizadas visa garantir que essas moléculas atravessem barreiras biológicas, alcancem seus alvos em concentrações eficazes e mantenham atividade por tempo suficiente para exercer o efeito terapêutico desejado. Parâmetros físico-químicos como lipofilia, solubilidade e permeabilidade são fundamentais na estimativa da absorção oral, e embora existam protocolos consolidados por agências regulatórias para sua determinação, a aplicação sistemática desses métodos a compostos inéditos ainda representa um desafio, sobretudo pela ausência de dados para diversas classes químicas. Neste trabalho, investigaram-se dois peptidomiméticos inéditos da classe dos dipeptídeos, sintetizados pelo grupo NEQUIMED (IQSC/USP), visando à caracterização comparativa de seus perfis farmacocinéticos por meio de abordagens cromatográficas. As moléculas diferem por variações estruturais mínimas, estrategicamente planejadas para avaliar o impacto sobre propriedades críticas à biodisponibilidade. O método cromatográfico foi ajustado conforme o parâmetro avaliado. Para estimativa do índice de retenção cromatográfica, ligado a lipofilia (log Kw), foi utilizada uma coluna biomimética à base de fosfolipídeos com detecção por DAD. Já os ensaios de solubilidade (log S) e permeabilidade aparente (PappCaco-2) empregaram coluna C18, com detecção por DAD e LC-MS/MS em modo MRM, respectivamente. Os dados obtidos revelaram que, apesar da lipofilia elevada (log Kw > 2) e da solubilidade limitada (log S > –2), ambos os compostos apresentam permeabilidade passiva elevada (PappCaco-2 > 10 x 10^{-6} cm s^{-1}), indicando alto potencial de absorção intestinal e provável categorização como BCS Classes II. A estratégia adotada permitiu identificar perfis promissores em compostos inéditos de mesma classe química, destacando a cromatografia como ferramenta útil na seleção de candidatos bioativos com propriedades farmacocinéticas adequadas, alinhada aos critérios preconizados no desenvolvimento de fármacos.

Acknowledgements: FAPESP (#2022/01393-5), CAPES, CNPq, Grupo BioMicS (IQSC/USP) e Grupo de Química Inorgânica e Analítica (IQSC/USP).

Addressing Analytical Challenges in Food and Beverage Testing with Tailored, Automated Solutions

Matthew Edwards[1], Rachael Szafnauer[2], Khaled Murtada[1], Jonathan Grandy[1]

[1]Markes International and SepSolve Analytical, 826 King St N, Unit 15, Waterloo, N2J 4G8, Canada
[2]Markes International, 1000B Central Park, Western Avenue, Bridgend, CF31 3RT, UK

Food and beverage products present significant analytical challenges due to their chemically complex matrices and the occurrence of both volatile and non-volatile compounds that define flavour, aroma, and quality. Detecting trace-level analytes, especially those contributing to subtle sensory characteristics or potential contaminants, requires more than conventional instrumentation can offer. Manual sample preparation adds variability and slows throughput, while traditional methods often lack the sensitivity and resolution needed for confident analysis.

To address these demands, Markes' Centri offers a personalised, modular approach to sample preparation and analysis, designed to adapt to diverse workflows and sample types. Centri combines best-in-class PAL3 robotic automation (CTC Analytics) with world-leading cryogen-free analyte refocusing. This powerful combination minimises manual intervention while maximising reproducibility and sensitivity. Advanced analyte enrichment technologies, such as immersive HiSorb, high-capacity sorptive extraction, enable broad compound coverage from even the most demanding matrices in a single run, revealing data that conventional methods may miss. Moreover, seamless integration of an olfactory detection port (ODP) further allows sensory characteristic analysis via gas-chromatography-olfactometry (GC-O), enabling correlations between the chemical data and human sensory perception – critical for flavour and aroma analysis.

These solutions are fully compatible with advanced separation and detection techniques, including comprehensive two-dimensional gas chromatography (GC x GC) and mass spectrometry (MS). This results in high-resolution, information-rich data of such complex samples, allowing analysts to gain a better understanding to support more informed decision-making throughout product development, manufacturing and quality control stages.

Together, these innovations empower analysts to meet regulatory standards, ensure product consistency, and uncover deeper insights into food and beverage composition with greater confidence and efficiency.

ADSORPTION OF L-ASPARAGINASE IN CRYOGELS FUNCTIONALIZED WITH NIACINAMIDE

Dayana Teixeira Botelho, Daniele do Carmo Costa*, Giovanni Aleixo Batista, Lizzy Ayra Alcântara Veríssimo*

Universidade Federal de Lavras

* Corresponding author: daniele.costa4@estudante.ufla.br

L-asparaginase (EC 3.5.1.1) is an enzyme of great interest to the food industry due to its ability to reduce the formation of acrylamide, a potentially carcinogenic compound produced during the heating of foods containing high levels of asparagine and carbohydrates. However, the purification and stability of this enzyme still pose challenges, particularly from an economic standpoint. The objective of this study was to develop a niacinamide-functionalized cryogel (cryo-VitB3) for the purification of fungal L-asparaginase. L-asparaginase was produced by solid-state fermentation (25 °C for 120 h) using 10 g of ora-pro-nobis fiber (Pereskia aculeata Miller), 10 mL of Khanna salt solution, 3 g of L-asparagine, and 10 mL of Aspergillus caespitosus spore suspension (10^7 spores/mL). The cryogels were synthesized at –12 °C for 24 h and functionalized via the epoxy method with niacinamide as the ion-exchange ligand. Adsorption tests were performed in batches using sodium phosphate buffer at different ionic strengths (0.0125 mol/L, 0.050 mol/L, and 0.100 mol/L) and pH values (3.0, 5.0, and 8.0). The total protein content was determined by the Bradford method, while enzymatic activity was evaluated using Nessler's reagent. One unit of enzymatic activity (U) was defined as the amount of enzyme required to release 1 µmol of ammonia per minute under standard assay conditions. The results were analyzed by Analysis of Variance (ANOVA), and the means were compared using Tukey's test at a 5% significance level. Significant differences ($p < 0.05$) were observed between the conditions applied in the protein adsorption process, with higher adsorption capacities (q, mg/g) obtained when using buffers with lower ionic strengths (0.0125 mol/L and 0.050 mol/L). The highest adsorption was observed at a concentration of 0.050 mol/L and pH 5.0 (q = 36.81 mg/g ± 2.30 mg/g), while the highest enzymatic adsorption capacity (qatv, U/mg) was observed under conditions of 0.0125 mol/L (66,038 U/mg ± 18,790 U/mg) and 0.100 mol/L (58,810 U/mg ± 18,597 U/mg), both at pH 5.0. It is likely that at this pH, the proteins and the adsorbent carried opposite surface charges, favoring adsorption by ion exchange. Overall, the results indicate that cryo-VitB3 is a promising preparative material for the purification of L-asparaginase from crude fermented extract.

Acknowledgements: FAPEMIG (APQ-00795-22) and CNPq (408779/2023-3).

AFFINITY SELECTION MASS SPECTROMETRY FOR IDENTIFICATION OF ACETYLCHOLINESTERASE LIGANDS IN STRYCHNOS SUBCORDATA

Fernando Cassas[1], Rebeca S França[1], Felipe MA da Silva[1], Quezia B Cass*[2]

[1]Universidade Federal do Amazonas
[2]Universidade Federal de São Carlos

* Corresponding author: qcass@ufscar.br

Affinity selection mass spectrometry (AS-MS) is a strategy for screening novel drug candidates. In this study, the technique was applied to identify ligands for acetylcholinesterase (AChE) from the aqueous extract of Strychnos subcordata Spruce ex Benth, an Amazon-endemic species traditionally used as a paralytic agent. The optimal gradient and stationary phase were first determined using a scouting protocol using four orthogonal columns based on their Fs values. The optimized method was subsequently applied in a high-resolution mass spectrometer (HRMS) for metabolite annotation by acquiring MS^2 spectra, which were compared against public databases, an internal database and in silico tools. For the AS-MS assay, 200 µg of eelAChE was immobilized on 10 mg of γ-Fe-amino-functionalized magnetic beads through Schiff's base using glutaraldehyde as the linker. Control samples were prepared under identical conditions, with enzyme inactivation achieved using 100% MeOH (60 min). Choline formation was monitored to assess enzymatic activity. The assay was conducted in four stages: incubation, separation, ligand dissociation, and ligand identification. Ligand identification was performed based on the ratio of mean peak areas for each ion between control (inactive) and experimental (active) groups, after normalization and alignment using MzMine software. The experiment was conducted in triplicate to calculate the affinity ratio (AR). In the scouting protocol, the ACQUITY® UPLC HSS T3 column was selected, and the gradient parameters (ΔB; tG) optimized to 10–30% and 16 min (ACN:HOH with 0.1% formic acid; flow rate 300 $\mu L \cdot min^{-1}$; STP conditions). Through HRMS data processing, 22 alkaloids, 17 glycosylated flavonoids, 5 benzoic acid derivatives, and 3 terpenoids were annotated. From the AS-MS assay, 232 ions were evaluated, among these, 17 ions displayed AR > 1.2 and were therefore considered ligands. The assay also revealed metabolites not identified in the dereplication approach due to their lower ionization or concentration. Moreover, the flavonoids showed AR

Acknowledgements: Acknowledgements: FAPESP (2023/15815-1; 2014/50244-6), CNPq (302464/2022-0; 172986/2023-0; 315040/2021-1) and CAPESP (Finance Code 001)

AFLATOXIN EXTRACTION FROM RICE BRAN PROTEIN CONCENTRATE: ADAPTATIONS OF THE QuEChERS METHOD FOR PROTEIN MATRIX

Caroline Senna, Marianna Veiga da Cruz, Manoelly Raquel Chaves, Larine Kupski*, Eliana Badiale Furlong

FURG

* Corresponding author: larinekupski@gmail.com

Quantifying aflatoxins in protein concentrates is a moderate challenge due to the complexity of the matrix, hindering the performance of the QuEChERS method, which is widely used for these contaminants in various food matrices. The lignocellulose-protein network has hydrophilic and hydrophobic groups that represent many possibilities for the formation of relatively stable interactions between the matrix and aflatoxins. To recover them, adaptations are necessary in the extraction and sample cleanup steps to minimize underestimation of detected mycotoxin levels. This study evaluated the QuEChERS method for the recovery of aflatoxins (AFB1, AFB2, AFG1, and AFG2) in defatted rice bran protein concentrate (DRBPC), with aflatoxin recovery as an indicator of efficiency. The extraction step of the method was modified, with adjustments in the proportion of acetonitrile (MeCN), acidification, partition salts ($MgSO_4$ and NaCl), and cleaning agents ($MgSO_4$, PSA, and C18). The dry residue was resuspended in 1 mL of the water:MeCN:methanol mixture (62:14:24, v/v/v) and quantified by HPLC-FL with a post-column photoderivatizer. Given the absence of protocols described in the literature for this matrix, different assays were performed. Assay 1 was performed using 1.2 g $MgSO_4$ and 0.3 g NaCl in the partition and 220 mg $MgSO_4$, 110 mg PSA, and 110 mg C18 in the clean-up and showed low recoveries for AFB1 (69%) and AFB2 (42%), in addition to high variability and recovery above 120% for AFG2, suggesting insufficient clean-up. Assay 2, with a higher proportion of partition salts (4 g MgSO4 + 1 g NaCl) and a greater amount of salts in the clean-up step (750 mg MgSO4 + 375 mg PSA), showed consistent recoveries for AFB1 (95%), AFG1 (94%), and AFG2 (109%), and low recovery for AFB2 (48%), with good reproducibility. Assay 3, with acidified MeCN (1% acetic acid) and the same proportions of partition salts and clean-up as assay 2, did not increase the recovery of AFB2 (44%) and compromised AFB1 (198%), evidencing inefficiency in the removal of interferents. The adaptations made in assay 2 promoted the best recoveries for aflatoxins, with the exception of AFB2. The values found were lower than the limits recommended by current legislation (70-120%) for AFB2. To reduce the effect of potentially hydrophobic interactions with the protein network, the composition of the extracting solvent and salt ratio are being evaluated. The facts confirm that even established methods for mycotoxin determination require specific validation for each type of matrix, since mycotoxins are formed by fungal metabolism using their components as substrates.

Acknowledgements: The authors thank for support and infrastructure of Federal University of Rio Grande (FURG) and development agencies for financing (CAPES, FAPERGS, and CNPq).

ALLYING HPLC AND MULTIVARIATE DATA ANALYSIS TO DISCRIMINATE HUMULUS LUPULUS L. BY THEIR COMERCIAL VARIATES APPLICATIONS

Bernardo Cardeal Darzé*[1], Débora Nascimento Eiriz[1], Natália Martins Libório[1], Licarion Pinto[2], Lucas Mattos Duarte[1]

[1]Institute of Chemistry, Fluminense Federal University
[2]Institute of Chemistry, Rio de Janeiro State University

* Corresponding author: bdarze@id.uff.br

In the brewing industry, hops (Humulus lupulus L.) represent one of the most important raw materials due to its wide range of chemical composition. Hops serve two main purposes in the beer making process: defining beverage bitterness and flavor. The standard method for quantifying the α-acids (humulones), responsible for the bitterness level, is mainly high-performance liquid chromatography (HPLC) coupled with different detectors. This study aims to combine the HPLC technique with chemometrical tools, attempting to distinguish the bittering capability of the raw material in a faster and qualitative way, reducing time and cost associated with the analysis. For this initial study, 14 varieties of hop pellets were bought and analyzed by HPLC-DAD in triplicate. A methanolic extract was analyzed in a HPLC-DAD, using a Thermo Accucore Phenyl-Hexyl column. The bitter acids separation was achieved using a binary mixture of 0.25% HCOOH in H2O (A) and 0.25% HCOOH in ACN (B). For detection, absorbance was measured at 330 nm. The collected data was initially studied using a series of preprocessing and transformation techniques that aimed to maximize the effectiveness of separation between the samples analyzed. Approaches that ranged from a simple autoscaling or mean centering to peak alignment (e.g. icoshift and PTW), besides smoothing, and derivative methods, were studied. To study the separation of classes, non-supervised algorithms were used, such as clustering techniques and parametric dimensionality reduction methods, that had its effectiveness evaluated visually and by a Hotelling T2 ellipse, calculated for each class. All calculations were done using MATLAB and R softwares. The results are promising in demonstrating that expensive and time-consuming calibration by using a analytical standard isn’t necessary in a fast assessment scenario, since a clear separation between high and low humulone content hops was achieved only using the chromatogram as data. Moreover, looking deeper into the new variables, it is possible to distinguish samples further into their composition, separating varieties based on different radical groups that distinguish intra acid group features. This information can be useful in a more sophisticated brewing industry.

Acknowledgements: CAPES, FAPERJ (E-26/210.614/2025), CNPq. Institutional support: LTPN and the Analytical Center, Faculty of Pharmacy (LCAN-CMF), Fluminense Federal University.

AN LC-MS/MS METHOD FOR THE MULTIRESIDUE DETERMINATION OF 142 PESTICIDES IN FRUITS USING A QuEChERSER METHOD

Igor Franceschi de Souza*[1], Gabriel Alexsander Barboza Prates[1], Douglas de Andrade[2], Osmar Damian Prestes[1], Renato Zanella[1]

[1]Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria - RS, Brazil
[2]Field Applications Specialist, Sciex Brazil, 06455-000 Barueri – SP, Brazil

* Corresponding author: igor.souza@acad.ufsm.br

Monitoring pesticide residues in fresh food is essential to ensure food safety and comply with regulatory standards. The large number of pesticides registered in Brazil, including several that are banned in other countries, presents a significant challenge for food safety monitoring and necessitates comprehensive multiresidue analytical methods. This work presents a multiresidue method for the determination of 142 pesticides in apples and peaches using a QuEChERSER [1] approach and LC-MS/MS. Instrumental conditions were optimized by evaluating two different analytical columns and varying the target cycle time to achieve an adequate number of data points per peak. For sample preparation, the QuEChERSER method was evaluated. Approximately 2 g of homogenized sample was extracted with 10 mL acetonitrile containing 1% (v/v) acetic acid. The mixture was shaken vigorously for 10 min and subsequently centrifuged at 3000 rpm for 3 min. A 100 µL aliquot of the supernatant was diluted with 900 µL of ultrapure water and filtered through a 0.22 µm nylon syringe filter. This dilution step was implemented to mitigate matrix effects without compromising the sensitivity required for multiresidue determination. Analyses were carried out in a 6500+ Qtrap system (Sciex) with ESI in positive and negative switching mode and scheduled MRM. Chromatographic separation was performed on a Kinetex Biphenyl column (100 × 3.0 mm, 2.6 µm) using a mobile phase consisting of (A) water:methanol (98:2, v/v) and (B) methanol:water (98:2, v/v), both with ammonium formate and formic acid, at a flow rate of 0.4 mL min^{-1}. The total run time was 20 min with 5 µL injection volume. The method was validated spiking blank samples at 2.5 and 5 µg kg^{-1}, with matrix-matched calibration curves ranging from 0.025 to 1.0 µg L^{-1}. For 118 pesticides, the method LOQ was 2.5 µg kg^{-1}, while for 24 pesticides it was 5 µg kg^{-1}. The method demonstrated satisfactory precision, with RSD ≤ 20%, and accuracy, with recoveries from 70 to 120%, in accordance with validation guidelines. This optimized approach provides a practical and efficient solution for the high-throughput routine analysis of food matrices.

[1] Monteiro, S. H.; Lehotay, S. J. et al. J. Agric. Food Chem. 69(4) (2021) 1234–1245.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM

ANÁLISE CROMATOGRÁFICA POR GC-MS DE ÉSTERES METÍLICOS DE ÁCIDOS GRAXOS (FAME) EM DIFERENTES MARCAS DE MANTEIGA E MARGARINA

Yasmim Eufrasio de Melo*, Ícaro do Nascimento Camêlo, Marcos Filipe Ramos e Silva, Lucas de Sousa Rodrigues, Nelson Roberto Antoniosi Filho

Laboratório de Métodos de Extração e Separação (LAMES), Instituto de Química (IQ), Universidade Federal de Goiás (UFG), Campus II - Samambaia, Goiânia, GO, Brazil.

* Corresponding author: yasmim.eufrasio@discente.ufg.br

A manteiga e margarina são produtos de alto consumo no mercado brasileiro, uma vez que possuem grande importância em termos sensoriais e nutricionais. Enquanto a manteiga é um derivado lácteo de gordura animal, a margarina é hidrogenada de forma parcial ou total a partir de óleos vegetais. Devido a importância deste produto no cenário brasileiro, este trabalho tem como objetivo, avaliar o perfil lipídico dos ácidos graxos de cada marca comercial de manteiga e margarina, identificar biomarcadores que classificam cada produto bem como quantificar e comparar os teores de acordo com as tabelas nutricionais. Para determinar obter os ácidos graxos esterificados, foi feita a transesterificação direta de 35 mg do produto segundo o método adaptado para microescala de Hartman e Lago. Depois da transesterificação direta, foi coletada uma alíquota de 1,5 ml e adicionados em vials para analisar no cromatógrafo a gás Shimadzu GCMS-QP2010 Ultra. A identificação dos compostos foi feita com o uso da biblioteca NIST11. Os resultados das análises confirmaram que os ésteres metílicos de ácidos graxos de cadeia C16 -C18. Há três principais FAMEs que foram majoritariamente identificados nas amostras. São eles: éster metílico do ácido hexadecanóico (C16:0), éster metílico do ácido 9,12-octadecadienóico (Z,Z) (C18:2) e éster metílico do ácido 9-octadecenóico (C18:1). Estes compostos representam, em conjunto, 77% da área total dos picos identificados (28.5%, 27.0 %, e 21.7% respectivamente). Também foi realizada análise hierárquica de cluster (HCA) para observar as tendências naturais de cada amostras e suas triplicatas, observou-se que a maioria das amostras seguiram suas tendencias e se agruparam em seus respectivos grupos, ou seja, margarinas tiveram alta similaridade, independente da adição de outras essências e manteigas tiveram alta similaridade entre si, independente da origem animal. Vale ressaltar que a predominância destes FAMEs torna evidente a compatibilidade com origem em triacilglicerídeos/fosfolipídeos de origem biológica, uma vez que a alta fração de ácidos (C18:2 e C18:1) pode indicar a predisposição à peroxidação lipídica. Diante do exposto, a análise de FAMEs por GC-MS é eficaz à diferenciação de produtos de origem animal e vegetal, bem como a identificação de FAMEs mais importantes para a classificação de cada grupo.

Acknowledgements: UFG, LAMES-UFG, CAPES, INCT-ALIM, FUNAPE.

Análise de bio-óleos produzidos pela técnica de extração de microalgas e esgoto sanitário por meio do GC/MS

Nicole Avila1, Juliana Otomo1, Marycel Cotrim1, Mariana Tango2, Luis Daniel2, Marcos Reali2, Oscar V. Bustillos1*.*

1. Instituto de Pesquisas Energéticas e Nucleares IPEN. 2. Instituto de Engenharia de São Carlos USP.

* Corresponding author: ovega@ipen.br

A produção de bio-óleos apartir de microalgas e esgoto sanitário foi desenvolvido para produção de compostos energéticos. Os produtos deste processo foram analisados por meio da técnica da cromatografia a gás acoplada à espectrometria de massas GC/MS. As amostras forma coletadas, filtradas e condicionadas durante o processo da produção dos bio-óleos. Uma alíquota, aproximadamente 5 mL de cada processo de produção foi separada e filtrada para as análises. As alíquotas foram diluídas em 1 mL do solvente dicloro-metano e posteriormente agitadas por 1 min no agitador automático da Quimis. Alocadas em vials de 1,5 mL as amostras foram numeradas e alocadas no sistema automático de análise do GC/MS (QP-5000 da Shimadzu). A coluna cromatográfica utilizada no GC, foi uma coluna apolar DB-5 (28,8x0,25 mm e 0,25 um) com gás Hélio de arrastre, o volume injetado foi de 1µL. O GC/MS equipado com um sistema automático de introdução de amostras facilitando o processo de análise das 73 amostras coletadas no processo. O espectrômetro de massas quadrupolar do GC/MS, possui uma fonte de íons por impacto de elétrons com 70 eV de energia e um detector de íons tipo multiplicador de elétrons, o modo de aquisição da leitura dos íons no quadrupolo foi o modo SCAN (varredura de íons) de 50 a 450 m/z para análise qualitativas. Foram analisados três lotes: Controle, RS e 1:50. Compostos tais como, ácidos graxos, carboxílicos, aldeídos e cetonas, ácidos oleicos, entre outros foram detectados em fases diferentes da produção de bio-óleos. Os resultados apresentados nestas análises, demonstram o potencial da produção de bio-óleos por meio da técnica de extração de microalgas e esgoto sanitário. Esta pesquisa revelou uma oportunidade de se aproveitar um passivo ambiental como o esgoto sanitário doméstico para gerar produtos de valor agregado que podem ser estudados em pesquisas futuras como fonte de nutrientes para cultivo de algas, poliaminas e poliamidas, produção de bioplásticos, amônia verde, produtos de hidrogênio, biocombustível e biodiesel e para matérias como supercapacitores e grafeno.

Acknowledgements: Ao CNPq, Fapesp e Capes pelo apoio financeiro.

ANÁLISE DE COMPOSTOS ORGÂNICOS VOLÁTEIS (VOCS) EM 4 TIPOS DE QUEIJOS VIA HS/GC-MS

Marcos Filipe Ramos e Silva*, Dayane Cristina da Costa, Nelson Roberto Antoniosi Filho

Universidade Federal de Goiás (UFG)

* Corresponding author: mfilipers@discente.ufg.br

O queijo é um alimento derivado do leite e presente em diversas culinárias sendo consumido puro ou aliado a outros alimentos. Os diferentes tipos de queijo proporcionam aromas e sabores variados o que permite sua utilização em diferentes contextos, desta forma é de grande importância conhecer a fração volátil dos queijos (VOCs), pois estes influenciam diretamente na percepção sensorial. Neste trabalho buscou-se entender as diferenças nos perfis voláteis dos queijos, para isso foram analisados quatro tipos diferentes de queijos que participaram do VI Concurso de Produtos Lácteos do Centro-Oeste, sendo 6 queijos prato, 6 minas padrão, 6 parmesãos e 9 muçarelas. Para estas análises realizou-se a extração por headspace (HS) e foi utilizada a técnica de cromatografia gasosa (GC) com detecção por espectrometria de massas (MS). Em cada análise pesou-se 7,0 gramas de amostra, seguida da extração por 30 minutos a 150 °C, a injeção foi realizada em modo split na razão de 1:50. Em seguida realizou-se a análise cromatográfica e após a obtenção dos cromatogramas e identificação dos picos foi possível observar diferentes perfis voláteis para cada amostra e padrões para cada tipo de queijo. Para os queijos muçarela, minas padrão e prato foi observado que a maior parte dos VOCs identificados foram ácidos carboxílicos (de 2 a 8 carbonos), cetonas e aldeídos, além disso, para esses três tipos de queijos as substâncias 3-metilbutanal, acetoína e ácido acético estiveram presentes em todas as amostras apresentando picos de alta intensidade. Já os parmesãos apresentaram maior quantidade de ácidos carboxílicos em relação as demais classes, além disso, os ácidos de maior cadeia carbônica apresentaram maior intensidade e foram identificados alguns compostos sulfurados como metanotiol, dissulfeto de dimetila e trissulfeto de dimetila. As diferenças nos tempos de maturação dos tipos de queijo e o tipo de bactéria utilizada no processo de produção são apontados como os principais fatores que diferenciam o parmesão dos outros três tipos. Essa distinção foi confirmada por uma análise de componentes principais (PCA) que indicou uma discriminação das amostras de parmesão em relação as demais. Por fim, através da análise via HS/GC-MS foi possível conhecer os principais VOC responsáveis pelos aromas de queijos e sua contribuição para as notas atribuídas ao sabor em análises sensoriais.

Acknowledgements: LAMES/UFG, IQ-UFG, EXPOLACO, ANP, INCT-ALIM, FUNAPE, CAPES.

ANÁLISE DE FENÓIS PRIORITÁRIOS EM ÁGUAS SUBTERRÂNEAS: UMA VISÃO DA PERFORMANCE DAS TÉCNICAS DE CROMATOGRAFÍA E ESPECTROMETRIA DE MASSAS

Giancarla Viviana Santa Cruz Mérida*[1], Juliana Ikebe Otomo[1], Diego Ricardo Araoz Prado[2], Elaine Aparecida Rodrigues[3], Delvonei Alves de Andrade[1], Oscar Vega Bustillos[1]

[1]Instituto de Pesquisas Energéticas e Nucleares IPEN-CNEN
[2]Pesquisador independente
[3]Instituto de Pesquisas Ambientais IPA

* Corresponding author: santacruz.viviana@usp.br

Com mais de 60 fenóis de ocorrência natural e de síntese industrial identificados em matrizes aquosas ao redor do mundo, esses compostos são poluentes prioritários devido à toxidade, bioacumulação e potencial carcinogênico. Sua detecção em águas subterrâneas é complexa pela diversidade estrutural e requer métodos convencionais e emergentes, como técnicas hifenizadas. Este estudo comparou a performance de técnicas cromatográficas e espectrométricas aplicadas à análise de fenóis prioritários em águas subterrâneas. A partir de uma revisão sistemática (PRISMA), conduzida em 2025 nas bases Web of Science e Scopus, foram recuperados 345 registros e selecionados de 52 estudos (1984 a 2023) que reportaram limites de detecção (LD) e quantificação (LQ) para 107 fénóis em 25 países, incluindo 11 prioritários (USEPA). Destacaram-se estudos na Romania, Croatia, Hungria e Irlanda com LC-MS/MS, com LD e LQ inferiores a 2 ng/L para 2,4-dinitrofenol, 2,4-diclorofenol e pentaclorofenol. A GC-MS apresentou desempenho comparável quando associada à derivatização, sobretudo com reagentes TMSDMC (Hungria) e BSTFA + TMCs (utilizado em estudos nos Estados Unidos, Brasil e China). Entre os métodos de preparo, a LPME foi a técnica mais utilizada, apresentou recuperação de até 94% para 2,4,6-trichlorofenol na Dinamarca. Na Irlanda, concentrações mínimas de até 1 ng/L de 2,4-diclorofenol, confirmou a elevada sensibilidade do LC-MS/MS. Concentrações críticas de fenol incluíram 40 mg/L nos Estados Unidos e de 866,140 ng/L na Alemanha, com GC-MS, acima do limite de 100 ng/L da União Europeia para água potável. Conclui-se que tanto a LC-MS/MS, especialmente quando combinada com as técnicas de extração SPE e/ou SPME, quanto a GC-MS se estabelecem como as abordagens mais sensíveis para a detecção de fenóis prioritários em águas subterrâneas. Ambas são capazes de garantir resultados consistentes a níveis traço, sendo que a GC-MS atinge esse desempenho satisfatório quando associada ao preparo adequado das amostras e à derivatização. A escolha criteriosa da técnica analítica é determinante para monitoramento confiável, formulação de políticas públicas e proteção da saúde humana e ambiental.

Acknowledgements: Os autores agradecem à CAPES, IPEN-CNEN e IPA pelo suporte técnico e institucional. À TVGD pelo financiamento da APC.

ANÁLISE DE MULTIRRESÍDUOS DE AMOSTRAS DE COCO RALADO USANDO O MÉTODO QuEChERS/GC-MS

Priscilla L. Maia[1], Cleidiane G. Lima[2], Luana G. Mendes[2], Jéssica R.P. Martins*[1], Micael de Andrade Lima[3], Maria Aparecida L. Milhome[1]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará, Campus Limoeiro do Norte- IFCE
[2]Núcleo de Tecnologia e Qualidade Industrial do Ceará- NUTEC
[3]University of Greenwich, Reino Unido.

* Corresponding author: jessica.r160@gmail.com

O coco ralado é um ingrediente versátil e nutritivo, amplamente utilizado em diversas receitas, desde bolos e doces até pratos salgados. Consumido com moderação, o coco ralado pode ser um excelente complemento para uma dieta balanceada, proporcionando sabor e benefícios à saúde. No entanto, o uso intensivo de pesticidas na agricultura, tem despertado a atenção dos pesquisadores sobre a presença desses contaminantes em produtos derivados do coco. Existem atualmente 28 princípios ativos de uso autorizado pela ANVISA para a cultura do coco, classificados em quatro grupos principais: organofosforados, carbamatos, organoclorados e piretróides. Este estudo teve como objetivo analisar e investigar a presença de 40 resíduos de pesticidas em amostras de coco ralado industrialmente. A extração de resíduos foi realizada usando o método QuEChERS, seguido por cromatografia gasosa com espectrometria de massas (CG-MS), uma técnica eficaz para analisar pesticidas em alimentos. O método utilizado apresentou seletividade satisfatória e linearidade entre 0,05 e 1,50 mg/kg ($R^2 > 0,99$), demonstrando excelente correlação entre a concentração e a resposta analítica. A exatidão e precisão variaram de 70 a 120% e de 0,56 a 10,12%, respectivamente. Os Limites de Detecção e Quantificação variaram de 0,005 a 0,05 mg/kg e de 0,015 a 0,15 mg/kg, respectivamente. Os níveis de pesticidas encontrados em todas as amostras estavam abaixo do limite de quantificação (LOQ), para todos os 40 compostos analisados. Os resultados demonstram a segurança do consumo de coco ralado industrialmente, desde que controles rigorosos sejam mantidos para prevenir riscos potenciais, e reforçam a necessidade de monitoramento contínuo e controle ambiental durante a produção.

Acknowledgements: INCT-ALIM (CNPQ), CNPQ, FUNCAP, CAPES, NUTEC, FAVILI.

ANÁLISE DE VITAMINAS A E D EM XAROPES MULTIVITAMÍNICOS: DESENVOLVIMENTO E VALIDAÇÃO DE MÉTODO POR CLAE-DAD

Adressa Nunes Furtado, Sthefany M. L. Cury, Sibele Guimarães*, André Colonese, Patrícia C. Lima, Soraya M. Ochs, Bianca S. Oliveira, Matheus N. Souza, Mychelle A. Monteiro

Instituto Nacional de Controle de Qualidade em Saúde (INCQS)

* Corresponding author: sibele.guimaraes@fiocruz.br

Os multivitamínicos, utilizados para complementar a alimentação de indivíduos saudáveis, são suplementos que podem ser estratégicos para sanar as deficiências nutricionais de uma alimentação pobre em nutrientes essenciais para a saúde humana. Dessa forma, os multivitamínicos podem ser aliados na prevenção de hipovitaminoses e prevenir as complicações advindas da deficiência de vitaminas que constitui um problema de saúde pública, principalmente nas regiões mais carentes. A determinação do teor de vitaminas é fundamental para garantir a qualidade, segurança e eficácia de multivitamínicos. No Brasil, o Instituto Nacional de Controle de Qualidade em Saúde (INCQS), integrante da Rede Nacional de Laboratórios de Vigilância Sanitária (RNLVISA), atua no controle de qualidade desses produtos. Neste estudo, foram analisadas amostras de xarope multivitamínico contendo vitaminas hidrossolúveis e lipossolúveis. Embora métodos descritos em compêndios oficiais sejam a primeira escolha, sua aplicação nem sempre é adequada, como observado para as vitaminas lipossolúveis. Nesse sentido, o objetivo do trabalho consiste em desenvolver e validar uma nova metodologia analítica adequada para essas amostras utilizando as técnicas de cromatografia líquida de alta eficiência com detecção por arranjo diodos (CLAE-DAD). Embora a metodologia descrita na United States Pharmacopeia (USP) tenha sido utilizada como referência inicial, observou-se perda dessas vitaminas durante a extração, comprometendo a eficiência do método. Assim, foram implementadas modificações no preparo das amostras e nos parâmetros cromatográficos, incluindo a substituição da fase móvel, adoção de gradiente de solventes, alteração do volume de injeção em razão da baixa concentração de vitamina D na amostra e aumento do fluxo cromatográfico visando à redução do tempo de análise. O método desenvolvido foi validado conforme os critérios estabelecidos na RDC 166/2017, demonstrando precisão, exatidão, linearidade e seletividade satisfatórias. Sua utilização no controle de qualidade de xaropes multivitamínicos assegura a verificação dos teores vitamínicos declarados, reforçando a proteção da saúde pública e ampliando a capacidade de atuação da Vigilância Sanitária.

Acknowledgements: Fundação Oswaldo Cruz, Instituto Nacional de Controle de Qualidade em Saúde, Fundação para o Desenvolvimento Científico e Tecnológico em Saúde.

Análise por HS/GC-MS da composição química volátil de cafés comerciais visando à identificação de marcadores de qualidade

Leonardo Silva Gonçalves*, Ana Luiza Reis Rodrigues da Cunha, Lilian Fernandes de Oliveira, Lucas Ferrão Marinho, Dayane Cristina da Costa, Nelson Roberto Antoniosi Filho

Universidade Federal de Goiás

* Corresponding author: gonc.leonardo@gmail.com

O café, reconhecido como uma das bebidas mais tradicionais e populares no mundo, destaca-se por sua variedade associada a diferentes espécies de grãos, grau de torrefação, origem geográfica e processo de extração. Esses fatores influenciam de forma significativa a composição química da bebida e, consequentemente, se expressam nas características sensoriais do produto. Dessa forma, diversos parâmetros como, aroma, sabor, acidez e corpo são resultantes da sinergia entre os compostos presentes no café. Dentre eles, os compostos orgânicos voláteis (VOCs) presentes no café podem ser considerados parte essencial no perfil sensorial. Nesse sentido, a análise dos VOCs se configura como fundamental para avaliar a relação entre os compostos químicos e os parâmetros que são utilizados para o controle de qualidade do café, assim como na aceitação do consumidor. O objetivo desse trabalho foi investigar o perfil químico aromático de amostras de cafés comerciais. Foram coletadas amostras de 28 cafés comerciais de classificação tradicional, extraforte, superior, gourmet e especial. O perfil químico aromático das amostras de pó de café foi determinado em triplicatas, sendo os compostos extraídos via headspace à 150 °C por 5 minutos sob agitação de 700 rpm. Um milílitro dos vapores gerados foram coletados e analisados em um cromatógrafo a gás Agilent 7890B equipado com espectrômetro de massas 7000D e coluna capilar DB-5ms (30m x 0,25mm x 0,25um). Foram identificados VOC de diversas classes orgânicas sendo as cetonas e pirazinas os grupos que apresentaram o maior número de compostos. O perfil volátil das amostras foi comparado e os cafés categorizados em sua embalagem com grãos arábica – e, consequentemente, cafés do tipo gourmet e especiais - apresentaram VOC que se distingue das amostras com outro padrão de grãos. Os dois principais compostos responsáveis por essa discriminação e suas características sensoriais foram 1-hidroxi-2-butanona (café doce, malte de grãos mofados, caramelo) e o 5-metilfurfural (caramelo de especiarias com bordo). Em suma, a análise via HS/GC-MS permitiu caracterizar o perfil volátil das amostras de café e identificar compostos responsáveis pelas características sensoriais presentes em cada categoria.

Acknowledgements: LAMES/UFG, IQ-UFG, CAPES, FUNAPE, INCT-ALIM.

ANALYSIS OF FERMENTATION BY-PRODUCTS IN DISTILLED ALCOHOLIC BEVERAGES

Tiago Rocha Nogueira*, Mairlane Silva de Alencar, Pedro Henrique Honorio Queiros, Fuad Pereira Nogueira Filho, Thales Rafael Guimarães Queiroz, Crisiana de Andrade Nobre

Nucleus of Technology and Industrial Quality of Ceará (NUTEC)

* Corresponding author: tiago.nogueira@nutec.ce.gov.br

Distilled alcoholic beverages are produced by fermenting musts derived from grape juice, barley, or other sugar sources, followed by distillation. During this process, volatile compounds are carried over with ethanol, contributing to the organoleptic properties of the beverage, which may also acquire additional characteristics when aged in wooden containers. Fermentation and distillation are critical stages, as they generate by-products regulated by control agencies that establish maximum limits for contaminants and congeners. In this study, an analytical method based on gas chromatography with flame ionization detection (GC-FID) was developed for the simultaneous determination of 10 analytes, using centrifugation as the sole sample preparation step. The method was validated according to INMETRO and MAPA guidelines, meeting requirements of linearity, detection and quantification limits, precision, and accuracy. Compared with methods reported in the literature, it allowed the identification of a broader diversity of compounds, aligned with green analytical chemistry principles. The method was applied to gin, rum, vodka, brandy, cachaça, aguardente, and whiskey, with results compared against legal limits and classified by chemometric tools.

Acknowledgements: Instituto Nacional de Ciência e Tecnologia em Química Analítica de Alimentos: Segurança de Alimentos e Caracterização de Alimentos Funcionais (INCT-ALIM)

ANALYSIS OF INORGANIC ARSENIC IN RICE BY LIQUID CHROMATOGRAPHY COUPLED WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR THE DEVELOPMENT OF A REFERENCE MATERIAL PROTOTYPE IN COLOMBIA

Andrés Madrid Montoya*[1], Elianna Castillo Serna[2], Ivonne Alejandra González Cárdenas[3]

[1]1 Universidad Nacional de Colombia – Sede Bogotá, Departamento de Química. Grupo de Estudios para la Remediación de Impactos Negativos al Ambiente (GERMINA). 2 Instituto Nacional de Metrología de Colombia – Subdirección de Metrología Química y Biología. Grupo de Investigación en Metrología Química y Biología (GIMQB)

[2]1 Universidad Nacional de Colombia – Sede Bogotá, Departamento de Química. Grupo de Estudios para la Remediación de Impactos Negativos al Ambiente (GERMINA)

[3]2 Instituto Nacional de Metrología de Colombia – Subdirección de Metrología Química y Biología. Grupo de Investigación en Metrología Química y Biología (GIMQB)

* Corresponding author: ammontoya@inm.gov.co

Refinement of risk assessments related to arsenic exposure in food requires reliable measurements not only of total arsenic content but also of individual arsenic species – particularly the more toxic inorganic arsenic (iAs), dimethylarsenate (DMA), and methylarsonate (MMA). We present the development and validation of a measurement method for iAs (As3+ and As5+) in rice, intended for evaluating homogeneity and stability in a reference material (RM) prototype that we also developed. RM prototype was prepared by fortification with As3+ and As5+ at the European maximum permissible level of iAs (0.25 mg kg-1) in a commercial polished rice flour sample. Freeze-drying and oven drying were compared before the prototype production. Anion exchange chromatography was used for the separation of arsenic species, with detection by inductively coupled plasma mass spectrometry (ICP-MS). Sample extraction was performed using 0.28 mol L-1 HNO3 in a thermostatic bath at 80 °C for 90 min, followed by filtration. The extract pH was then adjusted to 8.2 using an ammonia solution. Optimal chromatographic separation was achieved with a mobile phase gradient starting with 20 mmol L-1 ammonium formate, then 10 mmol L-1 ammonium phosphate buffer at pH 8.2. Mobile phases contained 1 % methanol to enhance the arsenic species sensitivity. MMA was used as a surrogate standard because it was present in insignificant amounts in the RM prototype, and the selectivity of the method was confirmed. Validation experiments were carried out using CRM NIST SRM 1568b, NRC BARI- 1, and the fortified RM prototype. Precision under repeatability and inter-day conditions was sufficient for homogeneity evaluation, and method bias was controlled for stability studies. RM prototype is expected to show uncertainty below the target uncertainty requirement.

Acknowledgements: This research was conducted as part of the project "Desarrollo de referencias de medición para la cuantificación de especies tóxicas de mercurio y arsénico en alimentos", funded by the Ministerio de Ciencia, Tecnología e Innovación de Colombia. We also acknowledge the participating institutions, current and former researchers, and students who were part of the project, for their valuable contributions.

ANALYSIS OF NAPHTHENIC ACIDS BY SOLID-PHASE MICROEXTRACTION COUPLED TO MASS SPECTROMETRY WITH DIELECTRIC BARRIER DISCHARGE IONIZATION (SPME-DBDI-MS)

Ana Beatriz Alves de Miranda Salata*[1], Glaucimar Alex Passos Resende[1], Allyson Leandro Rodrigues dos Santos[1], Rogerio Mesquita Carvalho[2], Iris Medeiros Junior[2], Leandro Wang Hantao[3]

[1]Institute of Chemistry, University of Campinas
[2]Leopoldo Américo Miguez de Mello Research Center (CENPES, PETROBRAS)
[3]Institute of Chemistry, University of Campinas; Center for Energy and Petroleum Studies (CEPETRO, UNICAMP); Center for Energy Planning (NIPE, UNICAMP)

* Corresponding author: a298906@dac.unicamp.br

The analysis and characterization of naphthenic acids (NAs) are of great analytical interest, especially in petroleum matrices. Mass spectrometry is one of the most powerful techniques for this purpose, with the ionization step being crucial to the success of the analysis. Dielectric barrier discharge ionization (DBDI) is an interesting ambient ionization technique for mass spectrometry. Recent literature indicates its ability to ionize analytes with a broader polarity range, when compared to electrospray ionization (ESI). The objective of this work was to develop a method for analyzing NAs using a commercial DBDI source. Analyte extraction and preconcentration were performed using solid-phase microextraction (SPME). The analytes were introduced to the ion source by thermal desorption of the sorbent phase. The ionization mechanisms occurring in cold plasma were investigated and compared with those of ESI. First, the ionization efficiency for NAs was evaluated in the positive and negative modes. Nitrogen was used as the base gas for plasma generation and tested under the following conditions: dry nitrogen, nitrogen humidified with water, and nitrogen doped with different reagents (acetone, methanol, and isopropanol) to observe the types of ions formed. Next, the mass spectra and ion profiles obtained by DBDI-MS were compared with those generated by ESI-MS, evaluating the extent of fragmentation and adduct formation in both sources. As the performance proved to be superior, the method optimized with the DBDE underwent semi-validation. The detection and quantification limits were determined, and linearity was evaluated using ten model NAs. The method using SPME-DBDE presented itself as an interesting alternative for analyzing NAs, with the potential to overcome some limitations of traditional ESI.

Acknowledgements: CAPES, CNPq, FAPESP, PETROBRAS, Plasmion GmbH.

ANALYSIS OF VOLATILE COMPOUNDS OF HONEY SPIRIT FLAVORED WITH AROEIRA, CUMARU AND PAU BRANCO

José Leitão Sena Lima Filho[1], Felipe Sousa da Silva[2], Mairlane Silva de Alencar[2], Crisiana de Andrade Nobre[2], Maria Aparecida Liberato Milhome[3], Laécio Galvão Maciel[3], Mayara Salgado Silva[3]

[1]Federal Instute of Education Science and Technology of Ceará - IFCE
[2]Nucleus of Technology and Indsutrial Quality of Ceará - NUTEC
[3]Federal Instute of Education Science and Technology of Ceará - IFCE;

The food industry has been advancing in the use of chromatographic techniques through the qualitative monitoring of volatile compounds (VCs) and bioactive compounds, which are related to product quality, in addition to the sensory aspect. Thus, the present study aims to qualitatively evaluate the VCs in honey spirit flavored with chips from caatinga trees. The species used were aroeira (Myracrodruon urundeuva), pau branco (Cordia oncocalyx), and cumaru (Amburana cearensis). The extraction of the flavored beverages was by Headspace Solid Phase Microextraction (HS-SPME), using SPME CAR/PDMS fiber (75 µm) exposed to 40 °C for 10 minutes, under constant agitation. The samples were identified by Gas Chromatography coupled with Mass Spectrometry, using a DB-5MS column (5% phenylmethylsiloxane) (30 m x 0.25 mm x 0.25 µm), operated in Full Scan mode, 35-400 m/z, electron impact ionization with an energy of 70 eV. Helium was used as carrier gas (1.0 mL/min) and splitless injection mode. To compose the volatile profile, compounds with a total area ≥ 0.2% and a similarity percentage ≥ 50% were considered. A total of 148 compounds were identified in the spirit with cumaru, 146 with pau branco, and 145 with aroeira. By analyzing the volatiles, it was possible to identify six compounds that share winemaking characteristics with honey brandy and its wood blends, such as Ethylalcohol, also called ethyl alcohol because it imparts an alcoholic, pungent, and slightly sweet flavor. Linalool, naturally occurring in plants and flowers, imparts woody, rose, citrus, lemon, and floral flavors. Propanoic acid imparts earthy, sweet, floral, and woody flavors. These results demonstrate common compounds regardless of the wood used, as it is plausible to investigate chemical characteristics that infer sensory perception of flavored brandies. Thus, the study emphasizes the importance of continuous monitoring of the use of aromatic woods to ensure the necessary quality control and food safety.

Acknowledgements: National Institute of Science and Technology – Food (INCT-ALIM);
Nucleus of Technology and Indsutrial Quality of Ceará (NUTEC);
Federal Institute of Education, Science and Technology of Ceará (IFCE) – Limoeiro do Norte Campus.

Analysis of volatile compounds of yerba mate from different geographical origins using HS-SPME-GC-MS

Rosangela Assis Jacques*[1], Helen C.dos S.Hackbart[1], Thiago J.T.da Luz[1], Manoela dias Varga[1], Eliseu Rodrigues[1], Ariana Helena de Oliveira Maia[2]

[1]Federal University of Rio Grande do Sul
[2]State University of Rio Grande do Sul

* Corresponding author: rosangela.j@iq.ufrgs.br

Yerba mate is a plant native and cultivated in Brazil, Argentina, and Paraguay, consumed mainly as an infusion of its leaves and branches. Its leaves have several nutritional and medicinal properties, attributed to their secondary metabolites, whose composition can vary depending on factors such as the type of cultivation, climate, agronomic conditions, and industrial processing. Given the above, the present study aimed to establish strategies for the elucidation of the volatile composition of yerba mate samples from different countries and growers.
Samples of yerba-mate (150 mg) were placed in a 15 mL vial. The vials were then heated at 52 ◦C for 10 min to equilibrate the sample temperature. Subsequently, volatile compounds were extracted using a fused silica fiber coated SPME triple phase 50/30 µm fiber (divinylbenzene/carboxen/polydimethylsiloxane) , which was exposed to the headspace within the vials containing the yerba-mate sample for 20 min at 52 ◦C . A blank fiber analysis was previously performed, following the above-described procedure, but using an empty vial. The chromatographic separation was performed on a DB-5 capillary column, 5% phenyl-95% dimethylpolysiloxane, 60 m , 0.25 mm internal diameter, and 0.25 µm stationary phase thickness. The carrier gas used was ultra-pure helium, at a flow rate of 1 mL.min-1. The temperatures of the injector, interface, and ion source were maintained at 280 °C. The energy for electron impact ionization was 70 eV. The mass range of detected ions was 45 to 450 Daltons, and the detector voltage was 1.4 kV. The linear temperature programmed retention indices (LTPRI) for the detected compounds were calculated using the Van den Dool and Kratz equation. Analysis of the volatile compounds in yerba mate using SPME-GC-MS showed that a total of 35 volatile compounds were identified and revealed that terpenes are the main group of compounds identified. Among the compounds, eucalyptol and α-farnesene stand out for their fresh and fruity fragrances, while caryophyllene has special notes. Analysis of the compounds in yerba mate revealed the complexity of its aromatic profile, with the presence of terpenes, alcohols, and esters. These compounds are essential for ensuring the authenticity and quality of the product, as well as enhancing its regional identity.

Acknowledgements: Acknowledgements: The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for financial support and scholarships.

ANALYTICAL EFFICIENCY AND SUSTAINABILITY WITH GC-BID: A GREEN AND MINIATURIZED POLYMER BIODEGRADABILITY TEST

Aline Vaz da Silva*[1], Amanda Alves Soares[1], Jhonatan Bispo de Oliveira[2], Patrícia Santiago de Oliveira Patrício[1], Patterson Patrício de Souza[1]

[1]Centro Federal de Educação Tecnológica de Minas Gerais
[2]Universidade Federal de Minas Gerais

* Corresponding author: aline.vzsilva@gmail.com

The accumulation of plastic has been a significant contributor to several environmental problems, including soil and water pollution, habitat degradation, and animal poisoning. As a result, these materials are considered one of the most problematic classes of solid waste. In this context, the search for biodegradable polymers has intensified. To attest biodegradability, the most used method is quantifying the CO2 evolved during the test. Typically, CO2 reacts with a barium hydroxide solution and the remaining excess base is titrated with a standardized hydrochloric acid solution. This method has several limitations, including the use of complex experimental apparatus, the need of large volumes of solution, the generation of significant toxic waste, and inability to detect low concentrations of carbon dioxide. In this sense, the present work aimed to develop a new miniaturized analytical method for determining the carbon dioxide released in a biodegradability test using Gas Chromatography coupled with a Barrier Discharge Ionization Detector (GC-BID). To build the calibration curve, CO2 was generated inside a 20 mL vial through the reaction of a standard sodium carbonate solution with 2M sulfuric acid, and the headspace was manually injected into the chromatograph through a 3 mL sample loop. The analytical method was validated with the following results: repeatability 9.58%, intermediate precision 14.51%, recovery 105.7%; Limit of Detection 0.0050 and Limit of Quantification 0.023 (mg of CO2). Due to the high efficiency of GC-BID in quantifying CO2, it was possible to reformulate the biodegradability test. In the original standard method, a set of twelve 5 L bottles is used as reactors; instead of that, in this work 20 mL vials were used as reactors (99.6% of miniaturization). The proposed method uses 100 mg of sample, does not employ any hazardous reagents, and generates zero waste. The methodology was applied to assess the biodegradability of polymeric materials. During the 6 days of the test, the positive control (cellulose) released about 500 mg of CO2, while the blank (organic compost) and negative control (high density polyethylene) released less than 0.2 mg. The new method presents itself as a more sustainable, precise and easier-to-perform alternative for determining the biodegradability of polymeric materials using GC-BID.

Acknowledgements: CEFET-MG, PPGMQ, CNPq, CAPES, Fapemig.

Analytical method for sulfonamides residues in whey protein supplements using LC-Orbitrap-HRMS

Hilton Wanderson de Souza e Sousa[1], Alexander Andrey Lopes da Silva[2], Vivian María Saez Martínez[3], Márcia Nogueira da Silva de la Cruz*[4]

[1]Universidade Federal do Rio de Janeiro, Escola de Química (EQ-UFRJ)
[2]Universidade Federal do Rio de Janeiro, Instituto de Química (IQ-UFRJ), LAGOA-LADETEC
[3]Universidade Federal do Rio de Janeiro, Instituto de Química (IQ-UFRJ), DQA/IQ
[4]Universidade Federal do Rio de Janeiro, Instituto de Química (IQ-UFRJ), LABITAN

* Corresponding author: marcianogueira@iq.ufrj.br

The dietary supplement market in Brazil, that produced more than 10 billion Reais in 2021, is growing significantly because of the use of Whey Protein (WP), specifically by practitioners of physical activities. Among the benefits of using WP are the contribution to the gain of lean muscle mass, aid in muscle recovery, improvement of the cardiovascular system, reducing cardiac risk, strengthening of the immune system, help in controlling blood pressure, and favoring the reduction of body fat. According to data from Associação Brasileira da Indústria de Alimentos para Fins Especiais (ABIAD), 59% of Brazilian homes have, at least, one person consuming WP. In 2022, whey protein consumption increased 25% compared to 2021. Whey protein production is sustainable because it is produced from milk byproduct. Nevertheless, there is great concern about food supplement quality. The use of sulfonamides, a common veterinary drug class for dairy cattle to treat infections, may cause the presence of residues in the milk and in its derivatives products, injuring consumers´ health. In Brazil, Anvisa is responsible for establishing residues limits in food, including supplements. The aim of this study was to develop and validate a method to identify and quantify sulfonamides in Whey Protein supplements, using Liquid chromatography coupled with mass spectrometry (LC-MS). The method is capable of separating, identifying, and quantifying eleven sulfonamides: sulfadiazine, sulfathiazole, sulfamerazine, sulfamethazine, sulfamethizole, sulfameter, sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole, sulfadimethoxine, and using sulfadimethoxine-d6 as an internal standard. The method demonstrated specificity, good linearity with an average linear correlation coefficient (r) of 0.96, good recovery (average of ~110%), and good repeatability (average of 11.57%). The analytical method was validated based on Directive 2002/657/EC and the Inmetro document DOQ-CGCRE-008. This approach aims to promote food safety and prevent unnecessary exposure to harmful substances, aligning with the integrity of quality control.

Acknowledgements: We gratefully acknowledge the Instituto de Química of UFRJ, and the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brasil (CAPES) – Financial Code 001.

ANALYTICAL STRATEGY FOR CHLORINE, SULFUR, BROMINE AND IODINE DETERMINATION IN RICE USING MICROWAVE-INDUCED COMBUSTION AND CHROMATOGRAPHIC/SPECTROMETRIC TECHNIQUES

Thauana Heberle[1], Marcia Foster Mesko[1], Gustavo Gohlke[2], Erico M. M. Flores[2], Priscila Tessmer Scaglioni[3]

[1]Universidade Federal de Pelotas - UFPel
[2]Universidade Federal de Santa Maria - UFSM
[3]Universidade Federal do Rio Grande - FURG

The determination of chlorine, sulfur, bromine, and iodine in food is an analytical challenge due to their low concentration, the possibility of losses during sample preparation, and the need for highly selective methods. Rice, a staple food worldwide, can accumulate these elements in different proportions, making the use of efficient digestion and analytical protocols essential. In this study, microwave-induced combustion (MIC) was employed, a technique that enables complete decomposition of the organic matrix with quantitative recovery of the target elements. In this procedure, 700 mg of sample were wrapped in polyethylene film and placed at the base of quartz holders containing a filter paper disk moistened with an ammonium nitrate ignition solution. The holders were inserted into quartz vessels containing 6 mL of ultrapure water (absorbing solution), properly sealed, pressurized with oxygen (20 bar), and subjected to the microwave oven. MIC presents important advantages over other digestion approaches, as combustion occurs in a closed and pressurized environment, minimizing volatilization losses – a critical factor when dealing with halogens. Furthermore, the use of ultrapure water as the absorbing solution eliminates the need for concentrated acids in the final stage, reducing the risk of contamination and simplifying preparation for chromatographic analysis. Two complementary techniques were applied for analyte determination: ion chromatography with conductivity detection (IC-CD) for chlorine and sulfur, and inductively coupled plasma mass spectrometry (ICP-MS) for bromine and iodine. IC-CD proved effective for quantifying Cl- and SO42- anions, providing high resolution and sensitivity, and enabling the distinction of different inorganic species in the digests. ICP-MS was chosen for bromine and iodine due to its high sensitivity, capable of detecting trace concentrations, and its robustness in handling the matrix obtained after MIC digestion. The results showed a wide variation in the concentrations of the elements: chlorine and sulfur ranged from 104 to 384 mg/kg and from 390 to 1138 mg/kg, respectively; bromine ranged between 0.3 and 1.3 mg/kg; and iodine showed concentrations below the quantification limit (0.04 mg/kg). In conclusion, MIC, combined with chromatographic and spectrometric techniques, constitutes a robust analytical strategy for the determination of halogens and sulfur in food.

Acknowledgements: CAPES, CNPq, and FAPERGS.

APLICAÇÃO DE SOLVENTE EUTÉTICO PROFUNDO NATURAL COMO FASE EXTRATORA NA TÉCNICA HF-MMLLE PARA DETERMINAÇÃO DE BIOMARCADORES DE CÂNCER DE PULMÃO EM URINA POR HLPC-DAD.

Amanda Vitória Santos*, Camila Will, Eduardo Carasek

Universidade Federal de Santa Catarina

* Corresponding author: amanda.vitoria@posgrad.ufsc.br

Hexanal e heptanal são considerados biomarcadores de câncer de pulmão que podem ser encontrados em diferentes matrizes biológicas, tais como sangue e urina. Eles têm sua determinação dificultada devido a sua volatilidade, baixa absorção na região UV, complexidade da matriz e as baixas concentrações em que são encontrados nas amostras, por isso para sua análise é necessária uma etapa de derivatização aliada ao preparo de amostras. Neste trabalho desenvolveu uma metodologia para a determinação de hexanal e heptanal analitos em urina utilizando solventes eutéticos profundos naturais (NADES) como fase extratora para microextração líquido-líquido de membrana microporosa de fibra oca (HF-MMLLE) acoplada a um sistema de placas de 96 poços de amostragem. O NADES otimizado (ácido dodecanóico:ácido hexanóico 1:3) foi impregnado na membrana e então submetido a extração em amostras de urina. Os experimentos foram realizados acoplando a técnica de HF-MMLLE ao sistema de placas de 96 poços de amostragem que permite a realização de até 96 extrações simultâneas, levando a um tempo de 1,09 min para o preparo de cada amostra. O modo de derivatização pós extração apresentou melhores resultados. O solvente de dessorção otimizado foi ACN:MeOH (1:1), com o tempo de dessorção de 5 minutos. Um planejamento fatorial completo mostrou que o tempo de derivatização não foi significativo, logo este foi fixado em 30 min. O tempo de extração, pH e quantidade de derivatizante foram estudados através de um planejamento box behnken que mostrou melhores resultados quando o pH da amostra foi mantido em 6, a proporção de derivatizante de 1:30 (aldeído:derivatizante) e extrações de 60 minutos. Os parâmetros analíticos de mérito foram obtidos através de curvas de calibração onde os valores de R^2 foram de 0,9973 para o hexanal e 0,9935 para o heptanal. Os LODs obtidos foram de 0,3 e 0,26 nmol mL –1 para hexanal e heptanal respectivamente, e os LOQs de 1,00 nmol mL –1 para hexanal e 0,87 nmol mL –1 para heptanal. Ensaios de precisão intradia e interdia variaram de 9 a 20% e de 17 a 20%, respectivamente. A exatidão do método foi avaliada pela recuperação relativa que apresentou resultados variando de 55,2 a 97,3%. A metodologia foi aplicada em amostras de urina de 3 voluntários nas quais as respostas apresentaram abaixo do limite de detecção do método.

Acknowledgements: Os autores agradecem aos órgãos governamentais FAPESC e CNPq.

Aplicação do Fast GC na análise de hidrocarbonetos de petróleo: Uma abordagem para aceleração de métodos convencionais

Alexandre Varão Moura[1], Lucas Pessôa de Araujo[1], Carlos Alberto Carbonezi[2], Leandro Wang Hantao*[1]

[1]Instituto de Química, Universidade de Campinas, 13083-970, Campinas-SP, Brasil
[2]Centro de Pesquisas, Desenvolvimento e Inovação Leopoldo Américo Miguez de Mello – CENPES, 21941-915, Rio de Janeiro-RJ, Brasil

* Corresponding author: wang@unicamp.br

O petróleo bruto é uma mistura complexa de compostos, e sua análise por cromatografia gasosa (GC) convencional apresenta tempo de execução elevado. A redução desse tempo permitiria o acréscimo no número de amostras analisadas em um mesmo intervalo, otimizando a rotina laboratorial. A cromatografia gasosa rápida (Fast GC) busca condições experimentais que reduzam a contribuição dos termos B e C (Equação de Golay), visando separações de altíssima eficiência. Desta forma, torna-se possível realizar experimentos de cromatografia mais rápidos, preservando-se a resolução dos pares críticos. Nesse contexto, os conceitos de Fast GC foram aplicados aos métodos de caracterização de petróleos. Para isso, foi utilizado um sistema GC-FID (Thermo Fisher Scientific, modelo TRACE1300). Os métodos estudados foram Whole Oil, Condensado e Carburane. O desenvolvimento de método visou a substituição do gás de arraste He por H2 , e as respectivas adequações nos demais parâmetros cromatográficos. Os resultados mostraram melhorias significativas no tempo de análise. Os métodos que utilizavam gás He como gás de arraste apresentavam tempos de corrida de 130 minutos para Whole Oil, 100 minutos para Condensados e 140 minutos para Carburane. Após a substituição por H2 , observou-se uma redução significativa nos tempos de análise: 17 minutos para Whole Oil (redução de ~87%), 36 minutos para Condensados (redução de ~64%) e 20 minutos para Carburane (redução de ~86%). Os novos métodos preservaram o perfil cromatográfico original, permitindo o uso destes novos métodos em estudos geoquímicos.

Acknowledgements: Petrobrás, CAPES, CNPQ e FAPESP

APPLICATION OF COUNTERCURRENT CHROMATOGRAPHY (CCC) FOR THE ISOLATION OF CHEMICAL CONSTITUENTS FROM SPECIES OF THE GENUS ZIZIPHUS (RHAMNACEAE)

Felipe Costa Cardoso*[1], Wallace Rodrigo de Jesus Barbosa[2], Fernanda das Neves Costa[1], Roberto Carlos Campos Martins[1]

[1]Walter Mors Institute of Research on Natural Products (IPPN), Federal University of Rio de Janeiro (UFRJ), RJ, Brazil
[2]Federal Institute of Education, Science, and Technology of Rio de Janeiro (IFRJ)

* Corresponding author: felipeccardoso@ufrj.br

Introduction: Countercurrent Chromatography (CCC) is a liquid–liquid partitioning technique that operates without a solid support, relying instead on the differential distribution of analytes between two immiscible liquid phases1. This feature eliminates irreversible adsorptive losses and enables the fractionation of crude extracts with high recovery rates. In this study, we applied CCC to the fractionation of ethanolic crude extracts from Ziziphus joazeiro (ELZJ) and Z. undulata (ELZU). Methodology: Solvent system (SS) selection was guided by the estimation of analyte partition coefficients (K). Aliquots of the extracts were partitioned in different SS, and metabolite distribution was assessed by Thin-Layer Chromatography (TLC). For the triphasic solvent system (TPSS), phase distribution was further evaluated by HPLC-DAD to obtain more accurate data. Systems in which compounds of interest exhibited balanced partitioning ($K \approx 1$) were selected. For ELZJ (400 mg), the biphasic solvent system (BPSS) HEMWat (n-hexane:ethyl acetate:methanol:water, 6:1:6:1, v/v/v/v) was chosen and applied to a P.C. Inc. Potomac chromatograph. Separation was carried out in normal elution mode (Head → Tail) at 2 mL/min and 800 rpm, with a stationary phase retention (Sf) of 86%. For ELZU (553 mg), a TPSS (n-hexane:methyl acetate:acetonitrile:water, 2:1:2:2, v/v/v/v) was employed on a Quattro HTPrep chromatograph. Fractionation proceeded in gradient normal elution mode, yielding an Sf of 89.3%. Results: Fractionation of ELZJ with the BPSS enabled the direct isolation of methyl pheophorbide A, identified by ^{1}H NMR. In contrast, fractionation of ELZU with the TPSS produced 104 fractions with distinct chemical profiles, demonstrating a broader selectivity window. Fractions from both experiments are currently under NMR analysis for the identification of additional constituents. Conclusion: The workflow, combining SS pre-selection via TLC and HPLC-DAD with CCC application, proved effective for fractionating complex natural product extracts. The BPSS was suitable for targeted, one-step isolation, while the TPSS provided greater versatility for exploratory separations.
1. A. Berthod, et al., J. Chromatogr. A 1216 (2009) 4206–4217.

Acknowledgements: The authors gratefully acknowledge the financial and institutional support from CNPq, FAPERJ, UFRJ, and IPPN.

APPLICATION OF HYDROPHOBIC DEEP EUTECTIC SOLVENTS IN DISPERSIVE LIQUID-LIQUID MICROEXTRACTION TO DETERMINE FLAME RETARDANTS IN SLUDGE SAMPLES BY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTOR

Letícia M. de Souza[1], Karen C. Ferreira[1], Guilherme Isquibola[2], Flávio J. Caires[2], Clóvis A. Ribeiro[1], Mario H. Gonzalez[3], Paulo Clairmont. F. de Lima Gomes[1]

[1]São Paulo State University (UNESP), Institute of Chemistry, Araraquara, SP, Brazil
[2]São Paulo State University (UNESP), School of Sciences, Department of Chemistry, Bauru, SP, Brazil
[3]São Paulo State University (UNESP), Department of Chemistry and Environmental Science, São José do Rio Preto, SP, Brazil

Polybrominated diphenyl ethers (PBDEs) are compounds used as flame retardants, which have been detected in environmental samples and are associated with risks to human health and aquatic ecosystems. Monitoring these compounds in complex matrices requires efficient sample preparation methods. In this context, hydrophobic deep eutectic solvents (HDES) have emerged as sustainable and versatile alternatives for miniaturized extraction techniques. Among them, dispersive liquid–liquid microextraction (DLLME) offers advantages such as reduced solvent consumption, rapidity, high extraction efficiency, and preconcentration capability. This study aimed to prepare HDES and evaluate their application as extraction solvents in DLLME for the determination of PBDE-28, PBDE-47, and PBDE-99 in sewage sludge samples using gas chromatography with electron capture detection (GC-ECD). The HDES was prepared using DL-menthol as the hydrogen bond acceptor (HBA) and organic acids (acetic and decanoic) as hydrogen bond donors (HBD). The HDES was characterized by Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Optimal DLLME conditions were 300 µL of HDES, 350 µL of acetonitrile, and a sample pH of 10. Limits of detection (LOD) and quantification (LOQ) ranged from 4.0 to 6.0 µg/L and from 13.0 to 20.0 µg/L, respectively. Intra and interday precision showed coefficients of variation (CV%) between 2.65% and 13.9%, demonstrating good repeatability. Linearity was observed in the analytical curves, with determination coefficients (R^2) ≥ 0.988, within the ranges of 20–140 µg/L for PBDE-28 and 13–91 µg/L for PBDE-47 and PBDE-99. Recoveries varied from 72.1% to 93.1%, despite significant matrix effects (ranging from 92.4% to 262%). Overall, the results confirmed the robustness of the method, with adequate precision and satisfactory recoveries. Moreover, HDES proved to be an efficient and sustainable solvent, highlighting its potential as a promising strategy for DLLME in the simultaneous determination of PBDEs in complex environmental matrices.

Acknowledgements: The authors wish to acknowledge the financial support from the FAPESP (grant #2022/02991-3 and #2024/02884-8) and São Paulo State University, Institute of Chemistry (Araraquara, Brazil).

APPLICATION OF MULTIPLE CHROMATOGRAPHIC TECHNIQUES IN THE ISOLATION OF FLAVONOIDS FROM Eugenia uniflora Linn

Camylla Janiele Lucas Tenório*[1], Anauara Lima e Silva[2], Josean Fechine Tavares[2], Janaína Carla Barbosa Machado[3], Mágda Rhayanny Assunção Ferreira[4], Luiz Alberto Lira Soares[5]

[1]NUDATEF, Dept. of Pharmaceutical Sciences, Federal University of Pernambuco (UFPE), Brazil; Post-Graduate Program in Therapeutic Innovation, UFPE, Brazil
[2]Post-Graduate Program in Bioactive Natural and Synthetic Products, Federal University of Paraíba (UFPB), Brazil
[3]NUDATEF, Dept. of Pharmaceutical Sciences, Federal University of Pernambuco (UFPE), Brazil; Post-Graduate Program in Pharmaceutical Sciences, UFPE, Brazil
[4]NUDATEF, Dept. of Pharmaceutical Sciences, Federal University of Pernambuco (UFPE), Brazil; Post-Graduate Program in Pharmaceutical Sciences, UFPE, Brazil; Dept. of Biomedical Engineering, Centre for Technology and Geosciences, UFPE, Brazil
[5]NUDATEF, Dept. of Pharmaceutical Sciences, Federal University of Pernambuco (UFPE), Brazil; Post-Graduate Program in Therapeutic Innovation, UFPE, Brazil; Post-Graduate Program in Pharmaceutical Sciences, UFPE, Brazil

* Corresponding author: camylla.tenorio@ufpe.br

Flavonoids from Eugenia uniflora L. (pitangueira) represent a class of metabolites of pharmacological relevance, often associated with the biological activities of the species. This study aimed to isolate and characterize flavonoids from its leaves. The plant material (Sisgen-A449575) was collected, identified, stabilized, and powdered, then extracted by turbolysis with acetone:water (7:3). After solvent removal and spray drying, an enriched fraction (EF) was obtained through sequential liquid–liquid extraction (LLE) with hexane (8x) followed by ethyl acetate (12x). EF was further fractionated on Sephadex LH-20 (SP), Flash Chromatography (Isolera®), and semi-preparative HPLC (Nexera®) using C18 columns and a mobile phase of methanol and acidified water (0.1% acetic acid). Subfractions were monitored by TLC (silica gel 60-F254, eluent 90:5:5 ethyl acetate:formic acid:water, derivatization with $AlCl_3$), characterized by LC-ESI(-)MS, and the isolates analyzed by direct-infusion ESI(-)MS/MS (50 to 1000 m/z). LLE enabled the concentration of polyphenols, which were subsequently separated into subclasses on SP, yielding flavonoid-enriched fractions (FrF, up to 19% w/w). From FrF, semi-purified subfractions rich in glycosylated flavonoids were obtained with the Isolera (SFlav, up to 41% w/w) and further isolated on the Nexera, leading to the identification of myricitrin (2.91 ppm), quercitrin (3.28 ppm), and afzelin (2.25 ppm). In addition, other putative flavonoids, such as myricetin-3-O-glucoside (3.52 ppm), myricetin-3-O-pentoside (2.85 ppm), myricetin-O-(O-galloyl)-rhamnoside (3.30 ppm), and isorhamnetin-O-glucopyranoside (3.14 ppm), were detected in subfractions. The integrated chromatographic strategy demonstrated effectiveness in isolating glycosylated flavonoids from E. uniflora, though some subfractions still need structural elucidation. As perspectives, these efforts will support more comprehensive phytochemical and biological studies and phytopharmaceutical potential.

Acknowledgements: CNPq/Brazil; iCEIS/UFPE; FACEPE.

Application of the isocratic mode in Countercurrent Chromatography for fractionation of phenolic compounds from the Dichloromethane Extract of Siparuna glycycarpa

Nayara Sales Ricardo*[1], Esthella Ariadny Souza Silva[2], Ana Beatriz S. Garcias[2], Diégina Araújo Fernandes[2], Simony Carvalho Mendonça[3], Suzana Guimarães Leitão[3], Gilda Guiramães Leitão[2]

[1]Programa de Pós-Graduação em Ciências Farmacêuticas (PPGCF/FF/UFRJ)
[2]Instituto de Pesquisa de Produtos Naturais (IPPN/UFRJ)
[3]Faculdade de Farmácia (FF/UFRJ)

* Corresponding author: nayara_sales0217@gmail.com

Siparuna glycycarpa (Siparunaceae) is a neotropical species native to the Brazilian Amazon, known for its chemical diversity, which includes alkaloids, chalcones, and flavonoids. The dichloromethane leaf extract (SGD) has demonstrated significant in vitro antiviral activity, with complete inhibition of the SARS-CoV-2 Spike (RBD:ACE2) interaction and 80% inhibition of the viral protease PLpro. Chemometric analyses conducted by our group pointed to alkaloids as key contributors to these effects. The aim of this work was to fractionate the dichloromethane extract of S. glycycarpa (SGD) leaves by countercurrent chromatography (HSCCC) for the isolation of potential anti-SARS-CoV-2 phenolic compounds. Several ratios of the hexane-ethyl acetate-methanol-water (HEMWat) solvent system (SS) were initially tested, and the one that gave a partition coefficient (K) near 1 for the target compounds was selected for SGD fractionation. Due to its complexity, part of the SGD extract was initially cleaned-up by liquid-liquid extraction with HEMWat 1:1:1:1 v/v and the lower phase (SGDL) was fractionated by HSCCC in the HTPrep apparatus with a 112 ml column (2.0mm i.d., flow rate 2.0ml/min) and HEMWat 7:3:6:4 as SS, in reversed isocratic elution mode and head-to-tail elution. In total, 110 fractions of 4 ml were collected (80 in the during elution mode and 30 in the extrusion mode). Fifteen final fractions were obtained by grouping according to TLC profiles, assessed under UV light (254 and 356 nm) and after derivatization with NP-PEG reagent. Fractionation of SGDL by CCC under the mentioned conditions was selective for the separation of phenolic constituents, yielding two dihydrochalcones, 2',6'-dihydroxy-4,4'–di-O-methyl dihydrochalcone - [M-H]-301 m/z - and 2',6'-dihydroxy-4'-O-methyl-dihydrochalcone - [M-H]-271 m/z - in fractions 20-25 and 36-56, respectively and identified by ^{1}H NMR. All the fractions were analyzed by LC-MS/MS that annotation 3 alkaloids with mass-to-charge ratios of [M+H] +330, [M+H] +282 and [M+H]+312 m/z in fractions 7, 8 and 9. Further studies are being done to isolate the alkaloids.

Acknowledgements: CAPES, CNPq and FAPERJ.

APPLICATION OF UHPLC-QTOF MS IN MONITORING DEGRADATION BY-PRODUCTS THROUGH ADVANCED OXIDATION PROCESSES

Gabrielly Machado dos Santos*[1], Eduardo Oliveira Marson[1], Lucas Gustavo da Costa[1], Carla Fernanda Grasel Frois[2], Raquel Wielens Becker[3], Carla Sirtori[3], Alam Gustavo Trovó[1]

[1]Federal University of Uberlândia
[2]Federal University of Rio Grande do Sul
[3]Federal University of Santa Maria

* Corresponding author: gabrielly.santos@ufu.br

Determining the transformation products generated by advanced oxidation processes in matrices containing persistent organic microcontaminants is crucial to assessing the efficiency and safety of the treatment. While these processes are effective at degrading target contaminants, they can produce by-products that are more reactive or toxic than the original compound. Therefore, identifying and characterizing these molecules is essential for understanding degradation pathways and estimating environmental and health risks. Thus, the transformation products formed from colchicine and nitazoxanide, present in tertiary wastewater and exposed to the advanced oxidation process H2O2/UVC, were determined by ultra-high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UHPLC-QTOF MS), operating in bbCID mode (MS: 4 eV; MS/MS: 25–50 eV). Separation was achieved on a C18 column, using 0.1 % formic acid (phase A) and HPLC-grade methanol (phase B) as the mobile phase under a programmed gradient: 0 min – 5 % B; 10 min – 90 % B; 12 min – 90 % B; 12.1 min – 5 % B; 17.1 min – 5 % B. The injection volume was 5 µL, with a flow rate of 0.5 mL min^{-1}. Data were acquired over the m/z range 50–1000, with a scan rate of 2 Hz, and processed using Data Analysis 4.2 software, with molecular formula assignment based on DBE and mass error ≤ 5 ppm. Four TPs were identified for nitazoxanide (retention times: 9.0, 4.1, 5.8 and 3.7 min) and four for colchicine (6.0, 6.1, 6.6 and 8.2 min). Notably, six of the eight transformation products were identified for the first time, with no prior reports in the literature, contributing to a better understanding of the degradation mechanisms involved. Therefore, applying the UHPLC-QTOF MS technique was essential to identifying the transformation products formed during the H2O2/UVC process. This approach allowed for efficient monitoring of advanced oxidation process, providing relevant structural data of the transformation products and contributing to the assessment of the environmental impact of persistent microcontaminants.

Acknowledgements: The authors thank CAPES, CNPq and RELAM-UFU for financial support and access to analytical infrastructure.

Approaches for Reducing the Environmental Impact and Increasing the Throughput of LC Separations

Arianne Soliven*[1], Matt James[2], Mark Fever[2], Tony Edge[2]

[1]Avantor, 1 The Markham Centre, Station Road, Theale, Reading RG7 4PE UK; Avantor, Minas y Cebollati, Montevideo, 11200 Uruguay.
[2]Avantor, 1 The Markham Centre, Station Road, Theale, Reading RG7 4PE UK

* Corresponding author: arianne.soliven@avantorsciences.com

Many analytical laboratories are increasingly focusing on approaches to reduce their environmental footprint. This is particularly important in high-throughput environments, where the large number of samples analysed results in significant solvent usage and waste disposal, detrimental to both the environment and running costs.

Significant reductions in solvent consumption and waste generated are possible, without compromising data quality, by translating existing LC methods to narrower bore columns. Additionally, this approach can also be used to enhance sensitivity for low detection level assays. This concept can be further extended by employing shorter columns packed with smaller particles to reduce analytical run times. This has a demonstrable impact on the electrical consumption per analysis, whilst providing the added benefit of improved laboratory efficiency and reduced running costs.

This poster explores the possibilities outlined above and demonstrates the potential gains that can be achieved for isocratic and gradient LC methods (e.g. up to 86.7% reduction in solvent use, 86.2% reduction in electrical consumption and 89.3% reduction in run time). Often, it is perceived that significant gains can only be made by upgrading to UHPLC instrumentation, however, it is often feasible to adapt established methods and better utilise existing equipment to realise substantial improvements. In one example, 71.9% reduction in solvent use and 57.3% reduction in electrical consumption and 60.4% reduction in analysis time was easily achieved on a 400 bar HPLC system. Finally, practical considerations, such as the impact of system dispersion on data quality when moving methods to narrower bore columns, are discussed.

Acknowledgements: Johnny Lima, Nova Analítica; Jose Cuadro, Zachary Stellbgerg, and Leandro Kasamatsu, Avantor for their additional support.

AQBD-GUIDED DEVELOPMENT OF A UHPLC STABILITY-INDICATING METHOD FOR CANNABIDIOL (CBD) AND ITS DEGRADANTS FOR PHARMACEUTICAL PRODUCT DEVELOPMENT AND QUALITY CONTROL

Ananda Pulini Matarazzo*[1], Bianca Furukawa de Godoi Passerine[2], Márcia Cristina Breitkreitz[2]

[1]Faculty of Pharmaceutical Sciences, State University of Campinas
[2]Institute of Chemistry, State University of Campinas

* Corresponding author: a237288@dac.unicamp.br

Cannabidiol (CBD) is a phytocannabinoid of great therapeutic interest, whose stability under different chemical stress conditions is essential to ensure the quality and safety of pharmaceutical formulations. This study aimed to develop and optimize a UHPLC stability-indicating method using the Analytical Quality by Design (AQbD) framework for the separation of CBD degradation products subjected to acidic, basic, and oxidative stress. In the screening phase, an A- and G-optimal design was applied to evaluate four chromatographic columns (CSH Fluoro-Phenyl, Cortecs C18, HSS T3, and Triart Phenyl), two organic modifiers (acetonitrile and methanol), pH values (3.0, 4.5, and 6.0), and column temperatures (30–40 °C). Flow rate was fixed at 0.3 mL/min, organic phase percentage ranged from 40 to 70%, injection volume was 2 µL, and detection was performed at 208 nm. The trend responses considered for evaluation were the number of peaks, the number of peaks with resolution >1.5 and >2.0, and peak tailing

Acknowledgements: The authors gracefully acknowledge the financial support provided by CAPES, Croda Pharma, and Ease Labs.

ASSESSMENT OF NITROSODIMETHYLAMINE GENERATION IN VETERINARY DRUG FROM FORCED DEGRADATION TESTS MONITORED BY HPLC-DAD

João Pedro Matos Silva*, Fábio Roberto Fogaça Filho, Anizio Marcio de Faria

Universidade Federal de Uberlândia

* Corresponding author: pjoao3369@gmail.com

The pharmaceutical industry is one of the largest sectors of the global economy. According to ANVISA, the sale of medications generates more than 130 billion reais annually in Brazil. This scenario implies large-scale production for consumption, making it essential to rigorously verify the quality and safety of medications to ensure that they do not pose health risks. Recently, studies indicated the formation of N-nitrosodimethylamine (NDMA), a potentially toxic compound, in medicines with the active pharmaceutical ingredient ranitidine hydrochloride. The ban on marketing was worldwide, and the episode revealed the need for greater control over production. Considering the possibility of formation of these compounds with carcinogenic potential, in the present work, a forced degradation study of the veterinary drug Ranivet 80 mg was carried out to evaluate their degradation products and the potential generation of NDMA. The powder drug (20 mg) was subjected to stress conditions: thermolysis, acid hydrolysis, basic hydrolysis, oxidation, and photolysis at 365 nm. Solutions after degradation studies were analyzed by high-performance liquid chromatography (HPLC), using a C18 column and mobile phase composed of ACN:H2O under gradient elution, and detection by a diode array detector at 228 nm. Forced degradation tests led to the formation of seven ranitidine degradation products (DPs). Under more extreme conditions (prolonged time and/or higher concentrations of degrading agents), complete degradation (>99%) of the drug was observed. Of these DPs formed, the formation of the toxic compound NDMA stood out, observed specifically in hydrolytic (acidic or basic) degradations under heating at 55 °C. Confirmation of the identity of NDMA was performed by comparing it with an analysis of the NDMA standard solution under the same analysis conditions. Ranitidine DPs were identified through chromatographic profile analysis and comparison with the ranitidine chromatograms and their impurities recorded by regulatory agencies. Thus, the forced degradation of Ranivet proved efficient and valuable in assessing the potential generation of toxic products, confirming the NDMA formation on the veterinary drug.

Acknowledgements: FAPEMIG (APQ-1901-22 and PCE-00390-25), CNPq, and FINEP (01.13.0371.00).

ASSESSMENT OF PAHs BY GC-MS IN FISH SAMPLES FROM THE MANGROVES OF THE CAETÉ RIVER ESTUARY, BRAGANÇA, PARÁ.

Luana Karla Araújo do Nascimento[1], Letícia Furtado dos Santos[2], Cássia Christina da Silva Rocha[2], Jaqueline Patrício da Costa[2], Rosivaldo de Alcântara Mendes[2]

[1]State University of Pará
[2]Evandro Chagas Institute

Mangroves are ecosystems of great biodiversity and ecological importance. They support the coastal food chain and serve as a source of livelihood for local populations, especially through fishing. However, these environments have been degraded due to human actions, such as pollution. Furthermore, contamination by toxic compounds, such as polycyclic aromatic hydrocarbons (PAHs), poses a risk to human health. Objectives: To evaluate the concentration of PAHs present in fish samples from the mangroves of the Caeté River estuary, Bragança, Pará. Materials and Methods: The study was conducted on the Bragança Peninsula, in the Caeté River mangrove. Seventy fish samples of different species with variable distribution were collected: bandeirado (Bagre bagre), corvina (Plagioscion squamosissimus), dourado (Brachyplatystoma flavicans), gó (Macrodon ancylodon), and yellow hake (Cynoscion acoupa). Initially, 2 g of each sample was weighed, followed by the addition of 5 mL of dichloromethane (CH_2Cl_2). Microwave-assisted extraction (MAE) was applied to accelerate the isolation of the compounds. The obtained extract was purified by solid-phase extraction (SPE) with C18 cartridges, silica gel, and anhydrous sodium sulfate to remove impurities. Elution occurred with dichloromethane and hexane, followed by concentration to 1 mL in a rotary concentrator. The purified samples were analyzed by gas chromatography coupled to triple quadrupole mass spectrometry (GC-MSMS). Results: The PAHs with the highest concentrations were naphthalene (12.83 µg/kg in Gó), fluorene (17.84 µg/kg in Bandeirado), and phenanthrene (20.53 µg/kg in Gó), all above the limit established by ANVISA. The average value of benzo[a]pyrene equivalent (BaP eq..) was 0.10 µg/kg, remaining below the risk level. The predominance of low molecular weight PAHs indicates petrogenic contamination in the mangrove, possibly associated with vessel traffic and fuel disposal. Conclusion: The results reinforce the need for continuous environmental monitoring and measures to preserve the ecosystem and food security for the local population.

Acknowledgements: National Research Council (CNPq) and the Amazon Foundation for Studies and Research Support of the state of Pará (FAPESPA) for their financial support.

AVALIAÇÃO DA BIOACESSIBILIDADE IN VITRO DE VITAMINA C EM KOMBUCHÁ EM PÓ COMERCIALIZADO EM FORTALEZA-CE POR HPLC

Luana Guabiraba Mendes*[1], Crisiana de Andrade Nobre[2], Antonia Fadia Valentim de Amorim[2], Fuad Prereira Nogueira Filho[2], Felipe Sousa da Silva[2], Antonia Carlota de Souza Lima[3], Luciana de Siqueira Oliveira[3], Maria Aparecida Liberato Milhome[4]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará - IFCE
[2]Núcleo de Tecnologia e Qualidade Industrial do Ceará – NUTEC
[3]Universidade Federal do Ceará – UFC
[4]Instituto Federal de Educação, Ciência e Tecnologia do Ceará – IFCE

* Corresponding author: luanagmendes@gmail.com

O kombuchá, uma bebida fermentada tradicionalmente consumida por seus benefícios à saúde, tem visto sua oferta se diversificar, com destaque para o formato em pó. Considerando que a simples presença de um nutriente não garante sua absorção pelo organismo, a avaliação da bioacessibilidade torna-se crucial. Neste contexto, este trabalho objetivou avaliar a bioacessibilidade in vitro de vitamina C (ácido ascórbico) em amostras de kombuchá em pó de diferentes sabores (K1: Amora, K2: Laranja, K3: Abacaxi) de uma mesma marca, comercializadas em lojas de produtos naturais de Fortaleza - CE. A metodologia consistiu na preparação das amostras conforme instruções do fabricante, seguida de simulação da fase oral da digestão. A quantificação do ácido ascórbico, antes e após a digestão, foi realizada por Cromatografia Líquida de Alta Eficiência (HPLC) com detector UV-Vis (254 nm), utilizando fase móvel de KH_2PO_4 0,2 M (pH 2,4) e vazão de 0,8 mL/min. O método analítico demonstrou linearidade, com curva de calibração na faixa de 5 a 80 $mg \cdot L^{-1}$ apresentando coeficiente de determinação (R^2) de 0,998. Os resultados revelaram teores iniciais significativamente diferentes entre os sabores, sendo 25,78 mg/100g (K1), 17,12 mg/100g (K2) e 10,01 mg/100g (K3). Após a fase oral da digestão, observou-se uma redução drástica e estatisticamente significativa ($p < 0,05$) nestes teores, com as concentrações caindo para 5,38 mg/100g, 0,52 mg/100g e 1,04 mg/100g para K1, K2 e K3, respectivamente. Estas reduções representam perdas de aproximadamente 79%, 97% e 90% da vitamina C inicial. Os dados indicam uma baixíssima bioacessibilidade do composto após a fase oral, possivelmente devido à degradação oxidativa acelerada pelas condições do processo digestivo, como variação de pH e presença de enzimas, ou por interações com outros componentes da matriz do pó. Conclui-se que as amostras de kombuchá em pó analisadas sofrem degradação deste nutriente durante a digestão. O estudo reforça a importância de avaliar a bioacessibilidade e sugere a necessidade de investigar estratégias de proteção ou estabilização da vitamina C nesta matriz específica.

Acknowledgements: National Institute of Food Science and Technology (INCT-ALIM); Instituto Federal de Educação, Ciência e Tecnologia do Ceará – IFCE.

AVALIAÇÃO DO EFEITO MATRIZ NA DETERMINAÇÃO DE AGROTÓXICOS EM HORTALIÇAS POR LC-MS/MS UTILIZANDO FONTES DE IONIZAÇÃO ESI E APCI

Renata de Oliveira Silva*[1], Cleidiane Gomes Lima[1], Denilson Gonçalves Queiroz[1], Felipe Sousa da Silva[1], Crisiana de Andrade Nobre[2], Mairlane Silva de Alencar[2], Ronaldo Ferreira Nascimento[2]

[1]Núcleo de Tecnologia e Qualidade Industrial do Ceará
[2]Universidade Federal do Ceará

* Corresponding author: renata.oliveira@nutec.ce.gov.br

Nos trabalhos de validação de métodos o estudo do efeito matriz é fundamental, especialmente quando se tratam da análise de amostras complexas, como alimentos. Como sabido, a análise de compostos de interesse pode sofrer interferência de outras substâncias, notadamente conhecido como efeito de matriz. Em LC-MS/MS essa interferência ocorre no momento da ionização em decorrência da competição no processo de ionização, fazendo com que o sinal do analito em questão seja intensificado ou suprimido. O objetivo principal é comparar o efeito matriz de agrotóxicos de diferentes classes em amostras de hortaliças, utilizando as fontes de ionização à pressão atmosférica (API), em um sistema LC-MS/MS: Ionização por Eletrospray (ESI) e Ionização Química à Pressão Atmosférica (APCI). Foram avaliadas as figuras de mérito como seletividade, limites de detecção (LD) e de quantificação (LQ), linearidade e exatidão, através de ensaios de recuperação. As curvas analíticas foram validadas estatisticamente, e apresentaram uma boa linearidade em ambas as fontes, com coeficientes de determinação acima de 0,99, estando de acordo com as normas adotadas pela ANVISA. Os resultados apresentaram uma variação de sinais tanto positivo como negativo para os compostos em ambas as fontes, confirmando a importância de se estudar curvas preparadas no extrato da matriz durante a etapa de desenvolvimento de métodos, principalmente por se tratar de amostras complexas. Na fonte ESI, ocorreu uma maior variabilidade (intensificação e supressão) de sinal entre os compostos nas nas três matrizes estudadas, na qual o percentual de efeito matriz destes compostos foram superiores ao determinado na APCI, principamente os agrotóxicos de maior polaridade. Na fonte APCI ocorreu uma supressão de sinal em praticamente quase todos os compostos. ESI e APCI se complementam, pois não há critério exclusivo para escolher a interface mais adequada e sensível quando novos métodos analíticos estão sendo desenvolvidos para pesticidas, especialmente em análise de multirresíduos.

Acknowledgements: INCT-ALIMENTOS, NUTEC e UFC

AVALIAÇÃO DO PERFIL DE COMPOSTOS VOLÁTEIS DO FRUTO E DA FARINHA DE CARNAÚBA (Copernicia prunifera) POR CROMATOGRAFIA ULTRA-RÁPIDA

Vanessa Rodrigues Lima*, Jéssica Roberta Pereira Martins, Laércio Galvão Maciel, Maria Aparecida Liberato Milhome, Virna Luiza de Farias, Daniele Maria Alves Teixeira Sá

Instituto Federal de Educação, Ciência e Tecnologia do Ceará

* Corresponding author: vanessa.rodrigues.lima08@aluno.ifce.edu.br

A carnaúba (Copernicia prunifera), uma árvore nativa do nordeste do Brasil, produz frutos comestíveis pouco explorados. O aroma é um fator-chave de qualidade que influencia a aceitabilidade do consumidor, e sua caracterização pode ajudar a valorizar o fruto e sua farinha. Este estudo teve como objetivo diferenciar os perfis de compostos orgânicos voláteis do fruto fresco da carnaúba e sua farinha processada usando sistema HERACLES Neo-Alpha MOS baseado em cromatografia ultra-rápida, o qual possui dois sistemas de detecção, permitindo uma detecção mais aprimorada dos componentes. Para cada amostra, 2,0 g de cada amostra foram colocados em vials de 20 mL de headspace e mantidos por 40 °C por 15 min sob agitação a 500 rpm. Posteriormente, 1000 µL do gás de headspace foram injetados no injetor a 200 °C, com dessorção térmica a 40 °C por 18 s. O hidrogênio foi usado como gás de arraste (10 mL/min), e a separação ocorreu em colunas MXT-5 e MXT-1701 sob um gradiente de temperatura de 50 a 250 °C, com o detector ajustado em 260 °C. Cada amostra foi analisada em triplicata. Os resultados da Análise de Componentes Principais (PCA) mostraram uma diferenciação clara e estatisticamente significativa entre os perfis de aroma da fruta fresca e da farinha, com amostras de cada grupo formando clusters distintos. De acordo com o índice Curvax, compostos correspondentes a acetaldeído, propenal, 1-propanol, 2-metilbutanal, 3-metilbutanal e L-limoneno foram encontrados no fruto, enquanto na farinha, compostos correspondentes a acetaldeído e 1-propanol foram identificados. A redução na diversidade de compostos voláteis nafarinha provavelmente se deve às etapas de secagem e moagem, que causam a volatilização ou degradação de moléculas aromáticas mais instáveis. O fruto da carnaúba apresenta um perfil aromático diversificado, e a farinha retém os compostos aromáticos do fruto, apesar das alterações sensoriais decorrentes do processamento. Esses resultados fornecem informações importantes para a utilização e valorização dessa matéria-prima regional ainda pouco explorada.

Acknowledgements: INCT-ALIM (CNPq), FINEP, FUNCAP, CAPES, IFCE

BALLS-IN-TUBE MSPD METHOD FOR THE SIMULTANEOUS DETERMINATION OF PAHs AND ANTHRAQUINONE IN YERBA MATE USING GC-MS

Dylan Mehler Hoffmann*, José Dilson da Silva, Igor F. de Souza, Gabriel A. Prates Barbosa, Vagner Americo Dutra, Osmar Damian Prestes, Renato Zanella

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria -RS, Brazil

* Corresponding author: dylan.mehler@acad.ufsm.br

Yerba mate (Ilex paraguariensis), widely consumed in South America, is valued for its bioactive compounds, such as polyphenols and methylxanthines. However, during its traditional processing, primarily in the fire-based scorching and drying steps, polycyclic aromatic hydrocarbons (PAHs) and anthraquinone (AQ), compounds with potential carcinogenic effects, may be formed. This study aimed to develop and validate an analytical method based on the balls-in-tube matrix solid-phase dispersion (BiT-MSPD) technique, followed by gas chromatography-mass spectrometry (GC-MS), for the simultaneous determination of 16 priority PAHs and AQ in yerba mate samples. Key parameters, including sorbent type, extraction solvent, sample-to-sorbent ratio, and extraction time, were optimized. The validated method demonstrated good linearity ($r^2 > 0.99$), with limits of detection ranging from 1.8 to 3.6 µg kg^{-1}, recoveries between 70 and 120%, and acceptable precision (RSD ≤ 20%). The method was applied to 31 yerba mate samples, comprising 20 commercial products and 11 samples collected at different stages of the industrial processing. The majority of commercial samples contained detectable HPAs. In samples from different stages of processing, some had contamination levels above the limit allowed by the European Union. Anthraquinone was detected in 40% of the samples, with some levels above the permitted limit of 20 µg kg^{-1}. These results confirm that traditional scorching and drying practices contribute to the formation of these contaminants, underscoring the need to modernize industrial processing. The proposed BiT-MSPD method proved to be efficient, rapid, and sustainable, offering a promising tool for quality control and food safety monitoring of yerba mate.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

CALCULATOR TO PREDICT SAMPLE VAPOR VOLUME AND ANALYTE RECOVERY FOR SPLIT/SPLITLESS INJECTION IN GAS CHROMATOGRAPHY

Iris Araújo Silva*[1], Thiago Pacheco Virgínio[2], André Fernando de Oliveira[1], Maria Eliana Lopes Ribeiro de Queiroz[1], Claudia Moraes de Rezende[2], Fábio Junior Moreira Novaes[1]

[1]Federal University of Viçosa
[2]Federal University of Rio de Janeiro

* Corresponding author: iris.silva@ufv.br

An Excel spreadsheet was developed for Gas Chromatography (GC) users to quickly determine the best chromatographic conditions for sample introduction in split/splitless injectors. It is based on the Clapeyron equation to present a 3D graph of the volume of sample vaporized in the injection chamber (Vg) as a function of the chosen sample solvent, liner model, injection volume (Vinj, µL), temperature (T, °C), and pressure (P, psi) in the injector. The color-coded graphic representation enables the recognition of injector saturation conditions when Vg exceeds the liner's internal volume, as indicated by the calculated value and a red background color (backflash effect). Risk areas are shown in yellow, and potential efficiency areas for sample transfer to the capillary tube are shown in green. The spreadsheet was compared with others available online for consultation and download from companies that manufacture and sell GC equipment and consumables. The predictive values were equivalent, with particular emphasis on greater intuitiveness and quick visualization of the response through the three-dimensional graphical representation (Vg × T × P), which allows for the simultaneous comparison of multiple injection scenarios (liner model × sample solvent × Vinj × T × P), in just a few clicks, saving time and facilitating the identification of the best predictive injection conditions. The spreadsheet was validated through several injection experiments involving a saturated n-alkane mixture (C10-C40) to determine the sample transfer rate to the capillary by the total and individual area of its components. The results did not reflect the linear-decreasing behavior of the theoretical data, given the strong interaction between T and P, demonstrated by a quadratic mathematical model with curved response surfaces in the shape of an elliptical paraboloid. To the detriment of this study, it is recommended that new and experienced chromatographers use the developed spreadsheet and the obtained experimental graphs as a guide tool in choosing injection conditions before starting their work, considering the size of the hydrocarbon chain and/or the linear retention index of the analyte in question, whether for analytical or preparative scale (prep-GC).

Acknowledgements: To FAPEMIG for financial support with this project and to CAPES for the student research grant.

CARACTERIZAÇÃO QUÍMICA DO ÓLEO ESSENCIAL DE Hyptis crenata Pohl ex Benth E ANÁLISE DO COMPLEXO DE INCLUSÃO EM β-CICLODEXTRINA POR GC-MS.

Lohanne Conceição Sarmento*[1], Edenilson dos Santos Niculau[2], Daniel Augusto Barra de Oliveira[2]

[1]Universidade Federal do Sul e Sudeste do Pará
[2]Universidade Federal do Norte do Tocantins; Universidade Federal do Sul e Sudeste do Pará

* Corresponding author: lohanne@unifesspa.edu.br

A espécie Hyptis crenata é conhecida popularmente como Salva do Marajó, é nativa do Brasil e distribuída nas regiões Norte, Nordeste, Centro-Oeste e Sudeste. O óleo essencial (OE) desta planta possui atividades antibacterianas e antifúngicas. No entanto, o OE manifesta limitações quanto a solubilidade, biodisponibilidade e volatilidade, diante disso o microencapsulamento é uma forma de minimizar estas problemáticas atuando como uma barreira de proteção. Este trabalho visa determinar, semiquantificar os compostos químicos do OE da espécie H. crenata na forma livre e encapsulada em β-Ciclodextrina (β-CD) e avaliar a eficiência do complexo de inclusão. O OE foi obtido por meio da hidrodestilação em aparelho do tipo Clevenger durante 3 horas, usando 200 g de folhas frescas e 1000 mL de água destilada. O complexo de inclusão foi preparado através da técnica de maxalagem de dois modos: etanol (MAE) e água/etanol (MAAE) em uma combinação de β-CD e OE na proporção 1:1 baseado na massa molecular do 1,8-cineol. A identificação do perfil químico foi realizada por cromatografia gasosa aclopada ao espectrômetro de massas (GC-MS) e para a semiquantificação usou-se timol como padrão interno a 50 µg/mL. Em média a composição química do OE apresentou 49 compostos e identificados 37, cujo os majoritários foram: 1,8-cineol (153,30 µg/g), α-pineno (89,36 µg/g), cânfora (84,45 µg/g), β-pineno (66,62 µg/g), limoneno (31,82 µg/g), e borneol (22,89 µg/g). Em MAAE, os principais compostos foram: 1,8-cineol (3,9 µg/g 7), cânfora (2,54 µg/g) e α-pineno (1,05 µg/g); e em MAE: 1,8-cineol (4,56 µg/g) e cânfora (2,34 µg/g). Para o óleo total, em MAAE, foram semiquantificados: 1,8-cineol (22,75 µg/g), cânfora (17,31 µg/g), α-pineno (6,34 µg/g), β-pineno (6,59 µg/g), borneol (6,82 µg/g) e α-terpineol (5,24 µg/g); e em MAE somente dois compostos majoritários 1,8-cineol (14,95 µg/g) e cânfora (10,26 µg/g). Com base nos resultados, o maior desempenho de encapsulamento foi em MAAE tanto em óleo total como também em superfície, pois o processo manteve a maioria dos compostos. Este melhor desempenho é devido ao etanol atuar como segundo solvente e favorecer maiores interações, entre elas a de Van der Waals. Estes dados demonstram que o encapsulamento pode ser uma alternativa promissora para evitar a degradação de compostos voláteis.

Acknowledgements: Agradecimentos: CAPES e INCT-ALIM (processo 406760/2022-5).

CARACTERIZAÇÃO QUÍMICA DOS ÓLEOS ESSENCIAIS DE POPULAÇÕES NATURAIS DE Lychnophora pinaster Mart. POR CROMATOGRAFIA GASOSA BIDIMENSIONAL ABRANGENTE

Júlio César Rodrigues Lopes Silva[1], Leila Gimenes[1], Roselaine Facanali[1], Leandro Wang Hantao[2], Marcia Ortiz Mayo Marques*[1]

[1]Instituto Agronômico (IAC), Campinas-SP, Brasil
[2]Instituto de Química (IQ), Universidade de Campinas-SP, Brasil

* Corresponding author: marcia.marques@sp.gov.br

Lychnophora pinaster Mart. é uma espécie medicinal e aromática endêmica dos campos rupestres de Minas Gerais. Popularmente conhecida como "arnica" ou "arnica-mineira", é amplamente utilizada na medicina tradicional devido às suas propriedades anti-inflamatórias e cicatrizantes, especialmente no tratamento de contusões e feridas. Suas populações naturais estão distribuídas em diferentes mesorregiões do estado, sob condições edafoclimáticas variadas, sendo sua diversidade química pouco explorada. A complexidade dos óleos essenciais (OEs) de L. pinaster é comumente associada a coeluições de seus constituintes químicos, e demandam técnicas analíticas avançadas para uma caracterização precisa. Nesse contexto, a cromatografia gasosa bidimensional abrangente (GC×GC) surge como uma ferramenta eficiente, permitindo a resolução de misturas complexas. Diante disso, este estudo teve como objetivo caracterizar a composição química dos OEs de populações naturais de L. pinaster de Minas Gerais, utilizando a técnica de cromatografia gasosa bidimensional abrangente (GC×GC). As folhas foram coletadas em dez populações naturais (GM, OD, ODMa, DI, DIMa, NLSC, RPS, SRM, SM e CTRA) localizadas em diferentes mesorregiões do estado (Norte de Minas, Jequitinhonha e Metropolitana de Belo Horizonte). Para cada população foram analisados dez indivíduos, totalizando 100 amostras. Os óleos essenciais foram extraídos por hidrodestilação (3 h) e analisados pela técnica de cromatografia gasosa bidimensional abrangente acoplada aos detectores de espectrometria de massas e ionização em chamas (GC×GC-EM/FID). Análises multivariadas (PCA, HCA e PLS-DA) foram aplicadas para avaliar as variações químicas entre as populações. Foram identificados 103 compostos, com predominância de sesquiterpenos oxigenados. As substâncias majoritárias observadas para a maioria das populações são derivadas de humuleno e cariofileno como o 14-acetoxi-α-humuleno (majoritário em NLSC e SRM), o 14-hidroxi-α-humuleno (abundante em GM, OD e DI) e o 14-hidroxi-9-epi-(E)-cariofileno (majoritário em ODMa). A população RPS destacou-se pelo elevado teor de β-pineno (47,16%). A técnica GC×GC mostrou-se eficiente na resolução de coeluições, como no caso do γ-cadineno e 4-oxo-15-nor-eudesmano-11-eno. A PCA revelou variações químicas significativas entre as populações, com maior homogeneidade entre aquelas das regiões Norte de Minas e Jequitinhonha. Os resultados demonstram que a GC×GC é uma ferramenta poderosa para a caracterização detalhada da composição química dos óleos essenciais de L. pinaster, revelando uma diversidade química significativa entre as populações naturais e destacando o potencial da espécie como fonte de substâncias bioativas em diferentes regiões de Minas Gerais.

Acknowledgements: FAPESP (2017/50338-9 e 2018/25812-1), CAPES e CNPq (307929/2022-1)

CHARACTERIZATION AND EVALUATION OF THE POTENTIAL OF TILAPIA DERIVED PYROLYTIC BIO-OIL FOR GREEN DIESEL FORMULATION

Nudson S. Santos*[1], Fabiana P. de Sousa[1], Leandro C. Fontoura[1], Euclésio S.[2], Lincoln C. S. de Oliveira[1], Carlos E. D. Nazário[1]

[1]Federal University of Mato Grosso do Sul (UFMS)
[2]State University of Mato Grosso do Sul (UEMS)

* Corresponding author: nudson.souza.obq@gmail.com

The use of drop-in biofuels is an important alternative to help reduce CO_2 emissions from fossil fuel combustion, thus plays a strategic role in mitigating climate change and ensuring national energy autonomy. These biofuels can be produced through various thermal processes, with the pyrolysis of fatty materials – including animal or vegetable oils – being one of the most relevant. Brazil is among the countries with the highest growth in fish farming, especially Nile tilapia, of which 68% is discarded as waste or fertilizer. In this study, oil was extracted from Nile tilapia residues (bones and tails) and converted via pyrolysis to produce bio-oil for potential use in green diesel formulation. The lipid profile of tilapia oil was determined by gas chromatography using a Shimadzu GC-FID system equipped with a BPX-70 column (30m × 0.25mm × 0.25µm). The analysis revealed a predominance of palmitic acid (C16:0, 23.37%) and oleic acid (C18:1, 34.73%), indicating compatibility with hydrocarbon chains typically found in diesel fractions. Additionally, the crude oil showed moderate oxidative stability (5 h), as measured by the RANCIMAT method. The TG and DTG curves indicated the onset of oil degradation at 240,37 °C in synthetic air atmosphere and 307,22ºC in nitrogen (N2). The DSC curve showed crystallization peaks at 2,31 °C and -26,43 °C, attributed to saturated and unsaturated compounds, respectively. After thermal cracking (500 – 670 °C), the analysis of bio-oil in Shimadzu GCMS-QP2010 system equipped with RTX-was column (30m × 0.25mm × 0.25µm) presented a composition of 77.9% fatty acids (23.4% palmitic acid and 17.7% oleic acid), 11.9% hydrocarbons, and 10.2% of other compounds (alcohols, ketones). The thermal degradation of the bio-oil began at 38.99 °C, close to the minimum required for fossil diesel (38 °C), and crystallization onset was observed at 9.58 °C, likely due to the high fatty acid content. The results demonstrate that, following pyrolysis process optimization (including the use of specific catalysts), tilapia derived oil shows strong potential as a sustainable raw material for production hydrocarbon rich bio-oil suitable for green diesel formulation.

Acknowledgements: My sincere thanks to CAPES, UFMS and Fuel Laboratory.

Characterization of Diesel Oil Using Comprehensive Two-Dimensional Gas Chromatography Coupled to Mass Spectrometry (GC×GC-FID/MS)

Lucas Gabriel da Silva do Carmo*, Nathan de Souza Coelho, Helvécio Costa Menezes

Universidade Federal de Minas Gerais, Department of Chemistry, Belo Horizonte, MG, Brazil

* Corresponding author: lgabrieldasil@gmail.com

Diesel oil is a complex mixture of hydrocarbons derived from petroleum primarily composed of paraffins, naphthenes and aromatics typically containing carbon chains between C9 and C25. It is very important for the economy because it is used as a fuel for transportation, heavy machinery and has many industrial applications due to its efficiency. Diesel's chemical composition varies depending on its source and refining processes, making its characterization essential for quality control, regulatory compliance, and environmental monitoring. So, the composition of diesel must meet strict regulatory specifications, including paraffinic content 15-62%, as defined by ANP (National Agency of Petroleum, Natural Gas, and Biofuels) regulations (Resolution 968/2024). Comprehensive Two-Dimensional Gas Chromatography coupled with Flame Ionization Detection/Mass Spectrometry (GC×GC-FID/MS) provides superior separation power for characterizing these hydrocarbons compared to conventional methods. This study focuses on optimizing GC×GC-FID/MS conditions to achieve complete separation and quantification of paraffinic compounds in diesel oil. The GCxGC-FID/MS system will allow the separation and identification of compounds in diesel, using columns of different polarities and optimizing critical parameters such as system temperature, injection volume, and modulation time to ensure an efficient and precise analysis. Given this, the best conditions found for the method was: the sample injection volume set at 1.0 µL, the injector temperature at 280 °C, the carrier gas used was H_2 with a constant flow rate of 1.0 mL min^{-1}, the initial oven temperature was 40 °C, increasing at a rate of 1.5 °C min^{-1} with a run time of 175 minutes, and the mass spectrometer temperature at 300 °C. 96 compounds were separated with peaks showing resolution (R) above 1.5 and a signal-to-noise ratio (SNR) above 10. Therefore, the method proved to be effective in separating the main components of diesel oil. In the next step, a validated analytical curve will be developed to accurately determine the paraffinic content within the specified regulatory range (15-62%), ensuring compliance with fuel quality standards. Following this, a chemometric model will be developed to correlate the paraffinic content, determined through GC×GC, with the physicochemical test data of the samples. This will allow the prediction of their physicochemical properties using only a single chromatogram.

Acknowledgements: Acknowledgements: The authors gratefully acknowledge the financial support provided by PRH-ANP (Resolution 918/2023) through FAPESP [Grant 2024/12554-5] and UFMG.

Characterization of Key Terpenes in Brazilian Seasonings Using Green Microextraction Coupled with GC×GC/MS and Odor Activity Value (OAV)

Jhonatan Bispo de Oliveira*[1], Helvécio Costa Menezes[1], Patterson Patrício de Souza[2], Zenilda de Lourdes Cardeal[1]

[1]Universidade Federal de Minas Gerais
[2]Centro Federal de Educação Tecnológica de Minas Gerais

* Corresponding author: jhonatanbo@hotmail.com

Brazilian culinary traditions rely heavily on a diverse array of aromatic seasonings, many of which derive their characteristic scents from terpenes. However, the comprehensive and eco-efficient identification of key aroma-active terpenes in such complex natural matrices remains challenging. In this study, we developed and validated a sustainable analytical protocol for the extraction, identification and sensory evaluation of terpenes in 26 traditional Brazilian seasonings. A novel sample preparation device was employed, consisting of a hydrophilic microporous cartridge (HMCart) made from expanded polytetrafluoroethylene (ePTFE), designed to enclose the sample and protect the extraction fiber during direct immersion solid-phase microextraction (DI-SPME). The extraction was performed using a 30/50 µm DVB/CAR/PDMS fiber, which provided broad selectivity toward both volatile and semi-volatile terpenes of varying polarity. Extraction conditions were optimized through a 2^{5-1} fractional factorial design, and the analytes were subsequently separated and identified by comprehensive two-dimensional gas chromatography coupled with mass spectrometry (GC×GC/MS). In total, 125 terpenes were identified across five chemical classes. Among them, oxygenated monoterpenes and sesquiterpenes were the most abundant and diverse. To assess their sensory relevance, odor activity values (OAVs) were calculated for 48 compounds. Notably, eucalyptol, linalool, pulegone, β-ocimene and geraniol exhibited extremely high OAVs, indicating their major role in the characteristic aromas of the analyzed seasonings. The analytical method showed excellent performance during validation. The limits of detection (LOD) ranged from 0.78 to 1.99 µg kg^{-1}, while the limits of quantification (LOQ) were between 2.37 and 6.04 µg kg^{-1}. Linearity was confirmed with R^2 values from 0.9533 to 0.9870 across the tested concentration range. Intra-day precision (RSD) ranged from 4.21% to 12.85%, and inter-day precision varied from 5.26% to 12.24%. Recoveries were satisfactory for all terpenes, ranging between 93% and 107%, complying with international guidelines for analytical accuracy. To visualize the contribution of individual terpenes to the perceived aroma, odor radar plots were generated based on the OAVs. These radars revealed that each seasoning exhibited a unique aromatic fingerprint composed of several sensory dimensions, including spicy, woody, floral, citrus, minty, camphoraceous, sweet, herbal, and resinous notes. For instance, curry and ginger were dominated by spicy and fresh notes due to high levels of eucalyptol and zingiberene, whereas herbs like oregano and rosemary displayed complex combinations of minty, floral, and woody attributes. These radar plots allowed a deeper interpretation of how individual terpenes shape the sensory identity of each spice and provided valuable information for potential applications in flavor design, gastronomy, and food innovation. This integrated approach—combining green sample preparation, high-resolution multidimensional separation, and sensory relevance quantification—represents a significant advancement in aroma chemistry. The methodology not only ensures analytical robustness but also aligns with green chemistry principles by eliminating excessive solvent use and reducing sample preparation steps. Furthermore, it contributes to the scientific valorization of Brazilian biodiversity, offering a sustainable and scalable platform for terpene analysis in natural products. The data generated can support developments in the food, fragrance, and pharmaceutical industries, especially in formulations where natural aroma profiling is essential.

Acknowledgements: National Council for Scientific and Technological Development (Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Chemistry Department of Federal University of Minas Gerais (UFMG), and the Federal Center for Technological Education of Minas Gerais (CEFET-MG).

CHEMICAL DEFENSES IN MELON (Cucumis melo L.) LEAVES AGAINST THE LEAFMINER FLY (Liriomyza sativae): INTEGRATING VOLATILES, SEMI-VOLATILES, AND WAX CONSTITUENTS

Hilton César Rodrigues Magalhães*[1], Fernando Antônio Souza de Aragão[2], Elaine Facco Celin[2], Ariana Veras de Araújo[2], Kirley Marques Canuto[2], Fernando Mauro Lanças[1]

[1]Instituto de Química da USP de São Carlos (IQSC)
[2]Embrapa Agroindústria Tropical

* Corresponding author: hiltoncesarr@usp.br

The leafminer fly (Liriomyza sativae) is the main pest affecting melons in Brazil, leading to significant drops in fruit quality and higher production costs. Due to the limited success of chemical control methods and the risk of developing insecticide resistance, resistant cultivars are considered a sustainable alternative. In this context, analyzing metabolites related to both innate and induced defenses is a promising strategy to identify chemical resistance markers that can be used in breeding programs. The study examined two contrasting pairs: A3.8 (resistant) × G1.S (susceptible), which are nearly genetically identical and ideal for metabolomic comparison, and AC13 (resistant) × GLD (susceptible), which are genetically different and represent real-world agricultural conditions. The genotypes were assessed at T0 (before infestation) and T2 (three days after infestation and mine appearance) using volatile analysis (SPME-GC-MS) and semi-volatile analysis (GC-MS of derivatized extracts from the apolar fraction). At T0, the susceptible genotypes (G1.S, GLD) showed accumulation of apocarotenoids (ionones, ciclocitral, oxoisophorone) and structural lipids (steroids, tocopherol, phytol, fatty acids), while the resistant ones (A3.8, AC13) had higher levels of leaf wax components, including n-alkanes, alcohols, and long-chain fatty acids. These results suggest a physical-chemical barrier present at the baseline level, indicating that antixenosis is not related to basal volatiles but may be partially linked to the leaf cuticle. At T2, the infested resistant genotypes exhibited a similar defensive profile, characterized by increased levels of GLVs (E-2-hexenal, hexanal), monoterpenes (limonene, isopinocarveol), and ketones (2-methyl-3-heptanone), indicating a rapid and coordinated defense response consistent with defense priming. In contrast, the susceptible genotypes maintained high levels of steroids, tocopherol, phytol, and fatty acids, indicating that membrane damage and oxidative stress were caused by larval mining. It can be concluded that A3.8 and AC13 share a chemical resistance pattern involving constitutive leaf wax barriers and the induction of GLVs and monoterpenes in response to attack, whereas G1.S and GLD exhibit vulnerability profiles. These metabolites are promising candidates as biomarkers of resistance in melon.

Acknowledgements: INCT-ALIM (CNPQ) and Embrapa Agroindústria Tropical

CHROMATOGRAPHIC ANALYSIS (GC-qMS) OF CYMBOPOGON DENSIFLORUS ESSENTIAL OIL AND PROSPECTION OF ITS BIOLOGICAL ACTIVITIES

Elina Bastos Caramão*, Rosianne Pereira Silva, Paulo Natan Alves dos Santos, Anaí Loureiro dos Santos, Laiza Canielas Krause

Universidade Federal de Sergipe

* Corresponding author: elina@ufrgs.br

Cymbopogon densiflorus (Family Poaceae), popularly known as "capim nagô," is an aromatic species native to Africa that is well-acclimated to Brazil. It is traditionally used in folk medicine, particularly for its notable antioxidant and antimicrobial activities [1-3]. The aim of this work was to identify the main compounds in the essential oil from the inflorescence of C. densiflorus. The oil was obtained by hydrodistillation using a steam distillation apparatus and provided by the rural producer. It was analyzed by GC/MS, and its main compounds were identified with the aid of linear relative retention indices (LPTRI). Monoterpenes and sesquiterpenes, oxygenated and non-oxygenated, were identified, with a prevalence of compounds having the basic structure of p-Menth-1-ene (1-Methyl-4-isopropyl-6-cyclohexene). The major compound was the monoterpene D-Limonene (p-Mentha-1,8-diene), (20%), followed by the oxygenated monoterpenes p-menth-2-en-1-ol (10.5%) and p-mentha-1(7),8-dien-2-ol (10%). Antioxidant activities were determined using three types of assays: DPPH, FRAP, and ABTS, for a better consistent conclusion. The results are presented below:

DPPH (2,2-diphenyl-1-picrylhydrazyl radical: Measures the antioxidant capacity of a given substance to scavenge the DPPH radical, reducing it to a hydrazine-like compound. (value = 1.80 mg Trolox Eq/g of sample)

FRAP (using the 2,4,6-tris(2-pyridyl)-s-triazine reagent): Evaluates the ability of an antioxidant to reduce the ferric ion (Fe^{3+}) to the ferrous ion (Fe^{2+}), forming an intense blue complex. (value = 188.5 mg Fe^{2+}/g of sample).

ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid): Measures antioxidant capacity by the reduction of ABTS through electron or hydrogen atom transfer from an antioxidant compound to a free radical. (value = 0,100 mg Trolox Eq/g of sample).

Note: All values obtained are consistent with potent antioxidants.

Thus, the analyzed essential oil of "capim Nagô" is rich in terpenes that possess a basic structure with an unsaturated six-carbon ring. This unsaturation can be considerable responsible for the antioxidant activity of this oil. The literature also cites antimicrobial activity for these compounds.

References:

[1] Fonseca, S.E. et al., Revista Fitos. Rio de Janeiro. 2022. DOI:10.32712/2446-4775.2022.1179

[2] Takaisi-Kikuni NB et al., Fitoterapia 2000 (71) 69-71. DOI: 10.1016/s0367-326x(99)00097-0

[3] Takaisi-Kikuni NB et al., J. Microbios 1996 (88) 55. DOI: 10.32712/2446-4775.2022.1179

[4] Zhao, J. et al., Journal of Ethnopharmacology, 2024 (330) 118181. DOI:10.1016/j.jep.2024.118181.

[5] Singh, S. et al., Food Bioscience, 2024 (61) 104931. DOI: 10.1016/j.fbio.2024.104931

Acknowledgements: Acknowledgements: authors thank to CAPES, CNPq and PETROBRÁS for financial support and to Elenito Hemes Lopes and Solange dos Santos Cerqueira for providing the essential oil studied.

CHROMATOGRAPHIC ANALYSIS OF CHLORPYRIFOS–MICROPLASTIC INTERACTION THROUGHOUT IN VITRO

Crisiana de Andrade Nobre*[1], Felipe Sousa da Silva[2], Fuad Pereira Nogueira Filho[2], Renata de Oliveira Silva[2], Maria Aparecida Liberato Milhome[3], Carla Bastos Vidal[1], Luciana de Siqueira Oliveira[1]

[1]Federal University of Ceará
[2]Nucleus of Technology and Indsutrial Quality of Ceará
[3]Federal Instute of Education Science and Technology of Ceará

* Corresponding author: cris.quimica@alu.ufc.br

The simultaneous presence of pesticide residues and microplastics in food has become a topic of great scientific relevance, raising growing concerns regarding food safety and public health. The literature already indicates that microplastics can act as vectors for chemical pollutants, including pesticides, heavy metals, and other emerging contaminants. However, their interactive behavior in complex food systems and under simulated human digestion conditions is still poorly understood. This study aimed to evaluate the interaction of chlorpyrifos with polyethylene microplastic (MP-PE) (200 and 100 µm). The in vitro digestion of heat-treated capuí beans (Vigna unguiculata) was assessed using an methodology adapted from INFOGEST 2.0. Contaminant analyses were conducted at each stage of digestion (oral, gastric, and intestinal) using high-performance liquid chromatography coupled with triple quadrupole mass spectrometry (LC-APCI-MS/MS), a widely validated method routinely applied to food matrices. The calibration curves obtained presented a wide linear range, ranging from 2.0 to 500 µg.L^{-1}, ensuring robustness and sensitivity. Multiple reaction monitoring (MRS) demonstrated high method selectivity, with no significant interferences detected in blank samples, thus ensuring the reliability of the results. Despite the high analytical sensitivity employed, chlorpyrifos was not detected in any of the samples evaluated, regardless of the in vitro digestion phase (oral, gastric, or intestinal) or the presence of MP-PE in the experimental matrix. Under the tested conditions, there was no measurable release of chlorpyrifos nor significant interaction with microplastics or the food matrix. This outcome may be explained by factors such as the low affinity of the compound for the polymer used, the absence of degradation under the simulated pH and digestion time conditions, or the strong retention of chlorpyrifos in structural components of the grains. Overall, this study highlights the importance of interdisciplinary approaches to investigate interactions between chemical contaminants and microplastics in food systems, thereby expanding knowledge on bioaccessibility mechanisms and potential health impacts. Although no measurable interaction between chlorpyrifos and microplastics in beans was observed under simulated digestion, the findings open promising avenues for future research on emerging contaminants and their implications for food quality.

Acknowledgements: National Institute of Science and Technology – Food (INCT-ALIM); NUTEC; IFCE and UFC.

CHROMATOGRAPHIC ANALYSIS VIA GC-MS OF FAME OBTAINED VIA DIRECT TRANSESTERIFICATION OF COMMERCIAL CHEESES

Lilian Fernandes de Oliveira*, Yasmim Eufrásio de Melo, Marcos Filipe Ramos e Silva, Dayane Cristina da Costa, Nelson Roberto Antoniosi Filho

Laboratório de Métodos de Extração e Separação (LAMES/UFG), Instituto de Química (IQ), Universidade Federal de Goiás (UFG)

* Corresponding author: lilianfernandes@discente.ufg.br

The lipid composition of cheese plays a fundamental role in the product's functional and sensory properties. Fatty acids and their derivatives, due to their wide variety, are responsible for producing unique textures and flavors in dairy products. Therefore, characterizing these compounds becomes an important tool for investigating product quality. In this context, chromatographic analysis stands out as a reference technique for the separation and identification of the lipid fraction in different types of cheese, allowing for a more detailed evaluation of the chemical composition. However, determining this profile requires the derivatization of fatty acids into compounds with greater volatility and thermal stability, such as Fatty Acid Methyl Esters (FAME). Thus, the objective of this study was to assess the possibility of verifying the diversity of lipid composition in commercial cheeses and relate it to their sensory characteristics, based on the chromatographic profile of fatty acid derivatives. A total of 26 samples of commercial cheeses were characterized, grouped into Minas Padrão (n = 6), Prato Lanche (n = 6), Mozzarella (n = 9), and Parmesan (n = 5). FAME were obtained through a direct transesterification process using the Hartman and Lago method adapted for microscale. The liquid FAME sample was analyzed on an Agilent 7890B gas chromatograph equipped with a 7000D mass spectrometer and a DB-WAX capillary column (30 m×0.25 mm×0.25 µm). Peak retention times were compared to Sigma-Aldrich standards. Chromatographic analysis revealed a profile of 22 FAME present in the transesterified organic phase of the cheeses. Among the identified compounds, the major ones in all four groups were palmitic, oleic, stearic, and myristic acids. These fatty acids are known to contribute to characteristics such as consistency and flavor, as well as to offer health benefits. Regarding the degree of saturation, Minas cheese showed a higher percentage of saturated FAME, while Mozzarella and Parmesan cheeses stood out for their high presence of unsaturated ones, a behavior that may be associated with milk composition or processing conditions. Statistical analyses such as Principal Component Analysis (PCA) highlighted the similarity between the lipid profiles of the samples. In this sense, the identification of the FAME profile was essential to evaluate the relationship between lipid composition and the sensory characteristics of the cheeses.

Acknowledgements: Acknowledgements: LAMES/UFG, IQ-UFG, FUNAPE, INCT-ALIM.

CHROMATOGRAPHIC EVALUATION OF THE THERMAL DEGRADATION OF LYCOPENE AND B-CAROTENE EXTRACTED FROM FRESH TOMATOES

Fernanda Dias Silva*[1], Maria Inês Gonçalves Leles[2], Nelson Roberto Antoniosi Filho[2]

[1]Universidade Federal da Paraíba – UFPB
[2]Laboratório de Métodos de Extração e Separação (LAMES). Instituto de Química – Universidade Federal de Goiás - UFG

* Corresponding author: dias.fernanda06@gmail.com

Lycopene and β-carotene are major carotenoids, widely recognized for their antioxidant properties and potential protective roles against chronic degenerative diseases. Both are abundant in tomatoes, a fruit extensively consumed worldwide in the form of sauces, purée, and extracts. The stability of these pigments is a critical factor during food processing, with heat and oxidation being the main causes of degradation. This study aimed to investigate the thermal degradation of lycopene and β-carotene extracted from fresh tomatoes, employing chromatographic techniques (RP-HPLC) and thermal analyses (TG and DSC). DSC analyses indicated that β-carotene exhibited an endothermic peak at 185°C, attributed to melting, whereas lycopene presented two endothermic peaks at 135°C and 165°C, likely corresponding to structural rearrangement and melting, respectively. Exothermic events were also observed at 220°C for β-carotene and 200°C for lycopene, associated with the volatilization of degradation products, as confirmed by TG data. However, HPLC analyses revealed that degradation occurred at lower temperatures than those indicated by TG, with significant losses detected from 100°C onwards. At 250°C, both pigments were reduced to near-minimal concentrations. Thermogravimetric curves showed the onset of mass loss at substantially higher temperatures compared to the HPLC profiles, suggesting that lycopene and β-carotene are initially converted into intermediate compounds, which subsequently volatilize at elevated temperatures.

Acknowledgements: We would like to thank the funding agencies CNPq and INCT-ALIM for their institutional support in the development of this research.

Chromatographic study of essential oil of Lippia rotundifolia Cham. from the Cerrado of Rio de Janeiro: Correlations with its pharmaceutical, dermocosmetic, and aromatherapeutic potential

Laiza Canielas Krause*, Rosianne Pereira Silva, Anaí Loureiro dos Santos, Elina Bastos Caramão

Universidade Federal de Sergipe

* Corresponding author: Laiza_canielas@hotmail.com

Lippia rotundifolia Cham. (Verbenaceae) is an aromatic species native to the Brazilian Cerrado, with a restricted occurrence in specific areas of the state of Rio de Janeiro. This study aims to determine the chemical composition of its essential oil and evaluate its potential for application in the pharmaceutical, dermocosmetic, and aromatherapy fields. The oil was extracted from fresh leaves by hydrodistillation in a mini-industrial still by the rural producer. The chromatographic analysis was performed by GC/MS, using retention indices (LPTRI) for the identification of its constituents. A total of 72 constituents were identified, with a predominance of monoterpenes and sesquiterpenes. The antioxidant activity was confirmed through DPPH, ABTS, and FRAP assays, revealing excellent activity. According to the literature, the main identified compounds have anti-inflammatory, antimicrobial, antioxidant, calming, toning, and skin-regenerating activities (Table 1), reinforcing the species' potential as a source of multifunctional functional ingredients. The results highlight the importance of the Cerrado's biodiversity as a resource for the development of high-value-added products, while also underscoring the need for conservation and sustainable management strategies for L. rotundifolia.

Table 1: Literature References on the Main Activities and Applications of the Compounds Identified in the Lippia Rotundifolia Essential Oil [1,2,3].

compounds(%)/class(*)	main activities found in the essential oil(**)					
	AA	AR	AO	AM	AT	IR	DES
Myrcene (13%)/MT(***)	yes	yes	yes	yes			
Camphor/OMT (13%)	yes	yes	yes	yes			
β-Caryophyllene/MT (9%)	yes	yes	yes				
α-Terpinolene (7%)/MT (***)	yes	yes	yes	yes	yes		
Tagetone (7%)/OMT	yes	yes					

Legend: (*) MT = monoterpene; OMT = oxygenated monoterpene; ST = sesquiterpene

(**) AA: Analgesic and anti-inflammatory; ASR = Antiseptic, Sedative, and Relaxant; AO = Antioxidant;

AM = Antimicrobial; AT = Antitumor; IR = Insecticide and Repellent; DES = Decongestant

(***) β-myrcene (13%) and β-caryophyllene (9%) exhibit a marked eutourage effect.

References: [1] Tavares, LS. Peptides, DOI:10.1016/j.peptides.2020.170317, 2020; [2] Gomide, M.S., Rev. Bras. Farmacog. DOI: 10.1590/S0102-695X2013000600006, 2013; [3] Camilo, C.J., Biocat. Agric. Biotech. DOI:10.1016/j.bcab.2022.102296, 2022

Acknowledgements: Acknowledgements: authors thank to CAPES, CNPq and PETROBRÁS for financial support and to Maria das Graças Ferreira Amim for providing the plants and essential oil studied.

COMBINING ION PAIR CHROMATOGRAPHY AND DIA-MS FOR REFINED METABOLOMICS OF HIGHLY POLAR COMPOUNDS IN CLINICAL RESEARCH

Andréa T. Faccio*, Jessica Silva Salgueiro, Karina Helena Moraes Cardozo, Adriana Lebkuchen, Valdemir Melechco Carvalho

Fleury Group, São Paulo, São Paulo, Brazil

* Corresponding author: andrea.faccio@grupofleury.com.br

Highly polar metabolites play essential roles in numerous biochemical pathways and are often implicated in disease mechanisms, making their accurate detection and identification critical for clinical application. However, their analysis remains challenging due to poor retention and co-elution in conventional chromatographic methods. We employed an untargeted metabolomics approach to assess the performance of an ion-pairing chromatography coupled to data-independent acquisition (DIA) mass spectrometry for the separation and annotation/identification of polar metabolites in plasma and urine. The method demonstrated exceptional resolving power, effectively separating biologically relevant isomeric compounds that are typically indistinguishable by standard techniques. These include leucine, isoleucine, and allo-isoleucine; alanine, β-alanine, and sarcosine; 2-methylhistidine and 3-methylhistidine; and α-aminobutyric acid, γ-aminobutyric acid, and 3-aminoisobutyric acid.

Metabolite annotation/identification was refined through DIA-based fragmentation and MS/MS deconvolution using MS-DIAL, with spectral comparisons against MassBank of North America, METLIN, mzCloud, and CarniBlast. Some identifications were confirmed using commercial standard mixture. Additionally, ^{13}C-labeled/unlabeled yeast extracts enabled isotope-assisted identification via MS-DIAL's tracking function, enhancing confidence in molecule annotation.

A key innovation of this study was the use of ^{13}C-labeled fragment ions to enhance metabolite identification. A Skyline library incorporating both labeled and unlabeled molecular formulas and fragment ions was built to validate identifications through retention time, isotope patterns, and fragmentation profiles.

Using the proposed strategies, either individually or in combination, 166 metabolites were annotated/identified (71 in plasma and 141 in urine). This workflow demonstrates the robustness of ion-pair chromatography combined with advanced MS techniques for comprehensive analysis of highly polar metabolites and introduces a new strategy for fragment-based identification using stable isotope labeling.

Comparative Study of Extraction Methods for Pesticide Determination in Chyme from Cooked Rice Bioaccessibility Assays

Maristela Barnes Rodrigues Cerqueira*, Alberto Kazutomi Ozaki Junior, Kamila da Rosa Acosta, Larine Kupski, Eliana Badiale Furlong

Federal University of Rio Grande

* Corresponding author: mariscerqueira@hotmail.com

The presence of pesticides in rice is a cause for concern among consumers. Dietary ingestion is the most important route of human exposure to pesticide residues. Bioaccessibility refers to the proportion of contaminants released from the matrix into the digestive solution of the gastrointestinal tract. Assessing the risk of dietary exposure to foods by combining in vitro exposure with in vivo digestion can also more accurately assess the amount of pesticides absorbed by the human body. In this sense, rapid, inexpensive, and reliable methods for determining these compounds are extremely important. Therefore, the objective of this study was to evaluate the QuEChERS method and salting-out induced liquid-liquid microextraction (SILLME) for the determination of multiclass pesticides in the chyme resulting from the bioaccessibility in vitro assay on cooked brown rice. Twenty grams of brown rice, previously contaminated with pesticides (pirimiphos-methyl, flutriafol, tebuconazole, fenpropathrin, and permethrin), were cooked with water, soybean oil, and table salt on a hotplate. After cooking, the bioaccessibility in vitro assay was carried out according to the method proposed by Versantvoort, Van de Kamp, and Rompelberg (2004). At the end of the assay, an aliquot of the chyme was removed for method evaluation. For SILLME, the extraction was performed using acetonitrile acidified with 1% acetic acid and partitioned using magnesium sulfate. For QuEChERS, the extraction was performed using acetonitrile acidified with 1% acetic acid, followed by partitioning with anhydrous magnesium sulfate and sodium acetate. In the clean up step, magnesium sulfate and C18 were used. After shaking and centrifugation, 1 mL of the extract was filtered and injected into a GC-MS. The recovery results obtained for SILLME ranged from 46 to 96%, with RSD < 53%. For QuEChERS, the results ranged from 68 to 121%, with RSD < 16%. The results indicate that the QuEChERS method was more suitable for extraction in the chyme resulting from the multiclass pesticide bioaccessibility in vitro assay on cooked rice.

Acknowledgements: Rio Grande do Sul State Research Support Foundation (Fapergs), project number 23/2551-0000946-3.

COMPARATIVE STUDY OF QUECHERS, PROTEIN PRECIPITATION, AND LOW TEMPERATURE PARTITIONING FOR PESTICIDE MULTIRESIDUE ANALYSIS IN VEGETABLE MILK BY HPLC-MS/MS

Heloísa Siqueira Santos, Yuri Arrates Rocha, Almir Custodio Batista Junior, João Victor Borges Assis, Lauanne Rocha Silva, Simone Nascimento^2

1 Instituto de Química, Universidade Federal de Goiás, Goiânia, Goiás, Brasil

Plant-based milks have become increasingly popular as alternatives to animal-derived milk, driven by plant-based diets, dietary restrictions, and environmental concerns. However, unlike animal milk, there is still a lack of studies investigating the presence of pesticide multiresidues in these products, as well as the validation of analytical methods for their detection—which raises concerns about food safety and potential health risks associated to contaminant exposure. In this context, the present study aims to compare the effectiveness of different sample preparation methodologies for pesticide residue extraction in plant-based milks, all using acetonitrile as the extraction solvent. According to AOAC International, the official sample preparation method for pesticide multiresidue detection in food matrices is QuEChERS, widely recognized for its efficiency and reproducibility; however, it involves multiple steps and a high consumption of solvents. A conventional method for animal milk samples is protein precipitation, which is quite simple and fast, it removes proteins but does not perform sufficient clean-up, since it applies cold solvent directly to the matrix. As an alternative, this study introduces an optimized liquid-liquid extraction method with low-temperature partitioning (LLE/LTP), enabling extraction and clean-up in a single step while minimizing solvent and reagent use. All techniques were evaluated based on the recovery of 27 pesticides from different classes through LC-MS/MS analyses. The results demonstrated excellent analytical performance in all three approaches, with a highlight on the LLE/LTP technique, which achieved 95 ± 1.2% recovery, while protein precipitation yielded 90 ± 0.9% and QuEChERS showed 82 ± 1.3%. The study concludes that the proposed LLE/LTP is equivalent to the official method while being simpler and more efficient. By comparing extraction techniques for pesticides in plant-based milk, this research aims to fill a critical scientific gap and provides reliable methodologies for food safety assessments.
Keywords: QuEChERS, LLE/LTP, plant-based milk, multiresidues, pesticides.

Acknowledgements: Acknowledgements: INCT-ALIM, CNPq, CAPES.

Comparative study of the use of Intra-Tube Flux Extraction Device and Solid Phase Microextraction for the Analysis of Polycyclic Aromatic Hydrocarbons in Surface Waters by GCxGC/MS

Victor Eduardo Almeida Pereira Silva*[1], Caroliny Regina da Silva Gonzaga[1], Jhonatan Bispo de Oliveira[2], Patrícia Santiago de Oliveira Patrício[1], Patterson Patrício de Souza[1], Patrícia Sueli de Rezende[1], Ildefonso Binatti[1]

[1]Chemistry Department, Federal Center for Technological Education of Minas Gerais (CEFET-MG)
[2]Chemistry Department, ICEx, Federal University of Minas Gerais (UFMG)

* Corresponding author: victoreduardoaps@gmail.com

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of persistent organic pollutants consisting of two or more fused aromatic rings and represents one of the largest classes of carcinogenic and mutagenic chemical compounds present in the environment. The determination of these contaminants in environmental matrices mostly requires chromatographic techniques, such as GC/MS or HPLC/DAD, associated with sample preparation steps to avoid matrix effects. Among the most widely used sample preparation techniques, Solid Phase Microextraction (SPME) stands out. However, despite its high sensitivity and ability to analyze trace levels, SPME presents limitations, such as high cost, fiber fragility, and unsuitability for passive sampling. Our research group from Laboratory of Integrated Technologies (IntechLab) developed the Intra-Tube Flux Extraction Device (IT-FEx), consisted of a GC Inlet Liner (straight type) internally coated with polydimethylsiloxane (PDMS) responsible for the adsorption of analytes present in the sample, combining sample collection and preparation in a single step, eliminating the use of solvents and showing potential application as a simple and low cost passive sampler. This study compared the analytical performance of commercial SPME device and IT-FEx for the analysis of PAHs in surface waters by comprehensive two-dimensional gas chromatography (GCxGC/MS) for detection and quantification. Both methods were optimized and validated according to EURACHEM criteria, presenting comparable results: good linearity ($R^2 > 0.9$ for both methods), high sensitivity (SPME – LOD: 0.001-19.163 µg L-1, LOQ: 0.002-19.183 µg L-1; IT-FEx – LOD: 0.005-8.107 µg L-1, LOQ: 0.024-9.197 µg L-1), satisfactory recoveries (SPME: 92-115%; IT-FEx: 87-116%) and acceptable precisions (SPME: RSD < 14%; IT-FEx: RSD < 14.8%). The results demonstrated that SPME and IT-FEx showed similar analytical performances, highlighting the new device as a promising alternative to SPME by combining similar performance, lower cost, operational simplicity and potential application in passive sampling, configuring itself as a viable and innovative solution for environmental monitoring of PAHs.

Acknowledgements: FAPEMIG, CNPq and CEFET-MG.

COMPLEMENTARY ANALYTICAL METHODS FOR THE INVESTIGATION OF NITROSAMINES DERIVED FROM CIPROFLOXACIN AND RELATED SUBSTANCES

Marisa de Jesus Silva Chaves*[1], Vanessa Paiva[2], Vanderson da Silva Bispo[3], Carla Beatriz Grespan Bottoli[1]

[1]Universidade Estadual de Campinas
[2]Universidade Federal de Minas Gerais
[3]Instituto de Excelência Farmacêutica - EPHAR

* Corresponding author: m238989@dacunicamp.br

Nitrosamines are organic impurities present in some drug products and classified as potentially mutagenic. Since this is a critical quality attribute of pharmaceuticals, the use of sensitive, robust, and selective analytical methods is necessary. However, acquiring analytical standards for nitrosamines is one of the main obstacles to carrying out investigative studies. Therefore, a complementary study using liquid chromatography coupled with diode array detectors (DAD), corona CAD (Charged Aerosol Detection), and mass spectrometry (MS) was conducted to investigate the nitrosation of ciprofloxacin and nine related substances containing different chemical substituents (fluorine, chlorine, hydroxyl, and N-oxide). To quantify the compounds evaluated in this study, as well as the possible nitrosamines formed during the reactions, an HPLC-DAD-CAD analytical method was initially developed using a YMC – Pack ODS – A analytical column (150 mm x 4.6 mm - 3 µm) maintained at 40°C and a mobile phase composed of water + 0.1% formic acid (A) and methanol + 0.1% formic acid (B) in gradient elution. Subsequently, to perform the structural confirmation of the nitrosamines formed, the method was transposed to LC-MS/MS, in which SCAN (for determination of the molecular ion) and Daughter SCAN (for determination of the fragmentation profile) analyses were performed. An electrospray ionization source operating in positive ionization mode (ESI+) was used. The desolvation gas flow rate, ion source temperature, and desolvation temperature were maintained at 600 L/hr, 130°C, and 500°C, respectively. In the CAD detector, the generated signal is directly proportional to the mass of analyte present in the sample. Therefore, using the DAD-CAD detectors, a UV-CAD relative response factor was determined for each analyte, enabling the quantification of nitrosamines, without the use of analytical standards. The proposed method was useful in evaluating the formation of nitrosamines in solutions from secondary amines and in verifying the influence of pKa and chemical substituents on the nitrosation kinetics. It was observed that smaller and more electronegative halogen substituents, such as fluorine, cause an increase in reactivity toward the nitrosation reaction, while halogens with larger atomic radius, such as chlorine, cause inhibition of the reaction. Such conclusions are useful in building more accurate mathematical models for mitigating nitrosamines in solutions.

Acknowledgements: We thank Laboratório Cristália for their support in this work.

COMPOSIÇÃO DE ÁCIDOS GRAXOS EM PRODUTOS PLANT BASED: ANÁLOGOS DO LEITE

Rafael Onilton de O. Sales[1], Esiana de A. Rodrigues[1], Maria Edlane A. da Silva[1], Séfura M. A. Moura[1], Cleidiane Gomes Lima[2], Mairlane Silva de Alencar[2], Rubens Carius de Castro[2], Maria Aparecida L. Milhome*[1]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará (IFCE), Limoeiro do Norte, Ceará, Brasil
[2]Fundação do Centro de Tecnologia Industrial do Ceará (NUTEC), Rua Rômulo Proença S/N, Pici, Fortaleza, Ceará, Brasil

* Corresponding author: maria.milhome@ifce.edu.br

O mercado de alimentos plant-based tem aumentado a cada ano, com o desenvolvimento de novos produtos. O consumo de alimentos de base vegetal, como os análogos ao leite, tem sido destaque. Com isso tem sido relevante a caracterização destes produtos, que tem se tornado cada vez mais presente na dieta alimentar. Os produtos plant-based utilizam geralmente ácidos graxos(AG) insaturados como principal fonte de gordura. Nessa perspectiva, torna-se essencial analisar o perfil de AG presentes em leites vegetais, uma vez que dependendo da composição da matriz a composição de AG pode variar. Assim, o presente estudo tem como objetivo analisar o perfil de AG em 3 amostras (A, B e C) de leite de castanha de cajú com sabores diferentes (castanha e aveia, castanha e cacau e castanha) de 3 diferentes lotes (n=9), disponíveis comercialmente na região do Vale do Jaguaribe-CE. As análises foram realizadas seguindo metodologia recomendada pelo Instituto Adolfo Lutz. Inicialmente, a gordura presente nas amostras foram extraídas pelo método Bligh-Dyer, seguida de reação de esterificação para produção dos metil-ésteres dos AG, que posteriormente foram quantificados por Cromatografia Gasosa com detector de Ionização em Chama-GC-FID (Thermo). A quantificação foi realizada pelo método de normalização com fator resposta. De acordo com os resultados obtidos foram encontrados em todas as amostras analisadas (A, B e C), AG saturado (0,62; 0,76; 0,72 g/100g), AG insaturado (1,95; 2,8; 3,09 g/100g), incluindo ômega 6 e 9, AG monoinsaturados e polinsaturados. Os principais AG encontrados nas amostras foram: Palmítico, Esteárico, Oléico e Linoleico. Não foi detectado ácidos graxos trans. A presença de AG nesse tipo de bebida mostra um grande potencial nutricional, podendo contribuir com o suprimento de ácidos graxos essenciais na dieta da população.

Acknowledgements: INCT-CNPQ, PRAPG-CAPES, FUNCAP e NUTEC.

COMPOSIÇÃO DE COMPOSTOS FENÓLICOS EM KOMBUCHAS SABORIZADAS.

Luana Guabiraba Mendes*[1], Francisco Flávio da Silva Lopes[2], Victor Borges Fernandes[2], Felipe Sousa da Silva[3], Antonia Carlota de Souza Lima[3], Maria Aparecida Liberato Milhome[1]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará - IFCE
[2]Universidade Estadual do Ceará – UECE
[3]Núcleo de Tecnologia e Qualidade Industrial do Ceará – NUTEC

* Corresponding author: luanagmendes@gmail.com

A kombucha é uma bebida fermentada resultante da ação simbiótica de bactérias e leveduras, tradicionalmente consumida na forma líquida. A liofilização ou desidratação possibilita sua obtenção em pó, conferindo maior estabilidade, facilidade de armazenamento e aplicação em formulações funcionais. Considerando a importância dos compostos fenólicos para o potencial bioativo da bebida, este estudo teve como objetivo identificar e quantificar esses compostos em amostras de kombucha saborizadas com diferentes matrizes vegetais (abacaxi, hibisco e acerola), por cromatografia líquida de alta eficiência com detecção por arranjo de diodos (HPLC-DAD). As análises foram realizadas em sistema de fase reversa, com acetonitrila e água acidificada como fases móveis em gradiente de eluição. O volume de injeção foi de 20 µL, e a detecção conduzida a 350 nm. A identificação baseou-se na comparação de tempos de retenção e espectros UV com padrões de referência, incluindo ácido gálico, clorogênico, cafeico, rutina, vanílico, isoquercitrina, p-cumárico e ferúlico. O ácido gálico foi identificado como principal composto fenólico, variando entre as matrizes avaliadas. Na kombucha de hibisco apresentou valores (0,00163 ± 0,00030 mg/g de extrato). Nas amostras de abacaxi e acerola, o ácido gálico esteve presente em níveis abaixo do limite de quantificação, impossibilitando sua determinação precisa. Outros compostos fenólicos investigados não foram detectados, possivelmente devido às baixas concentrações ou interferências da matriz. O uso de polidextrose como coadjuvante na secagem também pode ter contribuído para a redução da detecção. Em síntese, os resultados confirmam a presença de fenólicos, destacando o ácido gálico como marcador principal, e evidenciam que a escolha da matriz saborizante influencia diretamente o perfil e a concentração dos bioativos em kombucha em pó.

Acknowledgements: INCT-ALIM (CNPq) , Núcleo de Tecnologia e Qualidade Industrial do Ceará – NUTEC e Instituto Federal de Educação, Ciência e Tecnologia do Ceará (IFCE) – Campus Limoeiro do Norte.

COMPOSITIONAL STUDY OF "VAPE" (E-LIQUIDS) USING COMPREHENSIVE TWO-DIMENSIONAL GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY AND CHEMOMETRICS

Glaucimar Alex Passos de Resende*, Lucas Paines Bressan, Lucas Pessôa de Araujo, Leandro Wang Hantao

1 Institute of Chemistry, UNICAMP, 13083-862, Campinas, SP, Brazil; 2 National Institute of Science and Technology in Bioanalytics, SP, Campinas, 13083-862, Brazil

* Corresponding author: glaucima@unicamp.br

The modern e-cigarette has gained popularity as an alternative to the traditional cigarette. Popularly known as “vape”, e-cigarettes have a huge impact on human health [1]. E-cigarette uses e-liquids, and their composition primarily consists of propylene glycol, glycerol, and flavoring agents. The heating process in e-cigarettes produces aerosols, which can be harmful to humans [2]. This study aims to optimize the sample analysis of e-liquids and the aerosol component of e-cigarettes using headspace solid-phase microextraction (HS-SPME) and comprehensive two-dimensional gas chromatography coupled to mass spectrometry (GC×GC-MS). The optimization study was conducted by selecting the optimal unidimensional conditions for material fiber, NaCl solution concentration, and sample volume. Extraction time and temperature were optimized using a central composite design (CCD) to evaluate the total chromatographic area and the number of identified compounds. An aliquot of 100 µL of sample was diluted in 15 mL of 15% v/v NaCl solution. The resulting solution was extracted at 55 °C for 46 min, using a 50/30 µm DVB/CAR/PDMS SPME fiber. A mid-polar × polar configuration was used with modulation of 7 s. A total of 34 e-liquids were studied using hierarchical cluster analysis (HCA) and a heatmap generated from a peak table-based approach of 126 identified compounds. Clusters were formed based on their flavor: citric, fruity, creamy, and others. The aerosols formed during the heating process (5 levels of temperature and 5 levels of time) were analyzed by a pixel-based approach and principal component analysis (PCA). The heating time showed an increase in glycerin and a decrease in propylene glycol in the aerosol, with a total of 267 compounds identified. In conclusion, within the optimal extraction conditions studied, many compounds were identified in e-liquids and aerosols, and chemometric analysis tools helped characterize their chemical profiles.

References:
[1] World Health Organization. (2021). WHO report on the global tobacco epidemic 2021.
[2] Berenguer, C., Pereira, J. A., & Câmara, J. S. (2021). Microchemical Journal, 166, 106196.

Acknowledgements: The authors thank UNICAMP, CNPq, CAPES, Petrobras, and FAPESP for funding our research

COMPREHENSIVE MOLECULAR CHARACTERIZATION VIA GC×GC-TOFMS OF ORGANIC COMPOUNDS FROM PETROGENIC PRODUCT CO-PROCESSED WITH DIFFERENT BIO-OILS

Yasmin Guimarães Pedro*[1], Nathalia dos Santos Pontes[1], Vinicius Barreto Pereira[1], Adriana Moret Borges[2], Andrea de Rezende Pinho[2], Raquel Vieira Santana da Silva[1], Gabriela Vanini[1], Debora de Almeida Azevedo[1]

[1]IQ -UFRJ
[2]CENPES - Petrobras

* Corresponding author: yasminguim.pedro@pos.iq.ufrj.br

Growing energy and environmental demands have prompted the refining industry to adopt sustainable technologies, such as renewable currents into conventional refining units. Bio-oil, the liquid product derived from biomass pyrolysis, can be co-processed with heavy petroleum fractions to produce biogenic products that align with fuel market standards. This work aimed to chemically characterize organic compounds in liquid products from the delayed coking process of different bio-oils co-processed with crude oil distillation vacuum residue. The analysis was performed by comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS). Three liquid products were evaluated: 100% petrogenic product (PP), and co-processed with 10% fast (FBOP) and slow (SBOP) pyrolysis bio-oils from pinewood and eucalyptus, respectively. Samples were analyzed via GC×GC-TOFMS with DB-5 / DB-17 (D1/D2) column set, and processed by ChromaTOF® with a signal/noise ratio of 500:1 and ≥70% spectral similarity. The results revealed a predominance of aliphatic and cyclic alkanes, and alkenes. Bio-oil inclusion reduced the relative area of aliphatic alkanes, alkenes and cyclic hydrocarbons from 66.07% (PP) to 62.11% (FBOP) and 60.96% (SBOP), and sulfur compounds from 0.55% (PP) to 0.25% (FBOP) and 0.26% (SBOP). Conversely, the oxygenated compounds increased from 0.22% (PP) to 1.83% (FBOP) and 1.42% (SBOP). Phenolic compounds were identified in the liquid products, but in PP, only alkyl-phenols were identified. The alkylphenols relative area increased from 0.07% to 0.25% and 0.44%. In the co-processed products, additional phenolic groups were observed, such as methoxyphenols. The alkyl-benzenediols, alkyl-trimethoxybenzenes, dimethoxyphenol, and methoxy-benzenediol were detected exclusively in SBOR. Ketones were not detected in PP, only in FBOP and SBOP. Among them, C1 and C3 alkyl-cyclopentenones showed relative areas of 0.06% and 0.07%, respectively. Finally, the analysis enabled differentiation of FBOP and SBOP based on the exclusive compounds in SBOP, which showed higher diversity of O-containing compounds. These results demonstrate that GC×GC-TOFMS is effective in distinguishing liquid products from different conversion processes, and the detailed elucidation of oxygen compounds was only possible due to the high resolution of the GC×GC.

Acknowledgements: Petrobras, Capes, CNPq, and FAPERJ for financial support.

CONSTITUTIVE AND INDUCIBLE CHEMICAL DEFENSES IN RESISTANT MELON LEAVES AGAINST THE LEAFMINER FLY (Liriomyza sativae Blanchard)

Hilton César Rodrigues Magalhães*[1], Fernando Antônio Souza de Aragão[2], Elaine Facco Celin[2], Ariana Veras de Araújo[2], Kirley Marques Canuto[2], Renato Cardoso Leal Netto[1], Daniel Rodrigues Cardoso[1], Fernando Mauro Lanças[1]

[1]Instituto de Química da USP de São Carlos (ICSC)
[2]Embrapa Agroindústria Tropical

* Corresponding author: hiltoncesarr@usp.br

The leafminer fly (Liriomyza sativae) is a major pest of melon crops in Brazil, reducing fruit quality and increasing production costs. Because chemical control has limited effectiveness and can lead to insecticide resistance, developing resistant cultivars is a more sustainable approach. The metabolomic comparison between nearly isogenic lines, 56R (resistant) and 56S (susceptible), offers a precise method to study both constitutive and induced chemical defenses. The genotypes were evaluated at T0 (before infestation) and T2 (three days after infestation and mine appearance) using volatile analysis (SPME-GC-MS), semi-volatile analysis (GC-MS of derivatized extracts from the apolar fraction), and UHPLC-QTOF profiling of secondary metabolites. Volatile profiling showed that 56R did not have a higher abundance of volatile compounds compared to the genotype 56S at T0, indicating that the resistant genotype does not produce constitutive volatile compounds that repel L. sativae. Therefore, L. sativae is likely not deterred by volatiles from 56R and may even be more attracted to 56S, which exhibited slightly higher overall VOC levels. After infestation (T2), both genotypes showed clear changes in VOC profiles; however, 56R displayed a stronger induction of compounds like hexanal, (E)-2-hexenal, β-cyclocitral, D-limonene, and 4-oxoisophorone—associated with lipoxygenase, monoterpene, and carotenoid pathways involved in deterrence and indirect defense. Conversely, α-ionone was mainly detected in 56S, possibly acting as a susceptibility cue. Semi-volatile profiling revealed increased levels of long-chain fatty acids (hexadecanoic, octadecanoic, and linolenic acids) in 56R at T0, suggesting a thicker or more organized epicuticular wax layer likely responsible for antixenosis. Elevated levels of stigmasterols and tocopherols further supported this structural and antioxidant reinforcement. At T2, no consistent pattern was observed, reflecting metabolic adjustments following herbivory. Finally, UHPLC-QTOF analysis in positive ion mode demonstrated that 56R accumulated higher levels of cucurbitacins and other triterpenoids with known antifeedant activity, highlighting these compounds as strong biochemical markers of resistance to L. sativae.

Acknowledgements: Acknowledgments: INCT-ALIM (CNPQ) and Embrapa Agroindústria Tropical

CONTAMINAÇÃO POR FENÓIS EM ÁGUA SUBTERRÂNEA: O PAPEL DA CROMATOGRAFIA-ESPECTROMETRIA DE MASSAS AVANÇADA NA GESTÃO SUSTENTÁVEL

Giancarla Viviana Santa-Cruz-Mérida1, Juliana Ikebe Otomo1, Diego Ricardo Araoz-Prado2, Elaine Aparecida Rodrigues1,3,*, Delvonei Alves de Andrade1 and Oscar Vega Bustillos1*

1Nuclear and Energy Research Institute IPEN-CNEN, Av. Prof. Lineu Prestes, 2242 Butantã, São Paulo 05508-000, Brazil; 2Independent Researcher, São Paulo 04153-040, Brazil; 3Environmental Research Institute IPA, Av. Professor Frederico Hermann Junior, 345, São Paulo 05259-900, Brazil;

* Corresponding author: santacruz.viviana@usp.br

A contaminação das águas subterrâneas e seus impactos socioambientais são preocupações prementes da Agenda 2030, representando riscos à saúde pública e desafios à gestão sustentável. Compostos fenólicos, muitos deles classificados como poluentes emergentes e prioritários pela USEPA, destacam-se pelo risco que representam e que não são tradicionalmente monitorados. A seleção criteriosa de técnicas e métodos analíticos avançados é crucial para a detecção precoce da contaminação, priorização de áreas de intervenção e apoio a decisões estratégicas, especialmente em países do Sul Global. A pesquisa baseada em 52 estudos (de 1984 a 2023) de amostras ambientais em águas subterrâneas, identificou e mapeou 107 compostos fenólicos diferentes em 25 países. Dentre eles 11 são considerados como prioritários pela USEPA devido ao seu significativo risco para a saúde humana e o meio ambiente. Para a determinação de níveis traço (ng/L), LC-MS e LC-MS/MS destacaram-se como as principais abordagens analíticas, com LD e LQ extremamente baixos (

Acknowledgements: Esta pesquisa foi financiada pela Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES, 01). O APC foi financiado pela TVGD Holding.

COUMARIN, AN ANALYTICAL MARKER, FOR THE HPLC-DAD IDENTIFICATION OF CINNAMOMUN ZEYLANICUM AND CINNAMOMUM CASSIA IN METHANOLIC EXTRACTS

Elisa Missae Yamashita Umezu*, Marley Garcia Silva, Nizamara Simenremis Pereira

Federal Institute of Science and Technology of Brasília (IFB), campus Gama, Brasília, DF, Brazil

* Corresponding author: elisa.missae@gmail.com

Cinnamon is one of the world's most important spices and is widely used in the food industry. This spice exists in different varieties with distinct quality levels. Currently, cinnamon is classified into true cinnamon (Ceylon) and false cinnamon (Cassia). True cinnamon, which is rare and of higher quality, has a greater market value. In contrast, false cinnamon has a lower economic value. As a result, true cinnamon is susceptible to adulteration, with false cinnamon often used as an adulterant or a substitute for powdered true cinnamon. Therefore, the development of methods for characterizing different varieties and assessing the quality of cinnamon samples is important.
This study developed a method based on high-performance liquid chromatography (HPLC) for the authentication of cinnamon available on the market. Three samples of true cinnamon from different brands were purchased online. A 0.5 g sample was stirred for 30 minutes in a methanol-water (80:20) solution, subjected to an ultrasonic bath for 30 minutes, and then centrifuged for 10 minutes at 3000 rpm. Subsequently, the supernatants were filtered and reserved for analysis. The HPLC system consisted of a Shimadzu HPLC equipped with a diode array detector, binary pump, and degasser. LC separation was performed on a reversed-phase C18 column (200 mm × 4.6 mm, 10 µm) at ambient temperature. The mobile phase consisted of methanol–water (60:40) at a flow rate of 1.0 mL/min in isocratic mode, with detection at 280 nm. A standard calibration curve was obtained by plotting the peak areas against the concentrations of standard coumarin solutions in the range of 10 to 100 µg/mL. The curve showed good linearity, meeting the requirement of a correlation coefficient (R^2) ≥ 0.999. Grubbs' test was applied to confirm the absence of outliers. The plot of residuals versus concentration showed a random distribution of points, demonstrating the method's homoscedasticity. The method demonstrated adequate accuracy (96%–104%) and suitable precision, with %RSD values below 2% (calculated according to the Horwitz ratio). The limit of detection (LOD) was determined to be 2.06 ppm, and the limit of quantification (LOQ) was 6.26 ppm. Of the three cinnamon brands analyzed, two were adulterated, and only the Sri Lankan cinnamon was genuine. The coumarin concentration in false cinnamon (Cassia) was 16.3 ppm, whereas in true cinnamon (Ceylon), the coumarin level was below the method’s detection limit.

Acknowledgements: The authors thank FAPDF and IFB for their financial support.

CROMATOGRAFIA DE TROCA IÔNICA NA SEPARAÇÃO ISOTÓPICA DO LÍTIO

Juliana Ikebe Otomo1*, Daniela da Costa Gonçalves Santos1, Celso Maurício Serrano1, José Oscar Vega Bustillos1*

1Instituto de Pesquisas Energéticas e Nucleares/Comissão Nacional de Energia Nuclear (IPEN/CNEN)

* Corresponding author: julianaikebe@gmail.com

Em reator nuclear PWR, o principal componente para controlar o pH e a temperatura do sistema de refrigeração é a solução de LiOH enriquecida no 7Li. No mundo, somente dois países controlam o fornecimento deste isótopo, a Rússia e a China. A Rússia utiliza a técnica de eletromigração que emprega Mercúrio, que conhecidamente causa grande impacto ambiental e risco à saúde dos trabalhadores diretamente envolvidos. Por esta razão, têm sido investigadas outras técnicas para obtenção deste isótopo. Este trabalho propõe a técnica de cromatografia por troca iônica para obtenção do isótopo de lítio enriquecido à 99,95% partindo de sua abundância natural, 92,5%. No processo de separação isotópica do Lítio, é utilizado quatro colunas de 100 cm de altura e 1 cm de diâmetro interno, em série. Uma banda de lítio é formada na primeira coluna, por meio de saturação da mesma com solução de cloreto de Lítio 0,15 M. O deslocamento da banda é realizado com solução de acetato de cálcio na mesma concentração. Frações de 10 mL são coletadas na saída da quarta coluna, onde são medidos pH, condutividade elétrica e concentrações de Na, K, Ca e Li, além da razão isotópica 6Li/7Li. A banda de Lítio começa a sair na quinta fração, quando a condutividade aumenta de 1100 µS cm-1 para 2860 µS cm-1, por meio de análise em fotômetro de chama obteve-se a concentração de 203 mg L-1 de Lítio. A concentração de Li e a condutividade aumentam rapidamente na 6ª fração e estabiliza da 7ª à 79ª fração com uma média de 2100 mg L-1 e 14,9 mS cm-1, respectivamente. Ao final da banda de Li, é observado um aumento na condutividade que passa a ser superior a 16,67 mS cm-1, Li não é mais detectado, em seu lugar tem-se concentrações elevadas de Na e Ca, 4300 e 7400 mg L-1, respectivamente. Com relação a razão isotópica, é observado que nas primeiras frações (5ª à 17ª) houve enriquecimento do 7Li, com a razão variando de 0,047 para 0,079, mantendo-se constante até a fração de número 68, correspondendo a abundância natural de 6Li e 7Li. Nas 10 últimas frações onde se detecta Li, a razão varia de forma crescente de 0,084 à 0,124 demonstrando enriquecimento do 6Li. Conclui-se que a troca iônica é uma técnica adequada para enriquecimento isotópico do Li.

Acknowledgements: Os autores agradecem ao IPEN pela infraestrutura, à CBL pelo financiamento incial do projeto e a FDTE pela bolsa de pesquisa.

DESAFIOS NA ANÁLISE DE NITROSAMINAS EM METFORMINA DE LIBERAÇÃO PROLONGADA POR CROMATOGRAFIA LÍQUIDA DE ALTA EFICIÊNCIA ACOPLADA A ESPECTROMETRIA DE MASSAS

Bianca S. de Oliveira[1], Patrícia C. M. Dias[1], Matheus N. Souza[2], Jayane V. M. da Silva[2], André Colonese[2], Sthefany Maria L. Cury[2], Sibele Guimarães[2], Patrícia C. Lima[2], Soraya M. Ochs*[2], Mychelle A. Monteiro[2]

[1]Instituto Nacional de Controle de Qualidade em Saúde (INCQS)
[2]Instituto Nacional de Controle de Qualidade em Saúde (INCQS) - Fiocruz

* Corresponding author: soraya.ochs@fiocruz.br

A diabetes mellitus é uma doença metabólica que acomete cerca de 500 milhões de pessoas em todo o mundo e pode levar a complicações graves e morte quando não tratada adequadamente. A metformina, uma biguanida amplamente utilizada como fármaco de primeira escolha no tratamento do diabetes tipo 2 e gestacional, atua como sensibilizadora da insulina e inibidora da gliconeogênese pela ativação da AMPK. Nos últimos anos, entretanto, agências regulatórias como a FDA e a Anvisa emitiram alertas sobre a presença de impurezas de N-nitrosaminas (NA) em medicamentos contendo metformina. Essas impurezas, de reconhecido potencial carcinogênico e teratogênico, representam um risco relevante à saúde pública. Em 2019, foi instituído o Programa de Monitoramento de NA em Medicamentos, em parceria entre a Anvisae o INCQS, visando garantir a segurança de diferentes classes terapêuticas. A metformina de liberação prolongada (XR) apresenta vantagens farmacocinéticas decorrentes da formação de um gel no trato gastrointestinal, que prolonga sua absorção e reduz a frequência de administração. Contudo, essa característica impõe desafios à análise de impurezas, uma vez que o gel pode dificultar a extração dos analitos. Neste contexto, o presente trabalho teve como objetivo desenvolver e validar metodologia analítica por CLAE-EM/EM para identificação e quantificação de seis NA (NDMA, NDEA, NDIPA, NDBA, NEIPA e NMBA) em medicamentos de metformina XR, considerando os limites de ingestão diária estabelecidos pela RDC nº 677/2022. O método utilizou metanol e água em proporções que impediram a formação do gel, seguido de etapas de ultrassonicação e centrifugação. Foram analisadas 16 amostras de metformina XR de diferentes marcas disponíveis no mercado brasileiro. Todas as amostras apresentaram níveis de NA dentro dos limites aceitáveis estabelecidos pela legislação vigente. Os resultados demonstram a aplicabilidade do método desenvolvido e reforçam a importância do monitoramento contínuo da qualidade de medicamentos, contribuindo para a segurança, eficácia terapêutica e proteção da saúde da população que faz uso contínuo de metformina.

Acknowledgements: Anvisa, Fiocruz.

DESAFIOS NA ANÁLISE DE NITROSAMINAS EM METFORMINA DE LIBERAÇÃO PROLONGADA POR CROMATOGRAFIA LÍQUIDA DE ALTA EFICIÊNCIA ACOPLADA A ESPECTROMETRIA DE MASSAS

Bianca dos Santos de Oliveira*, Soraya de Mendonça Ochs, Matheus Nicolau de Souza, Patrícia Condé de Lima, Jayane Valente Meirelles da Silva, Andre Colonese, Sthefany Maria Libonati Cury, Sibele Guimarães, Mychelle Alves Monteiro

Fiocruz

* Corresponding author: bianca.deoliveira@fiocruz.br

A diabetes mellitus é uma doença metabólica que acomete cerca de 500 milhões de pessoas em todo o mundo e pode levar a complicações graves e morte quando não tratada adequadamente. A metformina, uma biguanida amplamente utilizada como fármaco de primeira escolha no tratamento do diabetes tipo 2 e gestacional, atua como sensibilizadora da insulina e inibidora da gliconeogênese pela ativação da AMPK. Nos últimos anos, entretanto, agências regulatórias como a FDA e a ANVISA emitiram alertas sobre a presença de impurezas de N-nitrosaminas (NA) em medicamentos contendo metformina. Essas impurezas, de reconhecido potencial carcinogênico e teratogênico, representam um risco relevante à saúde pública. Em 2019, foi instituído o Programa de Monitoramento de NA em Medicamentos, em parceria entre a ANVISA e o INCQS, visando garantir a segurança de diferentes classes terapêuticas. A metformina de liberação prolongada (XR) apresenta vantagens farmacocinéticas decorrentes da formação de um gel no trato gastrointestinal, que prolonga sua absorção e reduz a frequência de administração. Contudo, essa característica impõe desafios à análise de impurezas, uma vez que o gel pode dificultar a extração dos analitos. Neste contexto, o presente trabalho teve como objetivo desenvolver e validar metodologia analítica por CLAE-EM/EM para identificação e quantificação de seis NA (NDMA, NDEA, NDIPA, NDBA, NEIPA e NMBA) em medicamentos de metformina XR, considerando os limites de ingestão diária estabelecidos pela RDC nº 677/2022. O método utilizou metanol e água em proporções que impediram a formação do gel, seguido de etapas de ultrassonicação e centrifugação. Foram analisadas 16 amostras de metformina XR de diferentes marcas disponíveis no mercado brasileiro. Todas as amostras apresentaram níveis de NA dentro dos limites aceitáveis estabelecidos pela legislação vigente. Os resultados demonstram a aplicabilidade do método desenvolvido e reforçam a importância do monitoramento contínuo da qualidade de medicamentos, contribuindo para a segurança, eficácia terapêutica e proteção da saúde da população que faz uso contínuo de metformina.

Acknowledgements: Anvisa, Fiocruz.

DESENVOLVIMENTO DE MÉTODO ANALÍTICO HS-SPME/CG-EM PARA ANÁLISE QUANTITATIVA DE HPAS EM CAFÉ PREPARADO POR INFUSÃO

Luiz Thiago Vasconcelos da Silva*[1], Fátima Itana Chaves Custódio Martins[2], Taís Coutinho Parente[1], Lucas Alexandre Nobre da Silva[1], Joaquim Rodrigues de Vasconcelos Neto[1], Jhonyson Arruda Carvalho Guedes[1], Jefferson Pereira Ribeiro[1], Ronaldo Ferreira do Nascimento[1]

[1]Universidade Federal do Ceará
[2]Universidade Estadual do Vale do Acaraú

* Corresponding author: thiago97@alu.ufc.br

O café, uma das bebidas mais consumidas mundialmente, é o principal produto de exportação do Brasil. Embora seja associado a benefícios para a saúde, sua composição química, especialmente os hidrocarbonetos policíclicos aromáticos (HPAs), ainda é um tema de preocupação. Durante o processo de torrefação, esses compostos podem ser formados e são conhecidos por suas propriedades mutagênicas e carcinogênicas. Este estudo teve como objetivo analisar qualitativa e quantitativamente 16 HPAs em amostras de café utilizando microextração em fase sólida (SPME) acoplada à Cromatografia Gasosa com Espectrometria de Massas (CG-EM). Foram analisadas 10 amostras de café, divididas entre marcas de alta qualidade e de qualidade comum. O perfil dos HPAs foi avaliado em cafés em pó e bebidas preparadas por infusão, todos da espécie Coffea arábica e provenientes do Brasil. O método analítico foi validado de acordo com parâmetros como seletividade, linearidade, precisão, limite de detecção (LD) e limite de quantificação (LQ). A precisão intra-corrida variou de 11% a 21%, com LD entre 0,39 µg/kg e 2,02 µg/kg, e LQ entre 1,20 µg/kg e 6,48 µg/kg. As recuperações dos HPAs variaram de 53% a 126%, e o coeficiente de variação foi inferior a 20%, indicando que o método foi eficiente, rápido e sensível. Nas amostras de alta qualidade, as concentrações médias de HPAs variaram de 0,6 a 2,8 µg/kg, com destaque para o naftaleno (0,9 a 1,4 µg/kg) e o fluoreno (0,6 a 0,7 µg/kg). Nas amostras de qualidade comum, foram detectados, além do naftaleno e fluoreno, compostos como dibenzo[ah]antraceno, benzo[ghi]perileno e indeno[1,2,3-cd]pireno, com concentrações de até 1,4 µg/kg. Esses compostos mais complexos, com maior número de anéis aromáticos, indicam a presença de impurezas durante a fabricação do café de qualidade inferior. A análise multivariada revelou que os cafés de alta qualidade predominam compostos com menor número de anéis aromáticos, enquanto as amostras de qualidade inferior apresentam níveis mais elevados de compostos com anéis adicionais, caracterizando a presença de "produtos não café" durante o processo de fabricação. Os resultados deste estudo destacam a importância de monitorar as substâncias presentes no café, principalmente os HPAs, para garantir a segurança alimentar e a qualidade do produto.

Acknowledgements: LAT-UFC, LMQPN-EMPRABA, INCT-ALIM e CNPq.

DESENVOLVIMENTO DE MÉTODO ANALÍTICO POR HPLC-DAD PARA QUANTIFICAÇÃO SIMULTÂNEA DE DEET, IR3535 E ICARIDINA EM REPELENTES COSMÉTICOS.

Fellipe Campos da Fonseca*, Jéssica da Silva Pinheiro de Carvalho Monteiro, Gabriela Teixeira de Lima, Ana Lúcia Ribeiro de Barros, Érica de Oliveira Costa, Matheus de Jesus Werly, Leonardo de Souza Lopes, Lauro de Sena Laurentino, Adriana Sant Ana da Silva

Fundação Oswaldo Cruz, Instituto Nacional de Controle de Qualidade em Saúde, RJ, Brasil.

* Corresponding author: fellipe.fonseca@fiocruz.br

As mudanças climáticas têm intensificado a incidência de doenças sazonais como as arboviroses, representando um desafio significativo para a saúde pública. No Brasil, doenças como dengue, zika, Chikungunya e Febre amarela, transmitidas pelo mosquito Aedes aegypti, representam uma preocupação constante. Em 2024, o país registrou 6,5 milhões de casos prováveis de dengue e 5.536 mortes confirmadas. Os repelentes cosméticos são ferramentas essenciais, tendo como principais ativos presentes o DEET (N,N-dietil-3-metilbenzamida), IR3535 (etil-butil-acetilaminopropionato) e icaridina (hidroxietil isobutil-piperidina carboxilato), atuando como uma barreira química que afasta mosquitos e reduz o risco de transmissão das arboviroses. O Instituto Nacional de Controle de Qualidade em Saúde (INCQS), busca o desenvolvimento de novas metodologias, no sentido de contribuir para o atendimento a emergências sanitárias e promoção da saúde, em especial para aqueles em que não existem metodologias oficiais, que é de extrema importância para o controle de qualidade, como os repelentes. Este projeto tem como objetivo desenvolver e validar um método analítico por cromatografia líquida de alta eficiência (CLAE), para quantificação simultânea dos ativos DEET, IR3535 e Icaridina, que são encontrados frequentemente nas formulações de repelentes. Para o desenvolvimento foi utilizada coluna C18 (250mm 4,6mm e 5um), eluição isocrática com fase ternária de ACN:MeOH:H2O e detecção por Arranjo de Diodos (DAD) utilizando o comprimento de onda em 220nm. As amostras foram preparadas em acetonitrila e avaliadas frente a potenciais interferentes comuns em repelentes, como conservantes (parabenos, fenoxietanol e isotiazolinonas). Os resultados preliminares demonstraram adequada resolução entre os analitos, boa seletividade com testes de pureza de pico e pureza espectral, robustez frente à complexidade da matriz, com desempenho estatístico satisfatório a partir da curva analítica mostrando linearidade adequada. O método mostrou-se aplicável para o controle de qualidade de repelentes, contribuindo para a disponibilidade de ferramentas analíticas em situações de emergência sanitária.

Acknowledgements: Fiocruz, Anvisa, ABIHPEC.

DESENVOLVIMENTO DE MÉTODO CLAE-EM/EM PARA MONITORAMENTO DE NICOTINA E CONTAMINANTES EM PRODUTOS DE TABACO

Tarsila Dantas de Farias*, Tawany Sandy Moraes, Larissa Valentina Teixeira Almeida, Maryana da Rocha Cruz, Silvana do Couto Jacob, Lísia Maria Gobbo dos Santos, Soraya de Mendonça Ochs, Mychelle Alves Monteiro

Fundação Oswaldo Cruz (Fiocruz) - Instituto Nacional de Controle de Qualidade

* Corresponding author: tarsilafarias@gmail.com

A Organização Mundial de Saúde (OMS) considera o tabagismo um dos principais problemas de saúde pública global. O uso do tabaco, associado a doenças graves como câncer e problemas cardiovasculares, causa mais de 7 milhões de mortes por ano. Essa situação é impulsionada pela presença de substâncias como a nicotina e nitrosaminas nos produtos de tabaco. Diante desse cenário, o Sistema Nacional de Vigilância Sanitária (SNVS) atua na fiscalização e regulamentação desses produtos, proibindo o uso de aditivos e aromatizantes e estabelecendo limites máximos para compostos como a nicotina, principal responsável pela dependência química. A análise rigorosa dos produtos de tabaco é essencial para atender às exigências sanitárias e subsidiar ações de controle. Neste contexto, o presente trabalho tem como objetivo desenvolver métodos para monitorar a nicotina e as substâncias a ela associadas, tais como produtos de degradação, impurezas e aditivos. Entre os compostos analisados destacam-se a nornicotina, a cafeína e nitrosaminas específicas, incluindo a N-nitrosonornicotina, N-nitrosoanatabina, N-nitrosoanabasina e 4-(metilnitrosamino)-1-(3-piridil)-1-butanona. O método em desenvolvimento utiliza cromatografia líquida de ultra performance acoplada à espectrometria de massas em triplo quadrupolo (CLAE-EM/EM). Testes com diferentes diluentes e fases móveis indicaram que metanol como diluente e uma fase móvel de água e metanol, ambos com 0,1% de ácido fórmico, proporcionam os melhores sinais analíticos. As demais substâncias estão em processo de otimização para detecção. O método desenvolvido permitirá o monitoramento confiável de contaminantes em produtos fumígenos, fornecendo subsídios técnicos à Vigilância Sanitária e fortalecendo as ações de controle, contribuindo diretamente para a proteção da saúde pública.

Acknowledgements: Agradecemos a agência nacional de vigilância sanitária (ANVISA) pelo financiamento do projeto

DESENVOLVIMENTO DE MÉTODO POR HS-SPME/CG-EM PARA ANÁLISE DE HPAS EM CAFÉS PREPARADO POR COZIMENTO

Taís Coutinho Parente*[1], Fátima Itana Chaves Custódio Martins[2], Luiz Thiago Vasconcelos da Silva[1], Lucas Alexandre Nobre da Silva[1], Joaquim Rodrigues de Vasconcelos Neto[1], Jhonyson Arruda Carvalho Guedes[1], Jefferson Pereira Ribeiro1[1], Ronaldo Ferreira do Nascimento[1]

[1]Universidade Federal do Ceará
[2]Universidade Estadual do Vale do Acaraú

* Corresponding author: taiscoutinhop@gmail.com

O café é uma das bebidas mais consumidas em todo o mundo, sendo o Brasil o maior produtor mundial. Durante o processamento do café, ele é submetido a elevadas temperaturas, favorecendo a formação de hidrocarbonetos policíclicos aromáticos (HPAs) que são associados ao aumento da incidência de diversos tipos de câncer nos seres humanos. Nesse contexto, é importante o desenvolvimento de métodos analíticos que proporcionem sensibilidade e seletividade, utilizando pequenas quantidades de amostra e solventes orgânicos e que sejam rápidos, simples e confiáveis. Assim, este trabalho objetiva desenvolver e validar métodos analíticos para a determinação de resíduos de HPAs em cafés da espécie Coffea arábica, de alta qualidade e qualidade comum, obtidas de produtores brasileiros, usando as técnicas microextração em fase sólida (HS-SPME) e cromatografia gasosa acoplada a espectrometria de massas (GC-MS). Neste caso, foi avaliado o perfil de 16 HPAs em 10 amostras de cafés em pó e preparos da bebida por cozimento, via análise multivariada por componentes principais (PCA). A preparação da bebida por cozimento foi feita de acordo com o rótulo, utilizando água ultrapura. O método foi validado de acordo com os parâmetros seletividade, linearidade, limite de detecção (LD), limite de quantificação (LQ), precisão e exatidão (recuperação), revelando ser bem adequado para detecção e quantificação em todas as amostras. Nas amostras do café em pó, as concentrações médias de naftaleno, acenafteno, acenaftileno, fluoreno, antraceno, fenantreno e benzo[a]pireno foram abaixo dos Limites Máximos de Resíduos (LMRs) estabelecidos para outras matrizes que não o café. Porém foi encontrada uma concentração para o fluoranteno maior que o LMR, 9,07 ± 0,37 µg. L-1 na amostra do café comum (coado), bem como a concentração de 5,50 ± 2,5 µg. L-1 no café expresso. Nas amostras do grupo de alta qualidade, preparadas por cozimento, foram quantificados naftaleno (1,4 ± 0,8 µg.kg-1) e fluoreno (0,7 ± 0,6 µg.kg-1) e detectados os compostos acenaftileno, antraceno e o acenafteno. Os cafés de qualidade comum apresentaram concentrações apreciáveis de HPAs com anel de pentose, o que caracteriza a adição de “produtos não café” durante a fabricação.

Acknowledgements: Laboratório de Análise de Traços - UFC, Laboratório Multiusuário de Química de Produtos Naturais - EMPRABA, INCT – alimentos.

DESENVOLVIMENTO E VALIDAÇÃO DE MÉTODO ANALÍTICO POR GC-FID PARA DETERMINAÇÃO DE CONGÊNERES E CONTAMINANTES EM CACHAÇA

Mairlane Silva de Alencar*[1], Tiago Nogueira Rocha[2], Pedro Henrique Honorio Queiros[3], Crisiana de Andrade Nobre[1], Cleidiane Gomes Lima[2], Felipe Sousa da Silva[2]

[1]Universidade Federal do Ceará; Núcleo de Tecnologia e Qualidade Industrial do Ceará
[2]Núcleo de Tecnologia e Qualidade Industrial do Ceará
[3]Universidade Federal do Ceará

* Corresponding author: alencarmairlane@gmail.com

A cachaça é a segunda bebida alcoólica mais consumida no Brasil e a terceira no mundo, apresentando grande relevância econômica para o país. Com o objetivo de assegurar a qualidade e a segurança do consumo, o Ministério da Agricultura e Pecuária (MAPA) estabeleceu a Portaria nº 539, de 26 de dezembro de 2022, que define limites para congêneres e contaminantes orgânicos. O controle desses parâmetros é fundamental tanto para garantir a conformidade legal e prevenir riscos à saúde humana, quanto para preservar as características sensoriais desejáveis da bebida. Diante disso, o presente trabalho teve como objetivo desenvolver e validar um método analítico em cromatógrafo gasoso com detector por ionização em chama (GC-FID) para a determinação simultânea de congêneres e contaminantes, conforme previsto na legislação brasileira, bem como aplicá-lo em amostras de cachaça. Os critérios de validação analítica seguiram os requisitos do MAPA e as diretrizes do INMETRO, considerando as figuras de mérito: faixa de trabalho, linearidade, limites de detecção (LD) e quantificação (LQ), exatidão e precisão. Os requisitos de validação foram plenamente atendidos quanto à linearidade, precisão e exatidão, os valores de LD e LQ foram compatíveis com os limites exigidos pela legislação vigente e permitiu a determinação dos analitos sem a necessidade de pré-concentração. Dez amostras de cachaça comercializadas em Fortaleza – CE foram analisadas após a validação do método, onde foram evidenciadas variações nos perfis de congêneres, algumas amostras apresentaram concentrações de metanol, mas todas dentro dos limites exigidos pela legislação vigente. O método desenvolvido e validado para a determinação de congêneres e contaminantes em cachaça por GC-FID mostrou desempenho confiável, robusto e adequado para a determinação de congêneres e contaminantes em cachaça, sendo uma ferramenta confiável para atender às exigências regulatórias e contribuir para a segurança e padronização desta bebida típica brasileira.

Acknowledgements: Núcleo de Tecnologia e Qualidade Industrial do Ceará; Universidade Federal do Ceará.

DESENVOLVIMENTO E VALIDAÇÃO DE MÉTODO DE ANÁLISE PARA A DETERMINAÇÃO DE 1-NITROSO-4-METIL PIPERAZINA EM MEDICAMENTOS CONTENDO O INSUMO FARMACÊUTICO ATIVO RIFAMPICINA UTILIZADOS NO TRATAMENTO DA TUBERCULOSE

Sthefany Maria Libonati Cury*, Rosane Gomes Alves Lopes, Magno Maciel Magalhães, Mychelle Alves Monteiro, Soraya de Mendonça Ochs, Sibele Guimarães, Matheus Nicolau de Souza, Bianca dos Santos de Oliveira, Patrícia Condé de Lima

INCQS - Fiocruz

* Corresponding author: sthefany.cury@fiocruz.br

A tuberculose (TB) é uma doença, que apesar de tratável e curável, ainda leva a óbito mais de um milhão de pessoas no mundo por ano. Os medicamentos contendo rifampicina (RIF) são utilizados no seu tratamento, porém, através de uma análise comparativa entre a Relação Nacional de Medicamentos e o banco de dados de registro da Agência Nacional de Vigilância Sanitária (Anvisa), nota-se que no Brasil não há medicamentos com registros ativos que sejam capazes de suprir as demandas do Sistema Único de Saúde. A possível falta de interesse da iniciativa privada e de investimento nas indústrias públicas brasileiras gera a necessidade de aquisição desses medicamentos por importação direta do Ministério da Saúde. Tendo em vista o alerta global da presença de 1-nitroso-4-metil piperazina (MNP), uma impureza de potencial mutagênico e carcinogênico do grupo das nitrosaminas, nesses produtos e a dificuldade encontrada pelas indústrias em controlar a sua presença, o Instituto Nacional de Controle de Qualidade em Saúde, laboratório de referência da Rede Nacional de Laboratórios de Vigilância Sanitária (RNLVISA), pode e deve contribuir na garantia da qualidade desses medicamentos. O presente estudo tem o objetivo de desenvolver e validar método de análise para a determinação de MNP em medicamentos contendo RIF utilizados no tratamento da TB no Brasil, de acordo com os critérios e normas de validação analítica da Anvisa. Foi verificado que todas as referências compendiais consultadas e utilizadas no país, contém metodologias de análise que utilizam a técnica de Cromatografia Líquida (CLAE) acoplada à detecção por espectrometria de massas, o que dificulta o atendimento à demanda de monitoramento dessa substância devido ao alto custo de manutenção e aquisição desses equipamentos. Entretanto, com a alteração do limite estabelecido para a MNP no Guia nº 50, versão 4 da Anvisa, tornou-se viável a quantificação dessa impureza empregando técnicas menos onerosas, como a CLAE com detecção por arranjo de diodos (DAD). A implementação da nova metodologia utilizando a técnica de CLAE-DAD possibilita a difusão do conhecimento entre os demais laboratórios públicos e da RNLVISA, contribuindo para a saúde pública e para o Sistema Nacional de Vigilância Sanitária.

Acknowledgements: Fiocruz; Fiotec; INCQS

DESENVOLVIMENTO E VALIDAÇÃO DE MÉTODO POR HPLC-DAD PARA DETERMINAÇÃO DE CANABINOIDES: AVANÇOS NO CONTROLE DE QUALIDADE EM ASSOCIAÇÕES DE PACIENTES

Matheus Nicolau de Souza*, Soraya de Mendonça Ochs, Letícia de Souza Fraga, Bianca dos Santos de Oliveira, Bruno Siqueira Antunes, Patrícia Condé de Lima, Mychelle Alves Monteiro

Fundação Oswaldo Cruz, Instituto Nacional de Controle de Qualidade em Saúde, RJ, Brasil.

* Corresponding author: matheus.nicolau@fiocruz.br

A Cannabis sativa L. é uma planta herbácea da família Cannabaceae, cultivada há milênios por suas fibras, sementes e, notavelmente, por seus metabólitos secundários. A Cannabis sativa produz compostos bioativos, notavelmente os fitocanabinoides (CBD e THC), que interagem com o sistema endocanabinoide humano para regular processos fisiológicos essenciais como dor, humor e resposta imune. Devido a essa ação, o óleo extraído da planta possui alto potencial terapêutico, sendo uma valiosa ferramenta no tratamento de condições como epilepsia refratária, dor crônica e ansiedade. Neste cenário, as associações civis de pacientes emergem como protagonistas no Brasil. Diante das barreiras regulatórias e do alto custo de produtos farmacêuticos importados, essas organizações sem fins lucrativos viabilizam o acesso ao tratamento com derivados de cannabis para milhares de famílias. Um dos principais desafios enfrentados pelas associações de pacientes é a carência de ferramentas analíticas para assegurar a qualidade de seus extratos, o que compromete padronização e a segurança terapêutica dos produtos. Com o objetivo de suprir essa necessidade, este trabalho desenvolveu e validou um método por HPLC-DAD para a quantificação simultânea de seis canabinoides de relevância clínica: CBD, Ácido Canabidiólico (CBDA), THC, Ácido Tetrahidrocanabinólico (THCA), Canabigerol (CBG) e Canabinol (CBN). As amostras foram preparadas por extração assistida por ultrassom com etanol 95%, seguida de agitação mecânica (inversão e vórtex), sonicação e centrifugação para separação do extrato etanólico da fase lipídica. A análise foi realizada em coluna C18 ACE 5 (150 × 4,6 mm), utilizando gradiente de ácido fórmico 0,1% em água e ácido fórmico 0,1% em acetonitrila, com detecção por DAD entre 200 e 240 nm, e quantificação a 220 nm. O método demonstrou aplicabilidade e robustez na análise de múltiplos lotes de produtos oriundos de três associações de pacientes, contemplando desde matérias-primas (extratos concentrados) até produtos (óleos diluídos) destinados ao consumo. Os resultados confirmam a viabilidade do método como ferramenta confiável para monitorar a qualidade de extratos de Cannabis, contribuindo para a padronização, segurança terapêutica e fortalecimento das práticas das associações de pacientes no Brasil.

Acknowledgements: Fiocruz, Anvisa, Emenda Parlamentar da Deputada Federal Sâmia Bomfim.

Desenvolvimento e validação de metodologia analítica para identificação de Novas Substâncias Psicoativas (NSP) utilizando Índice de Retenção e CG/EM

Maurício Leite Vieira*[1], Luciana Souto Ferreira[1], Gabriela Hamú Giudice[2], Jorge Jardim Zacca[1]

[1]Instituto Nacional de Criminalística - Departamento de Polícia Federal
[2]Agência Nacional de Vigilância Sanitária

* Corresponding author: mauricio.mlv@pf.gov.br

As drogas de abuso conhecidas como Novas Substâncias Psicoativas (NSPs) são classificadas pelas Nações Unidas como substâncias que não estão sob controle, seja pela Convenção Única sobre Entorpecentes de 1961, seja pela Convenção sobre Substâncias Psicotrópicas de 1971, incluindo suas atualizações. Elas apresentam um potencial de se tornar um problema de saúde pública, à medida que seu aparecimento no mercado ilícito de drogas tem desafiado as autoridades policiais, os químicos forenses e o sistema de saúde pública. Uma das maiores dificuldades enfrentadas pelos profissionais responsáveis pela identificação dessas substâncias é a ausência de padrões, devido à impossibilidade de os laboratórios manterem o passo diante de um mercado ilícito altamente dinâmico, em constante mudança nas tendências de oferta (até 2023 mais de 1250 destas substâncias foram relatadas, segundo o Sistema de Alerta Rápido da UNODC). O presente trabalho trata do desenvolvimento e da validação de um método analítico para a identificação de NSPs usando índices de retenção, baseado em cromatografia gasosa acoplada à espectrometria de massas de quadrupolo único (CG/EM). Foram avaliadas 22 diferentes substâncias representativas de grupos de NSPs como fenetilaminas, drogas clássicas, canabinoides sintéticos, piperazinas, triptaminas, catinonas sintéticas, opioides sintéticos e aminoindanos. Uma das principais contribuições para o presente trabalho foi a avaliação teórica do fator de tolerância do índice de retenção, em função do tempo de retenção do analito e do n-alcano usado como normalização do sistema cromatográfico. As figuras de mérito do método foram avaliadas, tais como a repetibilidade, precisão intermediária, robustez por análise fatorial. Os resultados obtidos neste trabalho permitiram a criação de um método simples e confiável para a avaliação de 22 substâncias de 10 classes diferentes, seletivo para análises de NSPs. Esta estratégia envolvendo o fator tolerância de índice de retenção tem permitido a extensão do método para outras classes de compostos, tais como agroquímicos e fármacos. Em última análise o trabalho servirá como mais uma ferramenta prática para avaliação de NSPs no uso de CG/EM pelos laboratórios de química forense da Polícia Federal.

Acknowledgements: Polícia Federal/MJSP, Agência Nacional de Vigilância Sanitária (ANVISA/MS), Universidade de Brasília (UnB).

DESENVOLVIMENTO E VALIDAÇÃO DE METODOLOGIA CROMATOGRÁFICA POR CLAE-UV PARA DETERMINAÇÃO DO CLORIDRATO DE ETAMBUTOL EM COMPRIMIDOS DISPERSÍVEIS

Patrícia de Castro Moreira Dias*, Sthefany Maria Libonati Cury, Sibele Guimarães, Andre Colonese, Patricia Condé de Lima, Soraya de Mendonça Ochs, Mychelle Alves Monteiro

Instituto Nacional de Controle de Qualidade em Saúde - INCQS (Fiocruz)

* Corresponding author: patricia.castro@fiocruz.br

O cloridrato de etambutol é um agente antituberculoso amplamente empregado em esquemas terapêuticos de primeira linha. A formulação em comprimidos dispersíveis representa um avanço para a adesão ao tratamento, especialmente em populações pediátricas e em pacientes com dificuldade de deglutição. A qualidade dessas apresentações depende de metodologias analíticas confiáveis, capazes de assegurar a correta identificação e quantificação do fármaco. Nesse cenário, a cromatografia líquida de alta eficiência (CLAE) com detecção no ultravioleta constitui ferramenta de destaque pela seletividade e aplicabilidade em ensaios de rotina. O objetivo deste estudo foi desenvolver, padronizar e validar uma metodologia cromatográfica para a determinação quantitativa do cloridrato de etambutol em comprimidos dispersíveis, contemplando ensaios de teor, dissolução e identificação, em conformidade com critérios nacionais e internacionais de qualidade. As análises foram conduzidas em sistema CLAE equipado com detector DAD, utilizando coluna C18 (150 × 4,6 mm; 5 µm), fase móvel de acetato de amônio/acetato de cobre II em água e metanol (80:20 v/v), fluxo de 1,0 mL/min, forno a 40 °C, volume de injeção de 20 µL, detecção em 270 nm e tempo total de corrida de 17 minutos. Os resultados evidenciaram perfil cromatográfico específico, sem interferência dos excipientes, com picos bem definidos e tempos de retenção reprodutíveis. A curva analítica apresentou linearidade ($R^2 > 0,999$), a precisão intra e interdia mostrou desvio-padrão relativo inferior a 2% e a exatidão situou-se entre 98 e 102%. No ensaio de teor, as amostras permaneceram dentro da faixa de 90–110% do valor declarado, e no teste de dissolução observou-se liberação superior a 75% em 30 minutos. O método também se mostrou robusto frente a pequenas variações na fase móvel e na temperatura, sem impacto significativo nos resultados. . A metodologia cromatográfica desenvolvida e validada foi adequada, precisa e confiável para o controle de qualidade de comprimidos dispersíveis de cloridrato de etambutol. E sua aplicação em ensaios de rotina contribui para a garantia da eficácia terapêutica e reforça o papel da cromatografia líquida como técnica essencial no monitoramento da qualidade de medicamentos antituberculosos.

Acknowledgements: Fiocruz, INCQS e Fiotec

DESIGN OF EXPERIMENTS-BASED OPTIMIZATION OF CARBOXYLIC ACID DERIVATIZATION FOR IMPROVED LC-MS/MS SENSITIVITY IN METABOLOMICS

Guilherme Garcia Rafael*, Carla Beatriz Grespan Bottoli

Universidade Estadual de Campinas, Instituto de Química

* Corresponding author: g291077@dac.unicamp.br

Metabolomics has emerged as a powerful tool for understanding biochemical processes, enabling the identification of biomarkers and the investigation of metabolic alterations under diverse physiological and pathological conditions. Among the broad range of metabolites, carboxylic acids play a central role in metabolism. However, their high polarity and low ionization efficiency pose analytical challenges, often resulting in weak LC-MS/MS signals. Derivatization has become a widely applied strategy in targeted metabolomics methods to improve the detection of poorly ionizable and poorly retained analytes. In this study, we applied Design of Experiments (DoE) approach to optimize reaction parameters for the derivatization of carboxylic acids using the hydrazine reagent isoniazid, aiming to enhance ionization efficiency. Several carboxylic acid standards, representing distinct structural classes, were included in the optimization, such as 2,5-dihydroxybenzoic acid, GABA, L-arginine, L-glutamic acid, pyroglutamic acid, pyruvic acid, kynurenic acid, and tryptophan. A fractional factorial design (2^{5}–1) was first employed to identify the most relevant factors—reaction time, temperature, derivatizing agent concentration (isoniazid), coupling agent concentration [carbodiimide (EDC)], and additive concentration [1-hydroxybenzotriazole (HOBt)]. The additive was found to be non-significant, and the remaining factors were subsequently refined using a central composite design (CCD) to evaluate interactions and optimize conditions. The models obtained were statistically significant ($p < 0.05$) and showed satisfactory R^2, adjusted R^2, and predicted R^2 values for most analytes. L-arginine, pyruvic acid, and tryptophan exhibited the best predictive performance, whereas 2,5-dihydroxybenzoic acid, pyroglutamic acid, and kynurenic acid showed more limited predictability. Response surface analysis revealed distinct reactivity profiles: several analytes demonstrated synergistic effects of temperature and reagent concentrations, while pyruvic acid displayed an opposite trend. Optimization using a desirability function confirmed that it was not possible to maximize the response of all analytes simultaneously, highlighting the need for compromises between analytes with divergent reaction profiles. Overall, the optimized conditions consistently improved derivative formation for most analytes. L-arginine, pyruvic acid, and tryptophan provided the most robust model fit and predictive performance. Notably, pyruvic acid required milder conditions to maximize signal intensity, in contrast to other analytes that benefited from higher temperature and reagent concentrations. These findings highlight the specific reactivity behaviors of different carboxylic acids and provide optimized derivatization conditions that will guide method validation and its application in clinical metabolomics.

Acknowledgements: INCT-Bioanalítica [FAPESP/INCT 2014/50867-3, CNPq 465389/2014-7], CNPq 313185/2021-2

DETERMINAÇÃO DE CIPROFLOXACINO RESIDUAL POR SPE-HPLC-PDA NA ÁGUA SUPERFICIAL DO RIO JOANES

Ana Paula Tojal*[1], Jeancarlo Pereira dos Anjos[2], Madson Nascimento[3], Edith Cristina Laignier Cazedey[1]

[1]Universidade Federal da Bahia
[2]Universidade do ABC Paulista
[3]SENAI-CIMATEC

* Corresponding author: aptojal@gmail.com

A presença de antibióticos como o ciprofloxacino (CIP) em águas superficiais representa risco ambiental e sanitário, principalmente pela indução de resistência bacteriana. Este trabalho teve como objetivo desenvolver e validar método analítico baseado em extração em fase sólida (SPE) e cromatografia líquida de alta eficiência com detector de arranjo de fotodiodos (HPLC-PDA) para a detecção de CIP na água do Rio Joanes, manancial estratégico para o abastecimento da Região Metropolitana de Salvador (BA). A otimização da SPE foi realizada com suporte de ferramentas quimiométricas, utilizando cartucho HLB e etanol como solvente extrator. A análise cromatográfica foi conduzida em coluna C18, em modo gradiente, com etanol como modificador orgânico da fase móvel. O método foi validado e apresentou limite de detecção (LD) de 0,05 $\mu g \cdot L^{-1}$ e limite de quantificação (LQ) de 0,2 $\mu g \cdot L^{-1}$. A curva analítica (0,2–10 $\mu g \cdot L^{-1}$) apresentou linearidade adequada, com recuperações entre 90% e 102% na matriz amostral. A validação demonstrou ainda boa seletividade, precisão e exatidão, de acordo com diretrizes analíticas vigentes. Foram coletadas 15 amostras de água em diferentes pontos do Rio Joanes, entre agosto e outubro de 2024. O CIP foi detectado em três amostras, com concentrações entre 0,06 e 0,1 $\mu g \cdot L^{-1}$. Esses níveis estão acima da Concentração Prevista Sem Efeito (PNEC) indicado para essa molécula, apontando um risco ecológico e potencial para seleção de microrganismos resistentes, com possíveis implicações para a saúde humana e veterinária, sobretudo em comunidades expostas à água contaminada. O estudo comprova a aplicabilidade do método desenvolvido para o monitoramento de contaminantes emergentes em recursos hídricos, contribuindo para estratégias de vigilância ambiental e ações regulatórias. A detecção de antibióticos em pontos de captação hídrica reforça a urgência de políticas públicas intersetoriais voltadas à proteção ambiental, ao uso racional de antimicrobianos e à prevenção da resistência microbiana.

Acknowledgements: Esse trabalho teve o apoio da Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES); da empresa Baiana de Saneamento – EMBASA; do SENAI-CIMATEC; e do Núcleo de Pesquisa e Análise de Medicamentos – NuPAM/UFBA.

DETERMINAÇÃO DE TRIHALOMETANOS PRESENTES NA ÁGUA POTÁVEL ENCANADA DE FORTALEZA – CE VIA SPME-GC-FID

Joaquim Rodrigues de Vasconcelos Neto, Antonia Carlota de Souza Lima, Patricia de Sousa Queiroz, Taís Coutinho Parente, Luiz Thiago Vasconcelos da Silva, Lucas Alexandre Nobre da Silva, Jhonyson Arruda Carvalho Guedes, Ronaldo Ferreira do Nascimento

Universidade Federal do Ceará

Os trihalometanos (THMs), Triclorometano (TCM), Bromodiclorometano (BDCM), Dibromoclorometano (DBCM), Tribromometano (TBM), são os principais subprodutos de desinfecção (SPD) resultantes da cloração no tratamento de água potável. O risco no consumo destes compostos está em seu potencial carcinogênico e na exposição constante que passamos diariamente. Tarefas cotidianas simples como, cozinhar um alimento, tomar banho ou escovar os dentes, já são formar de exposição a esses SPDs que podem ser assimilados por via dérmica, inalatória ou por ingestão. O presente trabalho apresentou uma alternativa para a quantificação e detecção dos THMs por SPME-GC-FID, na água tratada em bairros de Fortaleza e ETA-Gavião. A técnica de microextração em fase sólida (SPME, sigla em inglês) junto a cromatografia gasosa foram usadas na determinação dos THMs. A extração foi otimizada por meio de Delineamento composto central rotacional (DCCR) e validado (verificado) pelos testes de significância (teste F e teste t) a um nível de confiança de 95%. O método SPME-GC-FID foi tratado por meio do Método de Mínimos Quadrados Ponderados (MMQP) devido a constatação da heterocedasticidade. Este modelo forneceu um coeficiente de determinação de 0,999 para todos os analitos. A faixa de LD (0,16 – 0,76 µg L-1) e LQ (0,59 – 2,61 µg L-1) foram na mesma ordem de grandeza de alguns trabalhos feitos em GC com os detectores tradicionais ECD e GC-MS. As concentrações de THMs e carbono orgânico total (COT) nas amostras coletadas em Fortaleza e ETA Gavião (bruta e tratada) foram analisadas e avaliadas estatisticamente em (PCA). Apenas 3 bairros apresentaram concentrações abaixo de 100 µg L-1 permitido pela Portaria GM/MS nº 888, de 4 de maio de 2021. O TCM foi o que mais contribuiu para a concentração total dos THMs e o TBM o que menos contribuiu. A água bruta revelou uma maior concentração de COT (18,60 mg L-1) frente as amostras de Fortaleza, enquanto a tratada a maior concentração de THMs totais (256,69 µg L-1).

Acknowledgements: Laboratório de Análise de Traços - UFC, INCT – alimentos, CAPES

DETERMINAÇÃO DO PERFIL QUÍMICO VOLÁTIL DE BOLDO CHILENO (PEUMUS BOLDUS MOLINA) E BOLDO BRASILEIRO (PLECTRANTHUS BARBATUS ANDREWS) POR HS-SPME/GC-MS

Karen Leticia Gomes da Silva*, Edenilson dos Santos Niculau

Universidade Federal do Norte do Tocantins

* Corresponding author: karen.silva@ufnt.edu.br

No Brasil, o consumo de plantas medicinais por infusões é considerado uma prática cultural amplamente utilizada pela população, especialmente quando associada a benefícios terapêuticos. Dentre as principais espécies utilizadas, destaca-se o boldo chileno (Peumus boldus Molina) e o boldo brasileiro (Plectranthus barbatus Andrews) por suas potencialidades medicinais em tratamentos de distúrbios hepáticos e digestivos. O uso dessas plantas, contudo, é acompanhado por uma recorrente confusão entre as espécies, no contexto popular e científico, em razão das semelhanças em suas nomenclaturas populares e aplicabilidades tradicionais. Entretanto, ambas apresentam características químicas relevantes que podem subsidiar estudos sistemáticos que visem suas diferenciações. Em virtude disso, o presente estudo teve como objetivo determinar o perfil químico volátil de Peumus boldus Molina e Plectranthus barbatus Andrews por HS-SPME/GC-MS, utilizando a fibra de polidimetilsiloxano (PMDS). As análises por GC-MS possibilitaram a identificação de 60 Compostos Orgânicos Voláteis (COVs), sendo 32 detectados no P. boldus e 28 no P. barbatus, com distribuição predominante nas classes monoterpênicas e sesquiterpênicas. Dentre os COVs do P. boldus destacam-se como compostos majoritários o 1,8-cineol (19,16%), trans-ascaridol (18,96%) e a β-oplopenona (11,64%). Além disso, o perfil químico volátil desta espécie apresentou um percentual de 44,38% em monoterpenos oxigenados e 19,16% em monoterpenos hidrocarbonetos. Por outro lado, no P. barbatus o α-selineno (23,20%), (E)-cariofileno (19,58%) e α-copaeno (13,64%) foram identificados como os COVs majóritários da composição química volátil da espécie, sendo composta por 83,68% de compostos classificados como sesquiterpenos hidrocarbonetos e 4,48% de monoterpenos hidrocarbonetos. Em síntese, o estudo caracterizou individualmente os perfis químicos voláteis e evidenciou a presença predominante de compostos oxigenados no P. boldus e de sesquiterpenos no P. barbatus. Essas particularidades são fundamentais para subsidiar investigações comparativas e favorecer um uso terapêutico mais seguro e eficaz. Além de contribuir para a valorização do conhecimento etnobotânico, enfatizando sua importância no saber tradicional e no contexto científico.

Acknowledgements: Agradeço à UFNT, ao CNPq, à PROPESQ/UFNT (Edital nº 09/2024) e ao INCT-ALIM (processo 406760/2022-5) pelo apoio e contribuições durante realização deste trabalho.

Determination of abamectin and difenoconazole residues in Scaptotrigona postica: validation of a QuEChERS–UHPLC-MS/MS method and application in environmental samples

Gabriela Reani Rodrigues Garcia*[1], Joyce Oliveira Costa[1], Rafaela Garcia da Silva[1], Janete Brigante[2], Michaela Daam[3], Eny Maria Vieira[4]

[1]Institute of Chemistry of São Carlos
[2]2School of Engineering of São Carlos, University of São Paulo (EESC-USP)
[3]Independent researcher
[4]Institute of Chemistry of São Carlos, University of São Paulo (IQSC-USP)

* Corresponding author: gabriela.reani.garcia@usp.br

Bees are essential pollinators for biodiversity maintenance and agricultural production, yet populations have been declining due to the intensive use of pesticides. Compounds such as abamectin and difenoconazole, widely applied in crops, can cause sublethal effects or even mortality in native species such as Scaptotrigona postica, a stingless bee of ecological and socioeconomic importance.This study aimed to develop and validate a sensitive and selective analytical method for the determination of residues of abamectin and difenoconazole in S. postica tissue samples, using adapted QuEChERS extraction and UHPLC-MS/MS analysis. Validation was performed according to ANVISA Resolution RDC No. 166/2017 and demonstrated adequate linearity ($r^2 > 0.99$) for both analytes. In the biological matrix, the limits of detection (LOD) and quantification (LOQ) were 22.4 and 67.8 ng mL^{-1} for difenoconazole, and 26.5 and 80.2 ng mL^{-1} for abamectin. Intraday precision showed RSD values of less than 8%, while interday precision remained below 10%. Recovery rates were within the ANVISA acceptance criteria, ranging from 85% to 97%, and matrix effects were considered insignificant, ensuring method reliability.When applied to environmental samples collected from hives located near strawberry crops in Bom Repouso (MG, Brazil), only difenoconazole was detected and quantified. The presence of this pesticide evidences environmental contamination and potential risks to colony health.The developed method proved to be robust and suitable for complex environmental matrices, representing a promising tool for monitoring studies and environmental risk assessment of native bees exposed to pesticides in agricultural landscapes.
Keywords: Scaptotrigona postica; UHPLC-MS/MS; QuEChERS; abamectin; difenoconazole.

Acknowledgements: The authors thank the University of São Paulo (USP), the São Paulo Research Foundation (FAPESP), and the LaQuAAE laboratory team for their support in conducting this research.

DETERMINATION OF ACENAPHTHYLENE, ACENAPHTHENE AND PYRENE IN COMMERCIAL SMOKED BACON USING SUPERCRITICAL FLUID EXTRACTION FOLLOWED BY HPLC-UV AND FLUORESCENCE DETECTION

Valentina Rojas*, Juan José Triviño, Verónica Arancibia

Facultad de Ciencias Químicas y Farmacéuticas. Universidad de Chile.

* Corresponding author: valentina.rojas.c@ug.uchile.cl

Polycyclic aromatic hydrocarbons (PAHs) are chemical contaminants having carcinogenic potential which accumulate in food through environmental depositions or are formed during its' thermal processing and incomplete combustion of constituent organic material1. The major thermal processes contributing in PAHs contamination in food includes smoking, barbequing, roasting, toasting, grilling, frying etc. Has been reported the quantitation of PAHs in meat products revealed the formation of only three PAHs including acenaphthylene (AcPy), acenaphthene (AcP) and pyrene (Pyr) in canned minced chicken and pork during processing with no significant difference in total PAHs between the meat types2.

This study describes a procedure for determining AcPy, AcP and Pyr in commercial samples of smoked bacon. In a first step, with spiked samples the SFE parameters (temperature, pressure, and time) were optimized using Bos-Behnken design (-1; 0; 1). Pressures of 1000-1750-2500 psi, temperatures of 40-50-60 °C and times of 10-25-40 min were applied, obtaining maximum values of AcPy, AcP and Pyr in these conditions: AcPy: 1000 psi-60oC-25 min, AcP 1000 psi-40oC-25min and Pyr 2500psi-50oC-40min.Then, HPLC technique with a UV detector was optimized because AcPy does not fluoresce. Different mobile phases and flow rates were tested, and calibration curves were constructed. Linear ranges between 200 and 1000 □g L-1 were obtained with detection limits (DLs) of 102.45, 43.03, and 34.12 □g L-1 for AcPy, AcP, and Pyr respectively. The method was subsequently validated using doped bacon, obtaining recoveries in the order of 53; 33 and 16 respectively. Finally, the methodology was applied to the analysis of bacon, finding that it had 20ng g-1. Furthermore, the electroanalytical methodology was optimized using a graphene screen-printed electrode (HCl 1 mol L-1), obtaining oxidation signals for the 3 PAHs close to 0.194 V. Subsequently, this electrode will be used as an HPLC detector to separate the signals corresponding to each hydrocarbon.

References:

1. L. Singha, T. Agarwala, J. Simal-Gandarab, Trends in Food Science & Technology 99 (2020) 487–506.
2. B.S. Inbaraj, Y-W Lai, B-H. Chen, Molecules (2024) 29, 4372.

Acknowledgements: Financial support by Universidad de Chile, Proyecto enlace 2025 (VA,VR), Fondecyt Regular Project No 1251804 (ANID, VA) and National Doctoral Scholarship No 21220946 (ANID, JJT) is acknowledged.

DETERMINATION OF ETHYLENE-BIS-DITHIOCARBAMATES AND THEIR DEGRADATION PRODUCT ETHYLENETHIOUREA IN TOMATO AND ITS PRODUCTS

Denise Carvalho Mello*, Eloisa Dutra Caldas

Universidade de Brasília

* Corresponding author: denisedcmello@gmail.com

Dithiocarbamates (DTC) are a group of fungicides widely used worldwide. Their chronic toxicity is attributed to some of their degradation products, mainly ethylenethiourea (ETU), a metabolite of the ethylene-bis-dithiocarbamate (EBDC) subclass, which is shown to be carcinogenic in animal studies. ETU can be formed during heating, a common step in tomato-based product manufacturing. Mancozeb, an EBDC, is the most sold fungicide and the second/third among all the pesticides sold in Brazil. In this study, a single analytical method for EBDC (includes metiram) and ETU determination in tomatoes and their products was validated. The method involves adding a L-cysteine-EDTA solution to the sample, followed by extraction with dimethyl sulfate solution in ACN and $MgSO_4$/NaCl, and dispersive clean-up using $MgSO_4$ and PSA. The extract was filtered and analyzed by UHPLC-MS/MS. A total of 45 tomato and tomato product samples were analyzed. The samples were first analyzed using the spectrophotometric method (determination as CS_2) and later by the validated method. This method involves acid hydrolysis of the sample, complexation in an ethanol-diethanolamine-copper acetate solution, and spectrophotometric detection at 435 nm. Six organic tomato samples contained no CS_2 residues, and a mix of these samples was used for the validation of the chromatographic method. Out of the 39 samples (17 tomato and 22 tomato product samples), 28.8% tested positive for CS_2, including one tomato sauce sample containing onion and garlic, which may have been a false positive as they contain sulfur compounds. The samples were analyzed using the validated chromatographic method to confirm the presence of EBDC, as the spectrophotometric method does not distinguish between possible dithiocarbamate compounds in a sample. This method also allowed for the confirmation of the presence or absence of EBDC in the tomato sauce sample containing onion and garlic, helping to verify whether a false positive occurred, thereby highlighting the relevance of this study.

Acknowledgements: Instituto Nacional de Ciência e Tecnologia-Alimentos; Laboratório de Toxicologia (UnB); Finatec; CNPq.

DETERMINATION OF MANCOZEB IN SOYBEAN LEAVES BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY COUPLED WITH SEQUENTIAL MASS SPECTROMETRY

Daiane Letícia Quirino de Souza, Carla Beatriz Grespan Bottoli*

Institute of Chemistry, University of Campinas (UNICAMP)

* Corresponding author: carlab@unicamp.br

Mancozeb is a fungicide widely used in Brazil for the control of Asian soybean rust, a disease that compromises leaf integrity and prevents full grain development. To evaluate its effectiveness and study its translocation in plants, sensitive analytical methodologies are required to enable quantification at low concentrations. However, due to its poor solubility in most solvents, mancozeb determination requires a derivatization step, yielding dimethyl ethylenebisdithiocarbamate (dimethyl EBDC), which is readily soluble in acetonitrile. In this work, the aim was to determine mancozeb in soybean leaves in order to assess the translocation of this compound after its application to the plant. For this purpose, the preparation of soybean leaf samples treated with formulations containing mancozeb, picoxystrobin, and tebuconazole was optimized, and quantification was carried out by HPLC-MS/MS.

Chromatographic separation was performed using a C18 column (150 × 4.6 mm; 5 µm) – Luna Phenomenex, with 0.1% (v/v) formic acid in water (phase A) and acetonitrile (phase B) under a gradient elution program, which proved selective for the quantification of dimethyl EBDC in soybean leaves. The variables studied in the derivatization reaction included the molar amount of EDTA-Na_2 (pH 9.5–10), cysteine, dimethyl sulfate, mancozeb dissociation time, and alkylation time of the intermediate. EDTA-Na_2 acted as a complexing agent for the released Mn and Zn species, cysteine was used as an antioxidant to prevent degradation of the dimethyl EBDC derivative, and dimethyl sulfate was employed for alkylation of the ethylenebisdithiocarbamic acid intermediate. Experimental design enabled the definition of optimal reaction conditions in acetonitrile, with a predictive accuracy of 84%. Evaluation of different QuEChERS methodologies demonstrated superior recovery using NaCl/$MgSO_4$ combined with PSA as a cleanup sorbent. The chromatographic method proved selective for the determination of dimethyl EBDC in the matrix, providing a working range of 50 µg L^{-1} to 1000 µg L^{-1}, with detection and quantification limits of 25 µg L^{-1} and 50 µg L^{-1}, respectively.

In conclusion, the optimized derivatization protocol combined with the developed chromatographic method demonstrated selectivity and efficiency, providing a reliable approach for monitoring mancozeb effectiveness in soybean crops.

Acknowledgements: The authors gratefully acknowledge the financial support provided by CAPES, INCT-Bioanalítica [FAPESP/INCT 2014/50867-3,CNPq 465389/2014-7], CNPq 313185/2021-2.

DETERMINATION OF MULTICLASS CONTAMINANTS IN BREAST MILK BY HS-SPME-GC-MS/MS: METHOD DEVELOPMENT AND OPTIMIZATION

Anna Carolina Nickel Meireles*[1], Ingrid Silva Wesz[1], Luciana Tavares de Oliveira[1], Sthefanie Lopes do Valle[1], Jean Lucas de Oliveira Arias[1], Karina Lotz Soares[1], Sergiane Caldas Barbosa[1], Vanusa Pousada da Hora[2], Josias de Oliveira Merib[3], Ednei Gilberto Primel[1]

[1]Universidade Federal do Rio Grande - FURG, Laboratório de Análise de Compostos Orgânicos e Metais - LACOM, Rio Grande, Rio Grande do Sul, Brazil, 96203-900
[2]Universidade Federal do Rio Grande – FURG, Faculdade de Medicina, Rio Grande, Rio Grande do Sul, Brazil, 96200-400
[3]Universidade Federal de Ciências da Saúde de Porto Alegre – UFCSPA, Departamento de Farmacociências, Porto Alegre, Rio Grande do Sul, Brazil, 90050-170

* Corresponding author: annacnmeireles@gmail.com

Breast milk is the main source of nutrition for newborns and infants. The WHO recommends exclusive breastfeeding for up to 6 months and supplementary breastfeeding up to 2 years or more. In human milk banks, milk undergoes microbiological quality control to ensure food safety for newborns. However, in Brazil, there are no standardized measures to assess the presence of contaminants in breast milk. Therefore, breast milk can be a potential vehicle for the transfer of contaminants from mother to child, such as pesticides, pharmaceuticals, and personal care products, which have toxic effects on the baby's development, such as neurological, gastrointestinal, and reproductive problems. Therefore, this study aims to develop an analytical method for the determination of emerging contaminants using HS-SPME and GC-MS/MS. Six SPME fibers were evaluated for the extraction of 13 analytes (9 parabens, caffeine, atrazine, bisphenol-A, and benzophenone-3) and polyacrylate was chosen due to its greater response for most analytes. After that, a CCRD 23 factorial experimental design was performed, using incubation and extraction temperature, ionic strength, and extraction time as variables. Therefore, the HS-SPME-GC-MS/MS method was performed as follows: 5 mL of sample solution (1:4, sample:water) and 1.5 g of NaCl, fiber conditioning occurs at 250 °C for 30 min, the sample is incubated at 80 °C for 10 min with shaking at 250 rpm, then the fiber is exposed for 80 min at 80 °C and finally desorption occurs for 5 min at 250 °C. The optimized method was validated according to INMETRO and SANTE guidelines. The analytical matrix superposition curves were evaluated by external calibration, showing linearity > 0.99 for most analytes. The method LODs ranged from 0.15 to 0.76 ng mL-1 and the LOQs ranged from 0.5 to 2.5 ng mL-1. The accuracy and precision showed recovery values ranging from 43 to 120%, with RSD The method will be further applied to the determination of contaminants in real samples.

Acknowledgements: The authors acknowledge the scholarship provided by CAPES and the financial support provided by CNPq, FAPERGS and FINEP.

DETERMINATION OF MULTIRESIDUE PESTICIDES IN SUNFLOWER SEEDS USING A MODIFIED QUECHERS METHOD WITH µSPE CLEAN-UP AND UHPLC-MS/MS

Alcides Ferreira Coradini, Vitória B. de Souza, Iuri R. C. Berni, Osmar Damian Prestes, Renato Zanella*

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria -RS, Brazil

* Corresponding author: renato.zanella@ufsm.br

Sunflower is one of the world's four largest oilseed crops, ranking behind only soybean, rapeseed, and cotton. Its prominence is due not only to the high quality of its oil, which is rich in vitamins, minerals, and antioxidants such as carotenoids and phenolic compounds, but also to its value as a production strategy. It serves as an excellent option for crop rotation (second harvest), helping to break monoculture cycles. In sunflower cultivation, chemical control through pesticides application is a highly effective method for field management. However, the extraction and analysis of pesticides in this matrix present significant challenges mainly due to its high lipid content. This work evaluated the feasibility and efficiency of using a micro-solid-phase extraction (µ-SPE) well plate as an alternative clean-up method to traditional dispersive solid-phase extraction (d-SPE) for QuEChERS extracts. Three different QuEChERS buffering versions were evaluated. For the d-SPE clean-up, a mixture of PSA (25 mg) and C18 (125 mg) sorbents with 150 mg of $MgSO_4$ was used, followed by agitation and centrifugation. A high-throughput µ-SPE procedure was proposed using a well plate containing (40 mg) of EMR-Lipid sorbent, with a simple elution step using a solution containing 20% ultrapure water. Extracts from both methods were five-fold diluted and filtered through a 0.22 µm PVDF membrane prior to analysis by UHPLC-MS/MS in a system Xevo TQ-XS (Waters) with ESI source. Chromatographic separation was performed on an ACQUITY UPLC BEH C18 column (2.1 × 50 mm, 1.7 µm) maintained at 45 °C. The mobile phase consisted of (A) ultrapure water and (B) methanol/acetonitrile 1:1 (v/v), both containing formic acid and ammonium formate. The flow rate was 0.225 mL min^{-1} with gradient elution. The acetate-buffered QuEChERS method using µ-SPE for clean-up proved to be viable, providing recoveries between 70 and 120% with relative standard deviation (RSD) values ≤ 20% for the majority of compounds. The method limit of quantification (LOQ) was established at 10 µg kg^{-1} for 93 pesticides. This work provides a new perspective on sample preparation for fatty matrices such as sunflower seeds, offering a faster, simpler, and more efficient alternative for routine laboratory analysis.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CNPq, CAPES and FAPERGS.

DETERMINATION OF NAPHTHENIC ACIDS IN CRUDE OIL AND PRODUCED WATER BY LIQUID CHROMATOGRAPHY COUPLED TO HIGH-RESOLUTION MASS SPECTROMETRY USING HILIC MODE

Allyson Leandro Rodrigues dos Santos*[1], Lucas Paines Bressan[1], Rogerio Mesquita Carvalho[2], Iris Medeiros Junior[2], Leandro Wang Hantao[3]

[1]Institute of Chemistry, University of Campinas (IQ, UNICAMP)
[2]Leopoldo Américo Miguez de Mello Research Center (CENPES, PETROBRAS)
[3]Institute of Chemistry, University of Campinas (IQ, UNICAMP);Center for Energy and Petroleum Studies (CEPETRO, UNICAMP); Center for Energy Planning (NIPE, UNICAMP)

* Corresponding author: allysonl@unicamp.br

Naphthenic acids (NAs) are a complex mixture of carboxylic acids naturally present in crude oil and produced water. High concentrations of NAs can cause operational problems, such as pipeline and equipment corrosion, the formation of deposits, and stable emulsions that are difficult to separate. Additionally, environmental impacts include toxicity to aquatic organisms. This makes the development of precise analytical methods essential. This study aimed to develop an analytical method for determining NAs in produced water and crude oil samples. Oil samples were subjected to solid-phase extraction (SPE), while produced water samples were processed using supported liquid extraction (SLE). NAs were determined using liquid chromatography coupled to high-resolution mass spectrometry (LC-HRMS). Hydrophilic interaction chromatography (HILIC) was used for the separation of NAs. The initial study involved evaluating the mobile phase composition, additives, pH, and flow rate. The optimized mobile phase consisted of acetonitrile and an ammonium hydroxide solution (pH 9), with a flow rate of 0.3 mL/min and a total run time of 15 minutes. The HRMS parameters were adjusted according to the chromatographic conditions by optimizing the capillary voltage and vaporization temperature. The primary measures included peak area, chromatographic resolution, selectivity, and the quality of the reconstructed peak. Calibration curves were determined for 15 NAs using solvents and matrix-matching, showing a linear range from 0.025 to 500 ng L^{-1}, adequate linearity ($r > 0.99$), and minimal matrix effect (

Acknowledgements: CAPES, CNPq, FAPESP, PETROBRAS.

DETERMINATION OF NONSTEROIDAL ANTI-INFLAMMATORY DRUGS IN AQUATIC ENVIRONMENTS USING DPX AND HPLC-UV

Isabella Felix de Almeida*, Maria Flávia Assunção Magalhães, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: isabella.felix@usp.br

Nonsteroidal anti-inflammatory drugs (NSAIDs) including naproxen, flurbiprofen, diclofenac, ibuprofen, and paracetamol are widely used and frequently detected in aquatic environments due to their indiscriminate consumption, posing risks to both aquatic biota and public health. Even at low concentrations, these compounds can cause toxic and reproductive effects in aquatic organisms, highlighting the need for sensitive analytical methods for their detection. High-performance liquid chromatography coupled with ultraviolet detection (HPLC-UV) is commonly employed owing to its robustness and accessibility, although analytical efficiency largely depends on an appropriate sample preparation procedure. In this context, the dispersive pipette extraction (DPX) technique emerges as a sustainable and effective alternative. In this study, graphene oxide anchored to β-cyclodextrin was employed as the sorbent phase a hybrid material that combines high surface area with molecular selectivity, enabling more efficient extraction in accordance with the principles of green analytical chemistry. Structural and spectroscopic analyses confirmed the successful anchoring of β-cyclodextrin onto graphene oxide. Preliminary tests were conducted using different desorption solvents (MeOH, ketone, ACN, and ACN:MeOH 1:1 v/v), with the highest recovery for ibuprofen (109%) obtained using ACN. Subsequently, different desorption volumes (100, 200, and 300 µL) were evaluated. The recoveries obtained for the target analytes were lower, and optimization of the experimental parameters is still in progress, aiming to establish a sustainable DPX–HPLC-UV procedure suitable for the multiresidue determination of NSAIDs in aqueous samples.

Acknowledgements: FAPESP [Grants 2017/02147-0; 2017/21984-0; EMU; 2017/21985-6 – EMU]; CNPq [Grants 308843/2019-3 and INCT-ALIM Grants 406760/2022-5; 125386/2025-7]; CAPES [Grant: 88887.005608/2024-00] financed this study.

DETERMINATION OF PAHs AND THEIR NITRATED AND OXYGENATED DERIVATIVES IN SETTLEABLE PARTICULATE MATTER USING AN OPTMIZATED DI-SPME-GC-FID METHOD

Alexandre Cristiano Vicente Campos*, Igor Corrêa Francisco, Zenilda de Lourdes Cardeal, Helvécio Costa Menezes

Universidade Federal de Minas Gerais

* Corresponding author: alexandrecvcampos@ufmg.br

Polycyclic aromatic hydrocarbons (PAHs) and their oxygenated (oxy-PAHs) and nitrated (nitro-PAHs) derivatives constitute a group of compounds that contain two or more condensed aromatic rings. Many of these compounds have proven carcinogenic and mutagenic properties, and their ubiquitous nature is evidenced by the fact that sixteen PAHs are considered priority pollutants by the USEPA (USEPA, 1998). The presence of these pollutants in the environment air may contribute to various human health problems, such as cardiovascular and cerebrovascular diseases, through mechanisms involving systemic inflammation, direct and indirect activation of coagulation, and direct translocation into systemic circulation. Given the risk attributed to PAHs and their derivatives, there is a need to develop robust and sensitive methods capable of determining these analytes in complex matrices, such as settleable particulate matter (SPM). This work were optimized the extraction conditions of direct immersion solid-phase microextraction (DI-SPME) and determination by gas chromatography with Flame Ionization Detector (GC-FID). The SPME fiber used was polydimethylsiloxane-divinylbenzene (PDMS-DVB) from Supelco®. The variables investigated were extraction time (30 to 60 minutes), temperature (40 to 70 °C), stirring (260 to 780 rpm), and acetonitrile as a modifier (50 to 200 µL), using a fractional factorial design 2^{4-1}. Only the variables time and temperature were significant in the screening step, based on the Pareto diagram at a 0.05 significance level. Thus, optimization was carried out by response surface methodology using a Doehlert matrix with triplicates at the central point. The optimal conditions obtained were 65 minutes of extraction at 80 °C. The most significant effect among the variables was time, possibly because the longer the fiber remains exposed, the more concentrated the analytes become. After optimization, the method will be validated and applied to PS samples collected at two sites on the UFMG campus in Belo Horizonte, Brazil.

Acknowledgements: FAPEMIG, PPG Química – UFMG, CNPq

Determination of pesticides in common black beans (Phaseolus vulgaris L.)

Kamila Rosa Acosta, Salvador da Silva Madruga Junior, Alberto Kazutomi Ozaki Junior, Lais Regina Maciel, Maristela Barnes Rodrigues Cerqueira, Jaqueline Garda Buffon, Larine Kupski*

FURG

* Corresponding author: larinekupski@yahoo.com.br

The common black bean (Phaseolus vulgaris L.) is widely consumed, especially in developing countries, due to its nutritional properties. Bean production depends on the use of pesticides, and Brazil was the world's largest consumer in 2021, accounting for 22% of the global total. This scenario reinforces the importance of applying effective methods for quantifying pesticides to ensure food safety. Therefore, the objective of this study was to validate a method for determining multiclass pesticides (atrazine, flutriafol, pirimiphos-methyl and procymidone) in black beans using QuEChERS and GC-MS. Extraction was performed using acetonitrile acidified with 1% acetic acid, followed by partitioning with anhydrous magnesium sulfate and sodium acetate. In the cleanup step, magnesium sulfate and C18 were used. After agitation and centrifugation, 1 mL of the extract was injected into a GC-MS. The method was validated by evaluating the following figures of merit: limit of detection (LOD), limit of quantification (LOQ), accuracy (recovery), and precision (repeatability). The validated method was used to determine contaminants in beans sold in the city of Rio Grande. For the occurrence survey, 80 samples of black beans (type 1 and out-of-type) were selected from five supermarket chains located in the city of Rio Grande, RS, collected in July 2024 and July 2025. Different brands were selected from each chain, and different lots within each brand. The method's LODs ranged from 0.015 to 0,05 µg/kg, and the LOQs from 0.05 to 0.5 µg/kg. The method's accuracy ranged from 75.6 to 100.8% for all pesticides, with deviations less than 17%. Pirimiphos-methyl was detected in 25% of the samples, at levels

Acknowledgements: FAPERGS- grant term 23/2551-0000927-7. CNPq grant term PQ 306194/2025-2.

DETERMINATION OF PHENOLIC ACIDS IN RED WINES BY HPLC-PDA: AN EFFICIENT APPROACH USING DIRECT SAMPLES INJECTION

Elizangela Gonçalves, Juliane Lima da Silva, Jaqueline Garda Buffon, Priscila Tessmer Scaglioni*

Universidade Federal do Rio Grande - FURG

* Corresponding author: priscilascaglioni@gmail.com

High-performance liquid chromatography coupled with a photodiode array detector (HPLC-PAD) was employed for the determination of phenolic acids in wine through direct sample injection. A total of 58 red wine samples were obtained from commercial outlets in the state of Rio Grande do Sul, Brazil. Sample preparation consisted of filtering 2 mL of wine through a 0.22 µm hydrophilic membrane, followed by direct injection into the chromatographic system. A reverse-phase C18 column was used, operating under isocratic elution with methanol and acetic acid–acidified water (20:80, v v^{-1}), at a flow rate of 0.7 mL min^{-1} and a temperature of 35 °C. Detection was carried out at two wavelengths, 280 and 320 nm, enabling the identification of different compounds. Nine phenolic acids were investigated (gallic, protocatechuic, chlorogenic, hydroxybenzoic, caffeic, ferulic, syringic, vanillic, and p-coumaric), with standards prepared from methanolic solutions. Quantification was performed using external calibration curves. The results demonstrated the presence of phenolic acids in all samples, with total concentrations ranging from 21.54 to 148.15 mg L^{-1}. Gallic, caffeic, and vanillic acids were detected in 100% of the samples, while chlorogenic, protocatechuic, syringic, p-coumaric, and ferulic acids were identified in more than 90% of the wines. Hydroxybenzoic acid showed the lowest detection frequency (65%), possibly due to its higher susceptibility to degradation processes during vinification. The analysis of individual profiles indicated predominance of gallic, caffeic, chlorogenic, p-coumaric, protocatechuic, and hydroxybenzoic acids in terms of concentration. Gallic acid stood out as the major compound, confirming its importance as a precursor of hydrolyzable tannins and as a product of oxidative reactions during wine aging. The high occurrence and diversity of phenolic acids highlight their relevance not only to sensory properties, such as color and astringency, but also to the antioxidant potential of the beverage. In summary, the chromatographic method applied proved efficient for characterizing the phenolic profile of commercial red wines, revealing significant variations among samples and demonstrating the influence of technological and aging factors on the final chemical composition. Furthermore, direct injection of filtered samples into the HPLC system minimized sample handling, reduced analysis time, and prevented potential losses or alterations of phenolic compounds.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN GREEN DIESEL USING SPME-GC-FID

Tainah Gomes de Jesus*, Vânya Márcia Duarte Pasa, Zenilda de Lourdes Cardeal

Universidade Federal de Minas Gerais

* Corresponding author: tainahgomezz@gmail.com

Burning fossil fuels increases environmental pollutants, releases harmful environmental pollutants, includingpolycyclic aromatic hydrocarbons and their nitrogenated and oxygenated derivatives (PAHs, Oxi-PAHs, and nitro-PAHs). he increasing demand for renewable energy sources has driven the adoption of biofuels as a strategy to reduce emissions and promote sustainability. Green diesel (HVO – Hydrotreated Vegetable Oil) is produced by hydrogenating vegetable oils and animal fats with catalysts that saturate fatty acids through three main reactions: hydrodeoxygenation (HDO), decarbonylation (DCN), and decarboxylation (DCX). In Brazil, ANP Resolution 842/2021 regulates green diesel, setting a maximum aromatic hydrocarbon content of 1.1% m/m, since these compounds affect thermal stability, combustion performance, and overall fuel quality. This work presents the development of a gas chromatography system equiped with flame ionization detection (GC-FID) for the determination of 15 PAHs (naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BAA), chrysene (CHR), benzo(b)fluoranthene (BBF), benzo(a)pyrene (BAP), indeno(1,2,3-cd)pyrene (IND), dibenzo(a,h)anthracene (DIB) and benzo(g,h,i)perylene (BZP), in green diesel. A direct immersion solid-phase microextraction (DI-SPME) method was developed for the determination of polycyclic aromatic hydrocarbons (PAHs) in green diesel, whereby a 10 µL aliquot was introduced into 20.0 mL of an aqueous solution using 1,4-dioxane as a dispersive solvent; extraction was performed with a polydimethylsiloxane (PDMS) fiber at 60 °C for 10 min, followed by thermal desorption in a splitless injector (280 °C for 1 min). Analysis was carried out on a GC-FID system (Clarus 600) with the FID maintained at 310 °C, using helium carrier gas at a constant flow of 1.0 mL min^{-1} and an oven temperature program starting at 80 °C and ramping at 5 °C min^{-1} to 300 °C. The method proved effective for PAH determination, yielding chromatograms with well-resolved peaks that allowed for clear distinction between compounds and successful validation of linearity and precision, demonstrating compliance with ANP resolution requirements for green diesel analysis.

Acknowledgements: Acknowledgements: The authors gratefully acknowledge the financial support provided by PRH-ANP (Resolution 918/2023) through FAPESP [Grant 2024/12554-5] and UFMG.

DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN PYROLIGNEOUS EXTRACT USING UALLE AND GC-FID

Antônio Miguel Gomes Lima*, Márcia Helena Scherer Kurz, Carlos Roberto Menezes Peixoto, Lenise Guimarães de Oliveira, Fábio Ferreira Gonçalves

Universidade Federal do Rio Grande - FURG

* Corresponding author: antoniosapgomes@gmail.com

In response to the escalating global demand for food, the use of biofertilizers, such as pyroligneous extract (PE), has gained prominence in modern agriculture. However, the presence of potentially carcinogenic polycyclic aromatic hydrocarbons (PAHs) in these products necessitates rigorous quality control. The objective of this study was to develop and validate a robust analytical method for the extraction and quantification of 16 priority PAHs, defined by the USEPA, from PE. The method employed a three-step procedure: Ultrasound-Assisted Liquid-Liquid Extraction (UALLE) of PAHs from the matrix using toluene, followed by a cleanup step with Solid Phase Extraction (SPE) C18 cartridges, and a final pre-concentration under an air flow. The quantification was performed using Gas Chromatography with a Flame Ionization Detector (GC-FID). The method was validated according to the criteria established by INMETRO and SANTE. Recoveries for the PAHs ranged from 38% to 109.5% with a relative standard deviation (RSD) below 13%. All compounds exhibited linearity with coefficients of determination (R2) greater than 0.99. The Limit of Quantification (LOQ) and Limit of Detection (LOD) values were in the range of 1.6 to 3 µg. L-1 and 0.53 to 1 µg. L-1, respectively. A significant matrix effect, characterized by signal amplification greater than 20%, was effectively compensated by the use of standard addition curves for calibration. The method was applied to real PE samples produced by small producers from the Paranhama Valley in the State of Rio Grande do Sul, Brazil, revealing total PAH concentrations between

Acknowledgements: CNPq, FAPERGS, PPGQTA and FURG.

DETERMINATION OF THE ANTICANCER DRUG 5-FLUOROURACIL BY LIQUID CHROMATOGRAPHY WITH AMPEROMETRIC DETECTION USING CARBONACEOUS SCREEN PRINTED ELECTRODE

Veronica Arancibia*, Arturo Salinas, Juan José Triviño

Facultad de Ciencias Químicas y Farmacéuticas. Universidad de Chile.

* Corresponding author: varancibia@ciq.uchile.cl

5-Fluorouracil (5-fluoro-1 Hpyrimidine-2,4-dione. 5-Flu) has held an important place in biomedicine over 50 years, due to its achievement in cancer chemotherapy of solid tumors. For several years it has been reported that Health care workers who prepare or administer Anticancer Drugs, or who work in areas where these drugs are used, can be exposed to these agents when they are present on contaminated work surfaces, drug vials and containers, contaminated clothing and medical equipment. Because of this, it is very important to have simple methodologies to determine 5-Flu in wastewater and urine of health workers.

Because 5-Flu can be oxidized at carbon electrodes, it is suitable for its determination either as an amperometric detector of Liquid chromatography or by direct measurements using electroanalytical sensors.

A commercial carbon screen-printed electrode (was chosen to perform the 5-Flu determination by anodic stripping voltammetry. In order to obtain a sensitive and selective methodology, a study was carried out based on supporting electrolyte, pH, accumulation potential, and time (Eacc, tacc).

The optimum experimental conditions chosen were Phosphate buffer 0.1 mol L-1 pH:7.0; Eacc: 0.0 V and tacc: 30 s obtaining a signal of oxidation of 5-Flu about 1.2 V. Peak current was proportional to 5-Flu concentration over the 0.2–6.0 mg L-1 range, with a 3σ detection limit of 0.17 mg L-1. The method was validated using 5-Flu spiked commercial urine with satisfactory results.

Then, HPLC technique with an Amperometric detector (CHIntruments) was optimized using a Phenomenex Gemini 5□-C18-110A (250 x 4.6 mm) column. Different mobile phases were tested, selecting 96% 5mM KH_2PO_4 (pH:6.0) 4% CH_3OH1. The circuit was completed with an HPLC pump, an injector, a column oven (25°C) and a special flow cell for screen-printed electrodes. A study was conducted based on the flow rate and applied potential required for electrochemical oxidation. The values chosen were a flow rate of 0.8 mL/min and a potential of 1.2 V. Linear ranges between 5.0 and 52.0 mg L-1 ($R > 0.99$) were obtained with a detection limit (DL) of 3.3 mg L-1.

Reference: 1. M. Hanif, M. Faheem-Akhtar, S. Naeema et al., Current Pharmaceutical Analysis, 14 (2018) 3-7.

Acknowledgements: Financial support by Fondecyt Regular Project No 1251804 (ANID, VA) and National Doctoral Scholarship No 21220946 (ANID, JJT) is acknowledged.

DETERMINATION OF THE HYDROTREATED VEGETABLE OIL (HVO) CONTENT IN HVO/FOSSIL DIESEL BLENDS USING GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY AND MULTIVARIATE ANALYSIS

Daniel Almeida Cozendey[1], Daniella Lopez Vale[2], Fábio Azamor de Oliveira[2], Cristiane Gimenes de Souza[2], Renan de Oliveira Muniz[1], Monica Costa Padilha[2], Luiz Antonio d'Avila[1], Débora França de Andrade*[2]

[1]EQ/UFRJ
[2]IQ/UFRJ

* Corresponding author: debora.franca.andrade@gmail.com

Low-carbon fuels, emitting less carbon than fossil fuels, are proposed to help in the transition to a sustainable, decarbonized transport sector. The new biofuels being studied and developed in this context include hydrotreated vegetable oils (HVO). Its chemical composition, which is the same as fossil diesel (primarily composed of linear chain hydrocarbons C12–C24), makes HVO (more homogeneous mixtures of paraffinic hydrocarbons C10–C20, containing no sulfur or aromatics) a fuel with slightly lower density than fossil diesel due to these characteristics. Therefore, it can be easily used in place of fossil diesel without the need for modifications to vehicle engines. However, this similarity means that when these fuels are mixed, differentiating and determining their respective concentrations becomes more challenging. ASTM D6866-22 is a standard that describes two tests for determining the carbon-14 (C14) in fossil and renewable fuels; however, both methodologies are expensive and time-consuming. To develop an alternative method to determine HVO in fossil diesel mixtures, a predictive model was created from the chemometric processing of total ion chromatograms obtained from gas chromatography-mass spectrometry (GC-MS). Forty-one mixtures were prepared in triplicate, with concentration levels ranging from 0% to 100% (v/v) HVO in fossil diesel. The samples were divided into training (96 samples) and testing (27 samples) datasets. The raw data obtained from the chromatograms was processed using Orange Data Mining using partial least squares regression. The validation parameters obtained from the predictive model generated by this method had a coefficient of determination of 0.991, mean absolute error of 1.714, and mean squared error of 12.648. The model developed obtained very satisfactory results for the HVO used in this study, however, it is always important to consider HVO's from other sources to strengthen the model.

Acknowledgements: The authors wish to thank CNPq and FAPERJ for the funding received.

DETERMINATION OF TYLOSIN, TILMICOSIN, SPECTINOMYCIN, AND STREPTOMYCIN IN CHICKEN MUSCLE BY LC-MS/MS: EVALUATION OF EXTRACTION METHODS FOR RESIDUE MONITORING

Rosana Gomes Ferreira, Letícia Leal Barros, Mararlene Ulberg Pereira, Amanda da Silva Rio, Lais Farias de Carvalho, Bernardete Ferraz Spisso*

1Instituto Nacional de Controle de Qualidade em Saúde – Fundação Oswaldo Cruz (INCQS/Fiocruz)

* Corresponding author: bernardete.spisso@fiocruz.br

The use of antimicrobials, including macrolides and aminoglycosides, is common in poultry farming. Therefore, monitoring residues from these classes in chicken muscle is of paramount importance. Analytical methods for the determination of antimicrobial residues are commonly based on liquid chromatography tandem mass spectrometry (LC-MS/MS), owing to its high specificity and sensitivity. Among all the steps involved in these methodologies, sample preparation is one of the most critical, as it entails the extraction of target compounds at microgram or nanogram per kilogram levels from complex matrices, often requiring purification of the extracts. The objective of this study was to evaluate different extraction and purification conditions for the determination of the macrolides tylosin and tilmicosin, and the aminoglycosides spectinomycin and streptomycin in chicken muscle using LC-MS/MS. The methods were based on five experiments involving acidic extractions, comprising one aqueous solvent step and one organic solvent step (acetonitrile). Additional sample purification steps were also performed, including the addition of hexane and octadecylsilane (C18) sorbent to the extracts. Recoveries were calculated by comparing the peak areas of substances spiked into blank matrices at the beginning of the procedure with those of blank samples extracted and spiked at the end of the process. The method that yielded the highest analyte recoveries and the lowest relative standard deviations (RSD) was the direct extraction method (Experiment 5), which employed an aqueous solvent - water containing 2% trichloroacetic acid - in the first step, followed by an organic solvent - acetonitrile acidified with 0.01 mol L^{-1} oxalic acid - in the second step. Recovery values ranged from 67% to 117%, with RSD between 7% and 15%. Additional purification steps did not improve recoveries compared to the direct extraction methods. Direct extraction method 5 proved to be more promising compared to the other tested approaches and those involving additional purification steps, offering lower cost and reduced execution time.

Acknowledgements: This study was supported by CAPES (Finance Code 001) and Secretaria de Gestão do Trabalho e da Educação na Saúde – SGTES/ Ministério da Saúde.

Development and application of a microextraction by packed sorbent method with ionic liquid-grafted silica–graphene oxide for multiclass pesticides in Spanish wines

Alessandra Timóteo Cardoso*[1], Gloria Domínguez-Rodríguez[2], Alejandro Cifuentes[2], Fernando Mauro Lanças[1]

[1]São Carlos Institute of Chemistry, Universidade de São Paulo, São Carlos, Brazil
[2]Foodomics Laboratory, Instituto de Investigación en Ciencias de la Alimentación, Consejo Superior de Investigaciones Científicas, Madrid, Spain

* Corresponding author: Alessandracardoso@usp.br

Monitoring pesticide residues in wine is essential to ensure food safety, as these compounds and their metabolites can persist in the final product and pose health risks. In this study, a hybrid sorbent was developed by anchoring graphene oxide onto amino-silica particles (GO@Sil) and functionalizing them with ionic liquids (ILs) via direct anion exchange. Among the tested materials, GO@Sil-[VHIm]$^{+}PF_6^{-}$ showed the best extraction performance due to its multiple interaction mechanisms with the analytes. This sorbent was integrated into a microextraction by packed sorbent (MEPS) system for the determination of six multiclass pesticides (carbendazim, thiodicarb, carbofuran, carbaryl, atrazine, and terbuthylazine) in wines, followed by HPLC-MS/MS analysis. Extraction conditions were optimized using univariate and multivariate approaches, establishing the following protocol: 3 mg of sorbent packed into a 1 mL polypropylene syringe, six extraction cycles of 1 mL wine (draw/eject), one washing cycle with ultrapure water to remove polar interferents, six desorption cycles with 200 µL of acetonitrile:methanol (50:50, v/v), and sorbent regeneration with 500 µL of acetonitrile to prevent carryover. The validated method provided excellent linearity ($r^2 \geq 0.9958$), satisfactory precision (RSD < 15%), and recoveries between 49% and 112%. Limits of detection ranged from 0.030 to 0.130 ng mL^{-1}, with negligible matrix effects in white, red, and rosé wines. The sorbent could be reused for at least six extractions, and batch-to-batch reproducibility met acceptance criteria (all RSDs < 20%), confirming the reliability of the synthesis. Additionally, the method demonstrated notable green advantages, including device reusability and low solvent consumption (0.7 mL per analysis). Sustainability assessments with AGREEprep and BAGI yielded favorable scores (0.52 and 57.5, respectively). Overall, this study introduces a promising and environmentally friendly analytical approach for multiclass pesticide monitoring in wines, with strong potential for routine application.

Acknowledgements: This study was financed, in part, by the São Paulo Research Foundation (FAPESP), Brasil (Process Numbers: 2023/06258-1, 2023/07159-7 and 2024/12325-6) and CNPq (INCT-ALIM, 406760/2022-5). Additional support was provided by projects PID2020-113050RB-I00 and PDC2021-120814-I00 (funded by MCIN/AEI/10.13039/501100011033 and the European Union Next Generation EU/PRTR), the INCGLO0019 project, and the Juan de la Cierva grant JDC2023-052516-I.

Development and Optimization of a LC-MS/MS Method for Determining Xanthines in Plasma Samples

Maria Eduarda Diniz*[1], Taís Betoni Rodrigues[1], Álvaro José Santos-Neto[1], Bryan Saunders[2]

[1]Laboratory of Chromatography (CROMA), São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil
[2]Faculty of Medical Sciences, University of São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: mariaeduaradadiniz2@usp.br

Regular physical activity is often associated with nutritional supplements aimed at improving performance, recovery, or muscle gain. Adequate supplementation can enhance athletic performance by optimizing muscle function and exercise tolerance. Among the substances studied, caffeine stands out as one of the most widely used in sports. However, the variability of results suggests that supplementation is not equally effective for all individuals, reinforcing the need for research to identify the determining factors for positive effects. In this context, the quantification of caffeine and its metabolites in biological matrices is essential for assessing individual responses. Therefore, this study aimed to develop an LC-MS/MS method for their determination in plasma samples. Plasma samples (100 µL) were subjected to protein precipitation with cold acetonitrile (400 µL) in the presence of an internal standard (caffeine-d9, 500 ng mL^{-1}). After vortexing and centrifugation (14,000 rpm, 10 min), the supernatant was dried in a SpeedVac (60 °C, 1h20). The residue was resuspended in H_2O:MeOH (90:10, v/v), centrifuged again, and the supernatant transferred to a vial with an insert. Then, 3 µL was injected into the LC-MS/MS. Analyses were performed on an ACQUITY UPLC system coupled to a Xevo TQ-MS triple quadrupole mass spectrometer (Waters, USA), equipped with an Acquity UPLC BEH C18 column (100 × 2.1 mm, 1.7 µm) and Vanguard pre-column (1.7 µm), maintained at 40 °C. The mobile phases were: (A) water + ammonium formate (5 mmol L^{-1}) and (B) methanol, with a flow rate of 0.3 mL min^{-1}, under a 15–95% B gradient, totaling an 8-min run. Detection was performed by ESI(+) in MRM mode. Data control, acquisition, and processing were performed using MassLynx software (Waters, USA). As a result, a concise and robust method for the analysis of xanthines was developed. However, column clogging was recurrent during method development, even with the use of a Vanguard pre-column, suggesting that the issue is related to sample preparation. Since the current protocol does not include lipid and phospholipid removal, an Ostro 96-well plate was acquired to assess whether the accumulation of these components is affecting chromatographic analysis of xanthines.

Acknowledgements: CNPq nº314731/2021-0 and 309282/2025-0; FAPESP nº 22/07258-2 , 21/06836-0 , 25/12047-9 , 23/07159-7, 17/02147-0; INCT nº 406760/2022-5.

DEVELOPMENT AND OPTIMIZATION OF AN HPLC-DAD-RID METHOD FOR MONITORING MUCONIC ACID AND METABOLIC INTERMEDIATES IN FERMENTATION PROCESSES

Lúcia Daniela Wolf*, Mariany da Silva Costa, Matheus Coutinho Gazolla, Cíntia Regina Sargo

Brazilian Biorenewables National Laboratory (LNBR), Brazilian Center for Research in Energy and Materials (CNPEM)

* Corresponding author: lucia.wolf@lnbr.cnpem.br

Muconic acid is a dicarboxylic organic compound of particular relevance to the polymer industry, due to its role as an intermediate in the synthesis of high-value polymers, such as PET and nylon-6.6. Its production through biotechnological routes from renewable substrates offers a more sustainable alternative to petrochemicals. To enable muconic acid biosynthesis, research efforts have focused on developing microbial platforms, combined with advances in systems metabolic engineering. In this context, high-performance liquid chromatography (HPLC) was used as a key tool to guide the genetic engineering of Escherichia coli, generating essential data for process optimization. In this study, eight metabolites were initially analyzed through a single sample injection using serially connected detectors: RID for glucose, glycerol, and ethanol; DAD at 262 nm for muconic acid; and DAD at 210 nm for acetic, succinic, formic, and lactic acids, as well as protocatechuic acid (PCA) and catechol - essential intermediates for the mass balance of the fermentation process. Separation was performed using an Aminex HPX-87H column (300 mm × 7.8 mm, 9 µm; Bio-Rad) at 50 ºC, mobile phase of 2.5 mM H_2SO_4 and a flow rate of 0.6 mL/min. During method development, analytical challenges were encountered, such as the isomerization of muconic acid (ccMA ⇄ ctMA), which required the quantification of both isomers. As no commercial standard is available for the ctMA isomer, it was produced in-house. Isomer separation and quantification were achieved using a C18 reverse-phase column (Acclaim 120, 4.6 mm x 150 mm, 3 µm; Thermo) at 45 °C, mobile phase of water:methanol:formic acid (80:20:0.16, v/v/v), a flow rate of 0.65 mL/min and DAD at 262 nm. The use of varied culture media contributed to the increased complexity of the matrices. In addition, the production of 3-dehydroshikimate (3DHS), a key intermediate in the muconic acid biosynthetic pathway and its co-elution with glycerol in RID prompted further method optimizations. As a result of the optimization process, all analytes were quantified using the same column, with a modified mobile phase consisting of 1 mM H_2SO_4 and a flow rate of 0.7 mL/min. Detection was performed at 236 nm for muconic acid, 3DHS, catechol, and PCA; 210 nm for acetic acid; glucose and glycerol were detected via RID. These results highlight the importance of employing flexible and integrated analytical strategies capable of accommodating experimental variability, thereby supporting robust process optimization and technological advancement.

Development and Optimization of an HPLC-UV Method for the Determination of Water-Soluble Vitamins in Dietary Supplements

Omar Costa Martins*[1], Jhonatan Bispo de Oliveira[2], Patterson Patricio de Souza[1]

[1]Centro Federal de Educação Tecnológica de Minas Gerais, Departamento of Chemistry, Belo Horizonte, MG, Brazil, 30421-169
[2]Universidade Federal de Minas Gerais, Departamento of Chemistry, City, Belo Horizonte, Brazil, 31270-901

* Corresponding author: omarmartins1997@gmail.com

Water-soluble vitamins, which include vitamin C and B-complex vitamins, are essential micronutrients that play an important role in human metabolism and are widely used in dietary supplements. In this context, high-performance liquid chromatography (HPLC) has established itself as one of the most commonly used analytical techniques for the determination of vitamins. The aim of this study was to develop and optimize HPLC-UV methods for the analysis of water-soluble vitamins, vitamin C and B-complex vitamins (B1, B2, B3, B5, B6, B7, B9, B12), using Design-Expert 13 software for experimental design, based on the official methods of the United States Pharmacopeia (USP). Factorial experimental designs (2^3 and 2^4) were applied to evaluate the effects of organic solvent concentration (varied within a 10% range of the total mobile phase composition), column temperature (25 to 45 °C), mobile phase flow rate (variation of ±0.3 mL/min, in accordance with the USP method), and aqueous phase adjustments: (i) replacement of phosphate buffer with trifluoroacetic acid (TFA) (C, B5, B7); (ii) testing with and without sodium 1-hexanesulfonate as an ion-pairing agent (B2,B5, B9, B12); and (iii) variation of phosphate buffer concentration (B1). In general, the percentage of organic phase controlled the retention and, consequently, affected the peak area, height, and number of theoretical plates. When it was increased in isolation, it decreased efficiency, but when it was adjusted in combination with flow rate, it restored height and plate number. Increased flow rate was the main factor for the decrease in area, height, and plate number, while higher temperature increased the number of plates by decreasing the viscosity of the mobile phase. At wavelengths ≤215 nm, replacing phosphate buffer with TFA increased baseline noise and thereby decreased peak height and area — as observed for B5 and B7; however, for vitamin C, the change had no significant effect on responses. The absence of anionic salt resulted in more asymmetric peaks and shorter retention times, with performance mainly determined by the percentage of organic phase and flow rate. With salt, retention increased, peak symmetry approached 1, and efficiency improved for B6 and B9, provided the organic phase was moderate. At high concentrations of the organic phase, the ion-pairing became weaker and the area/height decreased. The replicates of the central point of B6 showed low reproducibility without the salt, indicating that the method is not feasible without the ion-pairing agent. Increasing the phosphate buffer concentration in the B1 method increased the peak height, the number of plates, and improved the symmetry towards 1, but the gains decreased with higher organic phase and flow rate. Through optimization, it was possible to define the best conditions for each vitamin and highlight specificities and key points of chromatographic adjustment.

Acknowledgements: Laboratório de Tecnologias Integradas (Intechlab); Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG); Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

DEVELOPMENT AND VALIDATION OF A CHROMATOGRAPHIC ANALYTICAL METHOD BY SPE/IC-DC FOR CHLORATE ANALYSIS IN ACEROLA JUICE

Josália Liberato Rebouças Menezes, Tatiana Sainara Maia Fernandes*, Iuri Marques de Melo, Ronaldo Ferreira do Nascimento

Federal University of Ceara (UFC), Department of Analytical Chemistry and Physical Chemistry

* Corresponding author: tatisainara@yahoo.com.br

Inorganic contaminants resulting from the decomposition of chlorinated substances, such as chlorate (ClO3-), have been a concern for health and food safety authorities. Chlorate can contaminate food using fertilizers or even through chlorine-based sanitizers used to disinfect water, food, and production facilities. Since contamination occurs primarily through the ingestion of contaminated water and food, international regulatory bodies have established limits for the quantification of chlorate for the marketing of these products. Among the products most affected by chlorate contamination are fruits and vegetables, given the need to use water to irrigate these crops. As a major producer and exporter of fruit and vegetables, Brazil needs to comply with international parameters regarding the maximum permitted quantity of this substance so that it can compete with other exporting countries. Since the specifications for fruit exports allow very low concentrations of chlorate (maximum recommended limit of 0.05 mg/kg), sensitive, selective, and low-cost analytical methods must be developed for water analysis and monitoring during the production of these foods. Therefore, this study aimed to develop and validate a sensitive, selective, and more affordable chromatographic analytical method by SPE/IC-DC for the determination of chlorate in acerola juice, in accordance with the maximum residue levels determined by the European Union. For this purpose, samples of concentrated acerola juice were acquired in partnership with the producing industry and used for the development of the method and validation at the Laboratório Nucleo de Águas (LANAGUA) and Laboratório de Análises de Traço (LAT) of the Department of Analytical Chemistry and Physical Chemistry of the Federal University of Ceará. The results demonstrate that the SPE-IC-DC method for the analysis of concentrated acerola juice presented good selectivity, reduced matrix effect, low LOD (6.0 µg/L) and LOQ (18.0 µg/L) values for ClO3-, and good precision and accuracy (recovery). All samples analyzed showed chlorate levels within the limits established by EFSA and WHO, indicating suitability for use in food processes. This method proved to be a sensitive, effective, and lower-cost tool when compared to LC-MS or IC-MS techniques to control chlorate levels present in fruit juices, offering a practical alternative for routine analysis.

Acknowledgements: Federal University of Ceara (UFC), National Council for Scientific and Technological Development (CNPQ, Brazil), and CNPQ (406760/2022-5: INCT - CHAMADA Nº 58/2022).

DEVELOPMENT AND VALIDATION OF A MODIFIED QuEChERS METHOD FOR THE DETERMINATION OF HORMONAL HERBICIDES IN PLANT MATRICES BY UHPLC-MS/MS

Daniela Dall'Olivo Pereira, Cleusa Fatima Zanchin, Franciele Fátima Machado, Luana Floriano, Theo Samborski, Osmar Damian Prestes, Renato Zanella*

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900, Santa Maria – RS, Brazil

* Corresponding author: renato.zanella@ufsm.br

Hormonal herbicides, or auxin mimics, are a group of herbicides that act by mimicking the action of auxin, a natural plant hormone. They interfere with physiological growth processes, causing morphological abnormalities and, in more severe cases, plant death. This class is one of the most effective for controlling broadleaf weeds in grass crops such as corn, rice, wheat, sugarcane, and pastures. However, due to their high potential for drift, their application requires caution, as accidental contamination of sensitive crops can result in productivity losses and economic damage. Among the best-known compounds is 2,4-D, a systemic hormonal herbicide that acts selectively on dicotyledonous weeds, causing abnormal growth, senescence, and death. Due to its physicochemical properties, it is highly prone to volatilization, which favors drift and damage to adjacent crops. This study aimed to evaluate an analytical method for determining 7 hormonal herbicides (2,4-D, clopyralid, fluroxypyr, florpyrauxifen-benzyl, MCPA, picloram, and quinclorac), in addition to clomazone and metolachlor, applied in combination for weed control in plant samples. In this context, the three versions of the QuEChERS method (original, acetate, and citrate) were compared, in combination with $MgSO_4$, C18, and GCB in the cleanup step. The optimized method consisted of hydrating 3 g of sample, extracting with acidified acetonitrile with 5% (v/v) formic acid, partitioning with $MgSO_4$ and NaCl, and cleanup by d-SPE using 150 mg of $MgSO_4$ and 10 mg of GCB per mL of extract. Before injection, the extract was centrifuged, diluted 1:1 (v/v) in mobile phase, and filtered in a 0.2 µm PVDF filter. Analyses were performed on a Xevo TQ-XS UHPLC-MS/MS system (Waters) with an Acquity UPLC HSS T3 column. The accuracy and precision of the method were evaluated through recovery tests at the spike levels 5, 10, 25, and 50 µg kg^{-1}, with recoveries from 70 to 120% and RSD ≤ 20%, in accordance with SANTE guidelines. The linearity of the analytical curves was considered adequate ($r^2 > 0.99$), while the method limits of quantification (LOQ) and detection (LOD) were 5 and 1.5 µg kg^{-1}, respectively, indicating that the proposed method is efficient and suitable for the determination of such herbicides in plant samples.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

DEVELOPMENT AND VALIDATION OF A MULTIRESIDUE METHOD FOR PESTICIDES IN AVOCADO BY UHPLC-MS/MS: EVALUATION OF DIFFERENT SORBENTS FOR THE REMOVAL OF LIPIDS AND PIGMENTS

Cleusa Fatima Zanchin*, Osmar D. Prestes, Renato Zanella

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria - RS, Brazil

* Corresponding author: renato.zanella@ufsm.br

Avocado is a fruit of high nutritional value and growing importance in agricultural markets, notable for its high lipid content. While nutritionally beneficial, this characteristic poses significant challenges for determining pesticide residues due to the complex matrix and potential analytical interferences. The detection of residues above regulatory limits or of unapproved pesticides raises serious food safety and regulatory concerns. UHPLC-MS/MS is a fundamental technique for multiresidue analysis due to its high sensitivity, selectivity, and speed; however, its success depends critically on a carefully optimized sample preparation step to prevent issues like clogging, ion suppression, and unwanted co-extractives. In this study, a sample preparation protocol was developed and optimized for the multiresidue determination of pesticides in avocado. Various strategies were evaluated, including three variations of the QuEChERS method and seventeen different sorbents, such as C18, PSA, silica, EMR-Lipid, chitosan, Z-Sep+, CNT-CS, and diatomaceous earth, for the removal of matrix interferences. The validated method proved effective for the simultaneous extraction and quantification of 145 pesticides, meeting acceptable performance criteria for selectivity, linearity, sensitivity, accuracy, and precision. The low-temperature approach provided the highest recovery efficiency and effective removal of interferences, with recoveries ranging from 70 to 120% and relative standard deviation (RSD) values ≤ 20%. The method's LOQ was established at 1 µg kg^{-1}, and a low matrix effect was observed. Analyses were performed using a Xevo TQ-XS system equipped with an ESI+ source and an Acquity UPLC BEH C18 column (50 x 2.1 mm, 1.7 µm). The mobile phase consisted of ultrapure water and a 1:1 (v/v) methanol/acetonitrile mixture, both with formic acid and ammonium formate, using a gradient elution mode with a 5 µL injection volume. Detection was performed in SRM mode to monitor compound-specific transitions selectively. The developed protocol demonstrated high robustness and reliability for the quantification of pesticide residues at low levels in high-lipid-content samples like avocado.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

DEVELOPMENT AND VALIDATION OF A SALLE-UHPLC-MS/MS METHOD FOR THE MULTIRESIDUE DETERMINATION OF PESTICIDES IN HUMAN SERUM FOR EXPOSURE ASSESSMENT

Daniela Wouters de Medeiros*, Lais Pasinatto Santos, Adriana Zambenedetti Gehm, Renato Zanella, Osmar Damian Prestes

Universidade Federal de Santa Maria

* Corresponding author: daniwmedeiros@gmail.com

Pesticides are widely used in agriculture and domestic settings worldwide to prevent farm and postharvest losses, increase crop productivity, and control pests. However, the indiscriminate and inappropriate use of these chemicals can lead to human intoxication, making it crucial to monitor human exposure. This requires the development of analytical methods for identifying pesticide residues in biological matrices. Blood, serum, and plasma are particularly relevant for assessing exposure as they circulate throughout the body, allowing for the detection of parent compounds instead of just metabolites. Analytical techniques like ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS), combined with efficient sample preparation, enable the quantitative detection of numerous pesticides rapidly. This study evaluates the salting-out assisted liquid-liquid extraction (SALLE) method for sample preparation in human serum prior to UHPLC-MS/MS analysis. The method was rigorously validated by evaluating key parameters including recovery, precision, and matrix effects to ensure its reliability for assessing human exposure. Serum samples were extracted with acidified acetonitrile (1% (v/v) acetic acid), followed by the addition of an ammonium sulfate solution (5 mol L^{-1}). The extract was diluted with ultrapure water and filtered before injection. Analysis was performed on a Xevo TQ-XS (Waters) system using an Acquity UPLC™ HSS T3 column (100 × 2.1 mm, 1.8 µm). The mobile phase consisted of (A) ultrapure water and (B) methanol:acetonitrile (1:1, v/v), both containing 0.1% (v/v) formic acid and 5 mmol L^{-1} ammonium formate, at a flow rate of 0.500 mL min^{-1}. The injection volume was 5 µL. Electrospray ionization (ESI) was operated in +/- modes with detection in selected reaction monitoring (SRM). This method was validated for 155 pesticides. The recovery values ranged from 70% to 120%, with RSD≤20%. The LOQs varied between 0.2 and 2 µg L^{-1}. The validated method was applied to over 100 human serum samples and we found different pesticides (5 herbicides, 6 insecticides, and 3 fungicides). This work provides a robust, high-throughput analytical method that is essential for biomonitoring and human exposure assessment of a wide spectrum of pesticide residues.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM

DEVELOPMENT AND VALIDATION OF A SOLID PHASE EXTRACTION METHOD FOR MONITORING HERBICIDE BIOMARKERS IN HUMAN URINE BY UHPLC-MS/MS

Diogo Marchesan*, Franciele F. Machado, Gabriel A. B. Prates, Igor F. de Souza, Luana Floriano, Martha B. Adaime, Renato Zanella, Osmar D. Prestes

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria - RS, Brazil

* Corresponding author: diogo.marchesan@acad.ufsm.br

The indiscriminate use of pesticides in agriculture has led to a rise in human poisoning cases, posing a significant risk to public health. Urine is a common biological matrix for monitoring such exposure due to its non-invasive collection and ability to reflect recent contact. Consequently, it is essential to develop analytical methods capable of detecting multiple pesticide residues in a single procedure. This study developed and validated a method for the simultaneous determination of 2,4-D, 2,4-dichlorophenol, 2,4,5-T, atrazine, and MCPA in human urine using solid-phase extraction (SPE) followed by UHPLC-MS/MS analysis. Key parameters influencing extraction efficiency were investigated. Prior to extraction, urine samples were centrifuged at 4677 × g for 10 min at 20 °C. A 0.5 mL aliquot was diluted with ultrapure water. SPE extraction was performed on an Oasis® HLB cartridge (60 mg/3 mL), conditioned with methanol, acetic acid and ultrapure water. After sample loading, the cartridge was washed with ultrapure water containing 5% methanol, dried under vacuum, and eluted with methanol containing 1% acetic acid. The eluate was evaporated to dryness under a stream of N_2 at 40 °C and reconstituted in ultrapure water/methanol/acetonitrile. The final extract was filtered through a 0.2 µm PTFE syringe filter prior to UHPLC-MS/MS analysis. All compounds demonstrated linearity within the range of 0.5 to 5 µg L^{-1}, with determination coefficient (r^2) >0.99. Method recoveries ranged from 81.7 to 116.1%, with a relative standard deviation (RSD) ≤ 20%. The limit of quantification (LOQ) and the limit of detection (LOD) were 0.5 and 0.15 µg L^{-1}, respectively, for all compounds. When applied to 20 human urine samples, the method detected the target compounds 2,4-D and its metabolite 2,4-dichlorophenol at concentrations ranging from

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

DEVELOPMENT OF 3D PRINTED FLOW-THROUGH IMMOBILIZED TRYPSIN REACTOR FOR PROTEOMIC ANALYSIS

Joaquín Fernández-Martínez[1], Karem Henríquez-Aedo[2], David Arráez-Román[3], Mario Aranda*[1]

[1]Pontificia Universidad Católica de Chile
[2]Universidad del Bío-Bío
[3]Universidad de Granada

* Corresponding author: mario.aranda@uc.cl

In the last years, 3D print technology has become more affordable and now it is possible to find in several analytical laboratories. The technological advances on 3D print devices and software allows to prototype and produce more complex structures. Indeed, the ability to build complex structures increase the opportunity to take advantage of materials' structural, physical and chemical properties. The objective of this work was to 3D print an immobilized enzyme reactors (3D-IMERs) with the ability of coupling to advanced analytical instrumentation such as liquid chromatography mass spectrometry (LC-MS). This study describes the development of Nylon 3D printed IMER with an internal diameter of 0.2 x 0.32 mm, and 200 µL internal volume. Inside of the device channels, the enzyme trypsin was covalently bonded. This 3D-IMERs has the capability of carrying out protein digestion (BSA) in 10 minutes with a similar peptide profile to conventional enzyme digestion in solution but with a 98% reduction on digestion time. Food proteins were used as control and the digestion-formed peptides were quantified by high-performance thin-layer chromatography (HPTLC) using fluorescamine as derivatization reagent. The peptide mapping was performed off- and online by LC-MS. The combination of IMER digestion with 3D printed fabrication seems to be a good alternative for protein analysis, becoming a promising technology to develop lab-made analytical devices to accommodate specific lab necessities.

Acknowledgements: Thanks to FONDECYT N° 1251474 and 1251584; ANID Nº 21242151; Academy Installation Grant Nº 85220091 and FONDEQUIP EQY220018 and EQM210203

Development of a chromatographic methodology for the determination of adulteration markers in commercial ethanol fuel samples

Leonardo Silva Gonçalves*, Dyovanna de Sousa Costa, João Marcos Gonçalves Barbosa, Nelson Roberto Antoniosi Filho

Universidade Federal de Goiás

* Corresponding author: gonc.leonardo@gmail.com

With increasing environmental concerns about the use of fossil fuels, biofuels are emerging as a notable alternative. In Brazil, the main commercially available biofuel is bioethanol, which comes in two versions: the 'regular' and a higher-priced version containing packages of multifunctional chemical compounds where each brand or label may use a different additive package. Tracking of additives in other fuels, such as gasoline and diesel, has already been reported in the literature. However, there are no methodologies to assess the presence of additives in fuel ethanol, which raises questions from the fuel market and consumers. Therefore, this work aims to develop a method of distinguishing between fuel ethanol with additives (EHA) and ethanol fuel (EHC), identifying markers of additive presence, and evaluating the correlation of the selected markers with the leading brands available in the Brazilian market. For this study, gas chromatography coupled with mass spectrometry (GC-MS) was employed, followed by multivariate analysis. A total of 197 commercial fuel ethanol samples were analyzed, including 98 regular and 99 with additives samples. No natural discrimination was observed between EHC and EHA samples, but after supervised analysis, 17 compounds were selected by the multivariate model as discriminant markers. When evaluating the correlation of these markers with the leading brands, oleic acid, 2-ethyl-hexanol, and 1,4-diethylbenzene were selected to discriminate between EHA and EHC groups, achieving an accuracy of 95.7%. Thus, a rapid, robust, and highly accurate methodology was developed for distinguishing EHC from EHA, highlighting the differences in chemical composition among the main additive packages available in the Brazilian market and providing an unprecedented tool for quality control of fuel ethanol.

Acknowledgements: LAMES/UFG, IQ-UFG, FUNAPE, CAPES, ANP, INCT-ALIM.

DEVELOPMENT OF A DIRECT INJECTION LC-MS/MS METHOD FOR TRACE-LEVEL (ng/L) DETERMINATION OF MULTI-CLASS PESTICIDES IN WATER SAMPLES

Gabriel A. B. Prates[1], Igor F. de Souza[1], Douglas de Andrade[2], Osmar D. Prestes[1], Renato Zanella*[1]

[1]Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria - RS, Brazil
[2]Field Applications Specialist, Sciex Brazil, 06455-000 Barueri - SP, Brazil

* Corresponding author: renato.zanella@ufsm.br

Pesticides are frequently detected in drinking and surface water, with risks to human health and aquatic ecosystems. These organic compounds primarily enter the environment through agricultural use and inadequate waste disposal. To support the environmental monitoring of such pollutants, this study aims to develop and validate a multi-class and multi-residue method for the determination of pesticides in water and effluent samples. A direct-injection approach after preliminary filtration is being evaluated to ensure rapid analysis, accuracy, and high analytical sensitivity. Although the method is still under development, preliminary results have shown promising performance. Analytical curves exhibited excellent linearity ($r^2 > 0.99$) for approximately 180 compounds in the range of 2.5 to 500 ng/L. Preliminary recovery tests were conducted at 25, 50.0, and 100.0 ng/L and at pH 2.5 and 5.0. Based on official guidelines (Appendix F: Guidelines for Standard Method Performance Requirements - AOAC and DOQ-CGCRE-008), recoveries within 40–120% were considered acceptable for all analytes at the tested concentration levels. The best overall results were obtained at pH 5.0, where at the 25 ng/L concentration, 70 compounds showed satisfactory recovery rates, which were consistent at the other spiked levels (50.0 and 100.0 µg/L). The injection volume was 10 µL. The mobile phase consisted of (A) H_2O with 2% (v/v) MeOH and (B) MeOH with 2% (v/v) H_2O, both containing 5 mmol L-1 ammonium formate and 0.1% (v/v) formic acid, with a flow rate of 0.4 mL/min. Analyses were performed using an Exion liquid chromatograph equipped with a Kinetex® 2.6 µm Biphenyl 100 Å LC column (100 × 2.1 mm) coupled to a QTRAP 6500+ mass spectrometry system (Sciex). The MS method employed an ESI ionization source (+4000 V; –4500 V), ion source gases 1 and 2 at 40 psi, CAD gas at 9 psi (nitrogen), and acquisition in Scheduled Multiple Reaction Monitoring (sMRM) mode. These preliminary findings indicate that the proposed method is a promising tool for high-throughput monitoring of pesticide residues in water samples

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

Development of a DMSPE method using graphene oxide–silica functionalized with 1 vinyl 3 hexylimidazolium octane sulfonate for the determination of tebuconazole in orange juice

Alessandra Timóteo Cardoso*[1], Gloria Domínguez-Rodríguez[2], Alejandro Cifuentes[2], Fernando Mauro Lanças[1]

[1]São Carlos Institute of Chemistry, Universidade de São Paulo
[2]Foodomics Laboratory, Instituto de Investigación en Ciencias de la Alimentación, Spain

* Corresponding author: alessandracardoso@usp.br

Tebuconazole (TBZ) is a widely used fungicide with high efficacy and low toxicity [1], but it can pose health risks due to environmental accumulation and persistent residues in food. TBZ is authorized for use in Europe on certain citrus fruits, including oranges, which are highly nutritious. Orange juice is widely consumed in Spain, a leading producer both globally and within Europe [2]. Considering that TBZ is a predominantly hydrophobic compound (log K_ow = 3.7), Graphene oxide–silica functionalized with 1 vinyl 3 hexylimidazolium octane sulfonate (GO@Sil-[VHIm]+OS-) was evaluated for dispersive solid-phase microextraction (DSPME), with subsequent determination by LC-MS/MS. GO@Sil-[VHIm]+OS- showed superior sorption compared to other synthesized sorbents with different anions (PF6-, Br-) and to conventional sorbents (Strata-X and C8). Consequently, it was selected for further DSPME method optimization. The DSPME protocol, optimized by univariate and multivariate approaches, involved adding 5 mg of sorbent to 1 mL of orange juice (pH adjusted to 9 with 0.1 M NaOH), followed by ultrasonication (10 min) for extraction. After centrifugation (10 min, 14,000 rpm) and discarding the supernatant, desorption was performed with CPME:MeOH (46.43:53.57, v/v) under ultrasonication and centrifugation under the same previous conditions. The supernatant was filtered, dried, and reconstituted in 100 µL of mobile phase for LC-MS/MS analysis. The method was validated for orange juice following EU SANTE/11312/2021 guidelines. It provided satisfactory separation and detection, with linearity from 50–900 ng mL^{-1} (r^2 = 0.9972), RSDs below 15%, and recoveries of 105.7%, 117.1%, and 98% at 300, 600, and 900 ng mL^{-1}, respectively. LOD and LOQ were 0.06 and 0.19 ng mL^{-1}. The matrix effect was –15.3%, confirming method applicability. Sorbent reusability was demonstrated over five consecutive extractions at 100 ng mL^{-1}, with recoveries >60% and inter-extraction RSD of 13.1%. Eight natural orange juice samples purchased in Madrid were stored at –5 °C until analysis. TBZ was detected in two samples at 12.0 and 12.5 ng mL^{-1}, corresponding to 1.33% and 1.38% of the European MRL (900 ng mL^{-1}). These results confirm compliance with regulations and underscore the need for sensitive analytical methods to monitor low pesticide levels in beverages. Sustainability assessments using AGREEprep and BAGI yielded favorable scores (0.57 and 60.0, respectively), highlighting the environmental performance of the method. Overall, this study presents a promising and eco-friendly analytical approach for monitoring TBZ in orange juice.

REFERENCES
[1] Wang, K. et al. Food Chem 2025, doi:10.1016/j.foodchem.2025.142903
[2] Salar, F.J et al. Int J Food Sci Nutr 2024, doi:10.1080/09637486.2024.2303034.

Acknowledgements: Acknowledgements: This study was financed, in part, by the São Paulo Research Foundation (FAPESP), Brasil (Process Numbers: 2023/06258-1, 2023/07159-7 and 2024/12325-6) and CNPq (INCT-ALIM, 406760/2022-5). Additional support was provided by projects PID2020-113050RB-I00 and PDC2021-120814-I00 (funded by MCIN/AEI/10.13039/501100011033 and the European Union Next Generation EU/PRTR), the INCGLO0019 project, and the Juan de la Cierva grant JDC2023-052516-I.

DEVELOPMENT OF A GLUTAMIC ACID-FUNCTIONALIZED CRYOGEL FOR L-ASPARAGINASE ADSORPTION

Giovanni Aleixo Batista, Daniele do Carmo Costa*, Eduarda Alvarenga Naves, Jaime Vilela de Resende, Lizzy Ayra Alcântara Veríssimo*

Universidade Federal de Lavras

* Corresponding author: daniele.costa4@estudante.ufla.br

L-asparaginase (ASNase, EC 3.5.1.1) is an enzyme of great industrial interest, employed to mitigate acrylamide formation in thermally processed foods. However, its purification remains challenging, since conventional methods present limitations in selectivity, yield, and cost. In this context, ion-exchange cryogels are established chromatographic matrices. The aim of this study was to develop a glutamic acid–functionalized cryogel column (Cryogel-GA) for the purification of ASNase produced by Aspergillus caespitosus. The enzyme was obtained through solid-state fermentation carried out at 25 °C for 120 h, using 10 g of lyophilized ora-pro-nobis fiber as the support substrate. The medium was moistened with 10 mL of Khanna salt solution supplemented with 3 g of L-asparagine and inoculated with 10 mL of a spore suspension containing 10^7 spores per gram of substrate. The polyacrylamide cryogel (1.185 g of AAm, 0.3175 g of MBAAm, and 1 mL of AGE, with APS and TEMED) was synthesized by cryocopolymerization at –12 °C for 24 h and subsequently functionalized via the epoxy method, enabling amino acid immobilization. Cryogel-GA was characterized in terms of morphology, point of zero charge (pHpzc), and structural properties. Adsorptive capacity was optimized using a Central Composite Rotational Design (CCRD 2^2), considering pH (3.0, 6.0, 9.0) and ionic strength (20, 60, 100 mmol L^{-1}). Total protein was determined by the Bradford method, and enzyme activity by the Nessler reagent. Cryogel-GA exhibited a swelling capacity of 11.37 kg kg^{-1}, an expansion degree of 13.87 L kg^{-1}, a dry polymer fraction of 0.08, and a bound water fraction of 0.03. The macro-, meso-, and microporous fractions were 0.62, 0.25, and 0.87%, respectively, and scanning electron micrographs revealed interconnected pores ranging from 8 to 106 µm. The pHpzc values (3.2 and 6.3) confirmed the binding of COO^- and NH_2 groups of glutamic acid to the epoxy groups of the matrix. At pH 6.0, increasing ionic strength up to 100 mmol L^{-1} enhanced the adsorptive capacity to 38 mg protein g^{-1} cryogel, attributed to electrostatic interactions and increased enzyme solubility. Notably, the proteins immobilized in the column retained 68.01% of their catalytic activity, demonstrating that Cryogel-GA enabled the selective capture of ASNase. Thus, Cryogel-GA emerges as a promising chromatographic support for ASNase recovery from fermentation broths.

Acknowledgements: FAPEMIG (APQ-00795-22) and CNPq (408779/2023-3).

DEVELOPMENT OF A METHOD FOR CHARACTERIZING HUMAN HAIR BY PYROLYSIS COUPLED WITH GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION (Py-GC-FID)

Allyson Leandro Rodrigues dos Santos*, Glaucimar Alex Passos de Resende, Leandro Wang Hantao

IQ-UNICAMP

* Corresponding author: allysonl@unicamp.br

The launch of new products in the hair industry, such as wigs, extensions, and hairpieces, requires the development of effective methods to determine the origin of these products, ensuring regulatory compliance for commercial hair supply. In this study, a direct hair analysis method was developed using pyrolysis coupled with gas chromatography with flame ionization detection (Py-GC-FID). Rapid pyrolysis promotes the thermal decomposition of macromolecules into smaller molecules by heating samples at high temperatures (400–650 °C) for short periods (

Acknowledgements: CAPES, CNPq, FAPESP, Receita Federal

DEVELOPMENT OF A METHOD FOR DETERMINING ANTINEOPLASTIC AGENTS IN AQUEOUS MATRICES OF ENVIRONMENTAL RELEVANCE FOR ADVANCED OXIDATION PROCESSES CONTROL

Júlia Paula Neu*, Vitória Barbosa de Souza, Igor Franceschi de Souza, Renato Zanella, Carla Sirtori

Laboratory of Pesticides Residue Analysis (LARP) – UFSM, Brazil

* Corresponding author: juliapaula2011@gmail.com

Medications used in cancer treatment include antineoplastic drugs, which inhibit tumor cell growth, and therapeutic support drugs, which control side effects such as nausea caused by chemotherapy. This study addresses the validation of the method applied to: cyclophosphamide, cyproterone, pazopanib, methotrexate, nilotinib, ondansetron, and tamoxifen in water and simulated hospital effluent matrices. The validation parameters were evaluated according to the criteria established by INMETRO DOC CGCRE-08: linearity of the “low” analytical curve (1, 2, 5, 10, 20, and 50 µg/L) and “high” analytical curve (50, 100, 150, 300, and 400 µg/L); limit of detection (LOD) and limit of quantification (LOQ); in addition to precision and accuracy at concentrations of 10, 50, 150, and 400 µg/L. For the ultra-pure water matrix, LOD values ranged from 0.001 µg/L (anastrazole) to 0.175 µg/L (cyproterone). LOQs were equally low, ranging from 0.004 to 0.581 µg/L. Linearity was verified by means of coefficients of determination (r^2) greater than 0.97. Accuracy, expressed by recovery rates, showed satisfactory results, between 93% and 110%, with the exception of some drugs that obtained 117% to 135% in intermediate concentrations. Accuracy (repeatability and intermediate precision) showed variations of less than 10.6%, which is within the established limits. For the simulated effluent matrix, LOD values ranged from 0.003 µg/L (anastrozole) to 0.134 µg/L (methotrexate), while the LOQs ranged from 0.011 µg/L to 0.445 µg/L, demonstrating good sensitivity of the method applied. Linearity was confirmed for most compounds, with coefficients of determination (r^2) greater than 0.990 for all compounds. Accuracy showed acceptable percentage recovery variations, such as 78% (cyclophosphamide) and 108% (methotrexate), with the exception of nilotinib 128%. Precision, evaluated by the percentage variation in recovery (RSD%), ranged from 0.4% (ondansetron) to 4.0% (cyproterone). Intermediate precision remained within acceptable ranges for all compounds, such as 0.7% for nilotinib and 4.7% for cyproterone, meeting the criteria of the standard. Thus, in a future step, the methods developed will be applied in the evaluation of the efficiency of hospital effluent treatment by advanced oxidation processes.

Acknowledgements: CAPES (finance code 001), CNPq (Processo 306928/2023-0), UFSM, FATEC.

DEVELOPMENT OF A MINIATURIZED SYRINGE BASED DISPERSIVE SOLID-PHASE EXTRACTION METHOD FOR MULTIRESIDUE PESTICIDES DETERMINATION IN WATER BY UHPLC-MS/MS

Gabrielle Dias Pereira, Daniela Wouters de Medeiros, Theo Samborski, Osmar Damian Prestes, Renato Zanella

Universidade Federal de Santa Maria

In recent years, classical sample preparation techniques for determining organic compounds in environmental matrices have been gradually replaced by miniaturized methods. These novel approaches offer advantages such as lower cost, higher efficiency, reduced solvent consumption, and greater potential for automation. Although solid-phase extraction (SPE) is widely used for isolating and preconcentrating pesticides from water samples, new methods aim to be faster and more practical, while also reducing solvent and sorbent consumption and minimizing the equipment required for multiresidue analysis. The developed method utilized a 12 mL polypropylene syringe as the extraction device. The sample was adjusted to pH 2.5, and 20 mg of the Strata-X polymeric sorbent was added in a dispersive mode. After being spiked at 1 µg L^{-1} the blank samples were manually shaken. A 0.45 µm nylon filter attached to the syringe tip retained the sorbent along with the adsorbed analytes. Elution was performed using ACN:MeOH containing 1% (v/v) acetic acid, and the eluate was collected in a 1 mL vial.

Following a dilution, the samples were injected into a UHPLC-MS/MS Xevo TQ-XS (Waters) system equipped with a BEH C18 column (50 × 2.1 mm, 1.7 µm). The mobile phases consisted of (A) ultrapure water and (B) acetonitrile, both containing formic acid and ammonium formate.

The analysis was performed with an injection volume of 5 µL. Detection was carried out via positive electrospray ionization (ESI). Acquisition was performed in Selected Reaction Monitoring (SRM) mode. The method was evaluated for 75 compounds. Of these, 72 exhibited satisfactory performance, with determination coefficients (r^2) ≥ 0.98, recoveries between 60% and 130%, and relative standard deviation (RSD) ≤ 30%, meeting accepted criteria for multiresidue method validation. The procedure is simple and rapid, allowing for efficient manual execution. Furthermore, its potential for automation ensures high reproducibility, standardization, and feasibility for large-scale multiresidue analyses with minimal equipment requirements.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM

DEVELOPMENT OF A MIP-BASED PAPER SPRAY IONIZATION-MASS SPECTROMETRY METHOD FOR THE QUANTIFICATION OF CEFTIOFUR IN MILK.

Tauã Emanuel Silva*[1], Camila Cíntia Sousa Melo Brito[2], Eduardo Lima Nascimento[2], Heloísa Siqueira Santos[2], Jean Carlos Pereira Sousa[2], Andréa Rodrigues Chaves[2]

[1]Universidade Federal de Jataí
[2]Universidade Federal de Goiás

* Corresponding author: tauaemanuel99@gmail.com

Ceftiofur (CFT), a broad-spectrum antibiotic used to treat infections in cattle, can leave residues in milk, posing a public health risk. Monitoring these residues is necessary to mitigate the development of antimicrobial resistance and allergic reactions, which requires efficient detection methods to ensure food safety. In this context, ambient ionization techniques such as Paper Spray Ionization coupled with mass spectrometry (PSI-MS) emerge as promising alternatives due to their speed and minimal sample preparation requirements. To achieve the necessary selectivity in a complex matrix, the integration of Molecularly Imprinted Polymers (MIPs) onto the analysis substrate was employed as a selective extraction strategy. This work aimed to develop and validate an analytical methodology for the determination of CFT in milk, employing the MIP-functionalized PSI-MS technique. A MIP for CFT was synthesized directly onto cellulose membranes. Milk samples underwent a protein precipitation step with acidified methanol (1:1, v/v) and centrifugation. The supernatant was subjected to solid-phase extraction, in which the MIP-modified membranes were immersed in the extract for selective analyte capture. After a washing step, the membranes were analyzed by mass spectrometry using a Thermo LTQ XL instrument in Selected Reaction Monitoring (SRM) mode, monitoring the transition m/z 524 → 241. The method validation was conducted according to the Brazilian Health Regulatory Agency (ANVISA) guidelines (RDC 166/2017). The immobilization and characterization of the polymer were confirmed by the mass increase on the membrane (186.33 ± 26.90 mg) and by physicochemical analyses such as FTIR, SEM, and EDS. The comparative extraction capacity study demonstrated the superiority of the MIP-modified membrane over the Non-Imprinted Polymer (NIP) and the unmodified paper, evidencing the success of the molecular imprinting process. The method exhibited high selectivity, with negligible cross-reactivity in the presence of other antibiotics. In the validation parameters, the method proved to be linear in the 50 to 150 ng/mL range ($R^2 = 0.996$). The Limit of Detection was 12.39 ng/mL and the Limit of Quantification was 37.56 ng/mL, a value lower than the Maximum Residue Limit (MRL) of 100 ng/mL established by legislation, while the precision and accuracy assays showed results within the standard's acceptance criteria. The MIP-PSI-MS approach proved to be a rapid, selective, and sensitive tool for the determination of CFT in milk. The results validate the method as a robust and promising alternative for large-scale screening and residue monitoring in the dairy production chain, contributing to food safety assurance.

Acknowledgements: FAPEG, INCT, CAPES, UFG and UFJ.

DEVELOPMENT OF A MOLECULARLY IMPRINTED MONOLITHIC POLYMER FOR THE PIPETTE-TIP SOLID PHASE EXTRACTION OF CEFTIOFUR SODIUM FROM MILK SAMPLES

Bruna Bezerra de Melo*, Anizio Marcio de Faria

Federal University of Uberlândia, Institute of Exact and Natural Sciences of Pontal, Ituiutaba, MG, Brazil.

* Corresponding author: anizio@ufu.br

Cephalosporin antibiotics have been increasingly used in several animal species in recent years. In Brazil, ceftiofur is the most widely used antibiotic in bovine culture, and its residues in milk are a cause for concern. Milk is a complex sample, and monitoring ceftiofur residues requires efficient and selective sample preparation that allows pre-concentration of the analyte and meets the contemporary needs of chemical analysis. This work developed a new molecularly imprinted polymer monolithic sorbent with ceftiofur, molded in micropipette tips, to extract the antibiotic in bovine milk. The preparation of the polymeric monolithic sorbent via in situ thermal polymerization was optimized from a mixture design composed of trimethylolpropane triacrylate (TMPTA), methacrylic acid (MAA), and ethylene glycol dimethacrylate (EDMA) with isopropanol as porogen and 2,2'-azobisisobutyronitrile (AIBN) as radical initiator, aiming at the production of a hierarchically porous structure, with high permeability and molded at the 1 mL tip. The non-molecularly imprinted (NIP) monolith was optimized with 70% porogenic solvent, 7.5% MAA, 7.5% TMPA, and 15% EDMA polymerized at 60 °C for 20 h. For molecular imprinting of ceftiofur (MIP), five different ceftiofur:MAA molar ratios were evaluated from the previous reaction between MAA and the antibiotic at 70 °C for 2 h, followed by thermal polymerization under optimized conditions for NIP. The poly(TMPTA-co-EDMA-co-MAA) monoliths MIP and NIP were characterized for permeability, resulting in 2 mL/min flow rates, 55% total macroporosity, and 110 m2/g specific surface area. The structural and morphological properties of the MIP and NIP monoliths did not differ significantly. The ceftiofur:MAA molar ratio 0.55:1 (mmol:mol) resulted in the highest imprinting factor (IF) of 3.5, measured by pipette-tip solid-phase extraction of ceftiofur-spiked samples using the MIP and NIP monoliths. The recoveries of ceftiofur by MIP were higher than 70 ± 3 %, as determined by high-performance liquid chromatography with diode array detection. This indicates that the MIP monolithic sorbent produced was selective and efficient in extracting ceftiofur from milk samples.

Acknowledgements: FAPEMIG (APQ-1901-22 and PCE-00390-25), CNPq, and FINEP (01.13.0371.00).

DEVELOPMENT OF A MULTIDIMENSIONAL CHROMATOGRAPHIC APPROACH TO CHARACTERIZE FIXED-BED ADSORPTION PROCESSES

Larissa Silva de Oliveira Mota, Bruno Salarini Peixoto, Marcela Cristina de Moraes*

BioCrom – Laboratório de Cromatografia de Bioafinidade e Química Ambiental, Instituto de Química, Universidade Federal Fluminense

* Corresponding author: mcmoraes@id.uff.br

The increasing occurrence of emerging contaminants in aquatic environments has driven the development of efficient removal methods. Alternative adsorbents, such as biochars, have been investigated due to their sustainability and low cost. However, characterizing adsorption in multicomponent and continuous-flow systems remains challenging. In this work, a two-dimensional chromatographic approach was developed to investigate fixed-bed adsorption of the model contaminants salicylic acid (SA), caffeine (CAF), and isoniazid (ISO), using green coconut husk biochar (BC) as the adsorbent. The first dimension comprises a stainless-steel column (1 cm × 0.46 cm) packed with a mixture of BC and sand (1:9 w/w) responsible for adsorption. The second dimension consists of a C18 analytical column (5 cm × 0.46 cm, 5 µm) that enables separation of the analytes. Solutions containing the analytes, either individually or in mixture, were infused into the first dimension at 150 µM. In the second dimension, the mobile phase consists of ammonium acetate buffer pH 5.8 (75%) and methanol (25%), delivered at 0.6 mL/min. Coupling between the two dimensions was achieved via a six-port valve equipped with a 20 µL loop, which alternated between loading (2.8 min) and transfer (0.1 min, loop transfer), enabling real-time monitoring if the adsorption process. Quantification was performed using calibration curves obtained in the two-dimensional system without adsorbent in the first dimension, using a ternary solution at 500 µM in line B and ultrapure water in line A. Concentrations ranging from 5 to 500 µM were prepared by adjusting line proportions, with triplicate analysis. The method demonstrated that BC exhibits higher affinity for CAF, while ISO and SA displayed comparable adsorption behaviors. Adsorption in single-component systems was consistently greater than in binary and ternary mixtures, evidencing competitive interactions among the analytes for adsorption sites. A systematic roll-up effect of ISO and SA was observed in the presence of CAF in binary and ternary systems. This phenomenon, characterized by transient effluent concentrations exceeding the influent levels, results from the displacement of previously adsorbed species by compounds with higher affinity. In addition, adsorption of the ternary mixture was evaluated under different flow rates (0.5, 1.0, and 1.5 mL/min), revealing enhanced adsorption performance at higher flow conditions.

Acknowledgements: FAPERJ, CNPq, and CAPES.

DEVELOPMENT OF A NEW METHOD FOR ANTIBIOTICS RESIDUES QUANTIFICATION IN HOSPITAL SALINE SOLUTION BOTTLES

Nathalia da Rosa Luiz[1], Lara das Dores Santana*[2], Raquel Wielens Becker[3], Alexsandro Dallegrave[1], Osmar Damian Prestes[2], Carla Sirtori[2]

[1]Universidade Federal do Rio Grande do Sul
[2]Universidade Federal de Santa Maria - LARP
[3]Universidade Federal de Santa Maria

* Corresponding author: lara.santana@acad.ufsm.br

The presence of pharmaceutical residues in the environment is a growing concern due to their potential risks to both public health and ecosystems. Among these substances, antibiotics deserve special attention given their widespread use and the consequent risk of antibiotic-resistant bacteria, a critical global health threat. In hospital settings, antibiotics are commonly administered intravenously, diluted in saline solutions stored in polymeric bottles. Residual antibiotics in these bottles pose a challenge for hospital waste management, requiring specific disposal strategies and increasing operational costs. The development of analytical methods to quantify the presence of antibiotics residues in this kind of hospital waste is fundamental to understanding the risks and the magnitude of punctual contamination caused by the residue of antibiotics in the flasks after patient treatment. With the advance of technology, methods very sensitive based on liquid chromatography coupled with high resolution mass spectrometry (LC-HRMS) allow the quantification of antibiotics residues in different matrices in trace and ultra-trace levels. In this study, a new method was developed to quantify the presence of five antibiotics (Amoxicillin (AMX), Azithromycin (AZI), Ciprofloxacin (CIP), Levofloxacin (LEV), Trimethoprim (TRI)) in saline solution flasks after antibiotic administration. The goal is to understand the contamination after pharmaceutical administration, considering the residue of these compounds. To perform the analysis, saline solution was used as matrix and the method was developed in a UHPLC-QTOF MS equipped with an Atlantis T3 analytical column. Validation results demonstrated satisfactory repeatability and intermediate precision in accordance with AOAC guidelines. The method exhibited linearity for all compounds in the 10–500 µg L^{-1} concentration range. Limits of detection (LOD) were 0.64 µg L^{-1} (AMX), 0.09 µg L^{-1} (AZI), 0.06 µg L^{-1} (CIP), 0.06 µg L^{-1} (LEV), and 0.04 µg L^{-1} (TRI); while limits of quantification (LOQ) were 2.14 µg L^{-1}, 0.31 µg L^{-1}, 0.21 µg L^{-1}, 0.20 µg L^{-1}, and 0.13 µg L^{-1}, respectively. Despite the potential ion suppression effects associated with the saline matrix, the method demonstrated satisfactory analytical performance. This method provides an important tool for assessing antibiotic residues in hospital saline solution bottles, supporting improved waste management practices and contributing to broader efforts in environmental and public health protection.

Acknowledgements: Authors thanks CNPq (Processos 306928/2023-0 and 171802/2023-3)

DEVELOPMENT OF A NOVEL SPONGE-BASED SORBENT FOR LIPOPHILIC MATRIX CLEAN-UP AND UHPLC-MS/MS ANALYSIS OF PESTICIDES IN FISH

Franciele Fátima Machado*, José Dilson da Silva, Luana Floriano, Juliana B. Kuntz, Osmar D. Prestes, Renato Zanella

Universidade Federal de Santa Maria

* Corresponding author: francimachadote@gmail.com

Fish represent a significant nutritional source, being rich in high-quality proteins and omega-3 polyunsaturated fatty acids. However, the extensive use of pesticides in agriculture leads to environmental contamination, affecting aquaculture water bodies and promoting the accumulation of residues in fish tissues, which poses potential risks to human health. This study aimed to develop and evaluate an analytical method for the determination of 167 pesticides in fish with high fat content (Salmo salar). The method employs a novel sorbent based on a chemically modified vegetable sponge with acetic acid and deacetylated chitosan, designed to target the removal of lipophilic interferences. The sorbent material was characterized using FTIR spectroscopy. Analyses were performed by UHPLC-MS/MS using an Acquity UPLC™ system (Waters Corporation, USA) interfaced with a Xevo TQ™ triple quadrupole mass spectrometer. Chromatographic separation was achieved on a BEH C18 column maintained at 40 °C. The mobile phase consisted of (A) water with 2% methanol and (B) methanol with 2% water, both containing formic acid and ammonium formate. The flow rate was set at 0.225 mL min^{-1} under a gradient elution program, with a total run time of 20 minutes and an injection volume of 5 µL. For sample preparation, 2.5 g of fish muscle were extracted with acetonitrile acidified with 1% (v/v) acetic acid. A partitioning step involving the addition of salts (NaCl or $MgSO_4$). In the clean-up step, 150 mg of the vegetable sponge-based sorbent was used to remove co-extracted matrix interferences. The presence of lipid co-extractives was verified by full-scan analysis using gas chromatography-tandem mass spectrometry (GC-MS/MS), and the sorbent's phospholipid removal efficiency was evaluated. The method was validated through recovery tests at three fortification levels (5, 10, and 20 µg kg^{-1}; n = 3), yielding satisfactory results with relative standard deviations (RSD) ≤ 20% and accuracies ranging from 70% to 120%. Matrix-matched calibration curves exhibited excellent linearity ($r^2 > 0.99$) for all analytes. The method demonstrated a limit of quantification (LOQ) of 5 µg kg^{-1}, confirming its capability for the simultaneous, precise, and reliable quantification of multiple pesticide classes.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

DEVELOPMENT OF A SUSTAINABLE METHODOLOGY BASED ON THE DISPOSABLE PIPETTE EXTRACTION (DPX) TECHNIQUE USING A BIOSORBENT OF SILICA-GRAPHENE OXIDE MODIFIED WITH CHITOSAN FOR TRIAZOLES DETERMINATION IN FRUITS USING LC-MS/MS

Winnie Evelyn Valeria Perez Vite*, Rafael Oliveira Martins, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: winnieperez@usp.br

Some of the most consumed fruits daily in Brazil are tomatoes and bananas. However, their cultivation requires the use of pesticides for protection. Among these, triazole-class fungicides are currently among the most widely used worldwide. Despite this, these chemicals can harm human health and the environment. For this reason, their application is subject to various restrictions, making it necessary to develop appropriate methods for their detection and quantification. Miniaturized extraction techniques, such as Disposable Pipette Extraction (DPX), offer great versatility for evaluating complex matrices. In this context, developing new sorbents, especially those based on graphene oxide, has attracted considerable interest due to their physicochemical properties and ability to be modified to acquire enhanced and specific properties for various applications. Aiming to create hybrid sorbents, incorporating chitosan into graphene oxide emerges as a promising alternative for developing a new biosorbent with potential applications in the evaluation of pesticides in food matrices. In this study, a silica–graphene oxide@chitosan (SiGO@CS) sorbent was synthesized and employed to extract triazoles by DPX in tomato and banana samples. The sorbent characterization was performed using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), and Accelerated Surface Area and Porosimetry (ASAP), confirming the successful modification of SiGO@CS. Optimization was carried out on several parameters influencing DPX performance, including pH, salt effect, extraction and desorption cycles, sample and elution volumes, equilibrium time, and desorption solvents. The optimization and analytical application of the method are currently underway. We expect the method to be fully optimized and applied to evaluate triazoles in commercial fruit samples from São Carlos, Brazil, in the coming months.

Acknowledgements: Acknowledgments: CAPES [Grants: 88887.115332/2025-00]; FAPESP [Grants: 2023/15675-5; 2017/02147-0; 2017/21984-0 – EMU; 2017/21985-6 – EMU] and INCT-ALIM financed this study.

DEVELOPMENT OF A β-SUSTAINABLE METHODOLOGY BASED ON THE DISPOSABLE PIPETTE EXTRACTION (DPX) TECHNIQUE USING A BIOSORBENT OF SILICA-GRAPHENE OXIDE MODIFIED WITH CHITOSAN FOR TRIAZOLES DETERMINATION IN FRUITS USING LC-MS/MS

Fernando D. Lanças*[1], Helvécio Costa Menezes[1], Patterson Patrício de Souza[2], Zenilda de Lourdes Cardeal[1]

[1]Universidade Federal de Minas Gerais
[2]Centro Federal de Educação Tecnológica de Minas Gerais

* Corresponding author: fdlancas@gmail.com

Spices and dried herbs are widely consumed and highly susceptible to pesticide contamination, but are often overlooked in food safety monitoring programs. This study presents the development and validation of an environmentally friendly analytical method based on direct immersion solid-phase microextraction using a hydrophilic microporous cartridge (HMCart-DI-SPME) in combination with comprehensive two-dimensional gas chromatography and mass spectrometry (GC×GC/MS) for the multiresidue determination of organochlorine and organophosphorus pesticides. Optimization of the method was performed using a two-stage, full factorial design to evaluate the effects and interactions of critical variables such as extraction time, temperature, equilibrium time, agitation speed and solvent composition. Optimal conditions — 70 °C, 60 min extraction, 15 min equilibration, 600 rpm stirring and 100 µL ethyl acetate as a modifier — significantly improved analyte recovery and method sensitivity. The method showed excellent analytical performance with limits of detection between 0.10 and 0.87 µg kg^{-1}, recoveries between 88.36 and 109.86% and high precision (RSD < 13%). A total of 44 commercial samples of spices and dried herbs collected in Belo Horizonte (Brazil) were analyzed, and 41 samples tested positive for at least one pesticide. Prohibited substances such as dieldrin (up to 7.23 µg kg^{-1}), parathion (8.79 µg kg^{-1}) and heptachlor epoxide (5.84 µg kg^{-1}) were frequently detected. However, the chronic non-carcinogenic risk assessment based on estimated daily intake (EDI) and hazard index (HI) values did not reveal a significant risk to consumers (HI < 1 for all compounds). This method stands out as a sensitive, selective and sustainable alternative for routine monitoring of pesticides in complex plant matrices. Its practical application has been demonstrated by analyzing real samples and comparing it with conventional methods. It offers higher sensitivity, lower solvent consumption and a better environmental footprint (AGREE score: 0.67). The results underline the importance of continuous monitoring to ensure food safety and regulatory compliance.

Acknowledgements: National Council for Scientific and Technological Development (Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Chemistry Department of Federal University of Minas Gerais (UFMG), and the Federal Center for Technological Education of Minas Gerais (CEFET-MG).

DEVELOPMENT OF AN ANALYTICAL METHOD BY HPLC-FLD AND DAD FOR QUANTIFICATION OF MULTI-MYCOTOXINS IN MEDICINAL PLANTS

Marineli Aparecida Gelinsk*[1], Giovanna Araujo de Moraes Trindade[1], Gustavo Bertol[2], Roberto Pontarolo[1], Luana Mota Ferreira[1]

[1]Universidade Federal do Paraná
[2]Dall Phytolab SA

* Corresponding author: marineli.gelinsk@ufpr.br

Mycotoxins are produced by toxigenic fungal strains, mostly Aspergillus, Penicillium, and Fusarium (ELAMIN, 2023). The most damaging mycotoxins to medicinal herbs are aflatoxins, ochratoxins, fumonisins, zearalenone, and deoxynivalenol (ELAMIN, 2023). The prevention of mycotoxin contamination in medicinal plants in dried herbal drugs and in manufacturing and storage rooms is of great importance (STEVIC, 2012). Different detectors such as mass spectroscopy (MS), ultraviolet with diode array detector (DAD), and fluorescence detector (FLD) are used for analyzing mycotoxins by high performed liquid chromatography (HPLC). However, there are still gaps in the methods for detecting multi-mycotoxins in medicinal plants. So, this study aimed at quantifying multi-mycotoxins using DAD and FLD detectors. The determination of the mycotoxins was achieved using the Agilent HPLC, equipped with pump G7111B, autosampler G7129A, column oven G7116A, FLD detector G7121A, and VWD detector G7114A, with column Waters Cortecs Shield C18 2.7 µm, 4.6 x 150 mm. The mobile phase consisted of Water/Methanol/Acetonitrile in different proportions, because of the 3 injections pumped at a flow rate of 1 mL/min. In the first injection, aflatoxins can be quantified using a fluorescence detector and post-column derivatization at excitation/emission wavelengths of 360/ 440 nm while ochratoxin A can be quantified using the same method at 330/ 460 nm. In the second one, fumonisins were evaluated using derivatization with o-phthaldialdehyde reagent at excitation/emission wavelengths of 335/440 nm. Zearalenone was also evaluated in the previous injection, utilizing fluorescence at excitation/emission wavelengths of 276/460 nm, respectively. In this analysis, deoxynivalenol is quantified at a wavelength of 218 nm. HT2 and T2 toxins were quantified in the last injection at a wavelength of 191 nm. The method was developed using mycotoxin standards, and the subsequent step will be to test them for samples and validate them.

Acknowledgements: Universidade Federal do Paraná and the company Dall Phytolab SA for the support.

DEVELOPMENT OF AN ANALYTICAL PANEL FOR THE IDENTIFICATION OF EMERGING CHEMICAL CONTAMINANTS IN DRINKING WATER: FROM WATER TREATMENT PLANTS TO DOMESTIC FILTERS

Luana Figueiredo*, Álvaro José dos Santos Neto

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: luanafgrd@usp.br

In the face of the growing occurrence of new chemical contaminants in contrast with the use of traditional water treatment methods carried out by Water Treatment Plants (WTPs), there has always been a consensus about their effectiveness in the removal of chemical compounds from raw water. In this regard, it is necessary to evaluate the effectiveness of, and the gaps in, current water treatment methods. In this context, it is crucial to achieve low detection limits with the agility required for the analysis of multiple samples. The present work aims to develop and validate an analytical panel to determine contaminants in drinking water samples, covering several chemical classes, using Ultra-High-Performance Liquid Chromatography (UHPLC) coupled with Mass Spectrometry (MS). Furthermore, the analytical process will be improved through chromatographic miniaturization, comparing the results to the standard scale commonly used. Currently, qualitative detection of pollutants at a concentration of 100 ng mL^{-1} of analytical standards was accomplished using a capillary column in UHPLC-MS/MS, covering most of the contaminants originally predicted in the project, belonging to the classes of PFAS, pharmaceuticals, and personal care products. In the future, it is envisaged as an application of the methodology to develop a study on the most popular water purifier in Brazil, treating water samples previously fortified with the chemical compounds proposed by the analytical panel. The objective is to evaluate the efficiency of these filters in contaminant removal, quantifying the reduction of the original risk associated with their presence, using parameters established by Human Health Risk Assessment (HHRA). Based on the results, it will be possible to determine the effectiveness of different domestic treatment systems available on the market. With this work, we hope to identify the main failures in water treatment plant processes, if identifiable, and acquire subsidies that contribute to inferences about the impact/risk of prolonged exposure to contaminants.

Acknowledgements: This research is funded by CAPES [Grants: 88887.978023/2024-00] and CNPq [Grants: 314731/2021-0 and 309282/2025-0. The author acknowledges INCT-ALIM for the financial support for participation in this event.

DEVELOPMENT OF DIRECT MAGNETIC DEEP EUTECTIC SOLVENT SAMPLING (DMDESS) METHOD FOR CADMIUM DETERMINATION IN EDIBLE OIL SAMPLES BY FLAME FURNACE ATOMIC ABSORPTION SPECTROMETRY

Diego Prudencio dos Santos*[1], Maikon Thiago do Nascimento[1], Eduardo Costa de Figueiredo[2], César Ricardo Teixeira Tarley[1]

[1]State University of Londrina
[2]Federal University of Alfenas

* Corresponding author: diego.prudencio@uel.br

Vegetable oils are widely consumed for their high content of monounsaturated (omega-9) and polyunsaturated (omega-6 and omega-3) fatty acids, which help reduce the risk of chronic diseases such as cancer, diabetes, and cardiovascular disorders. Contamination by heavy metals, including arsenic, mercury, lead, cadmium, and zinc, is a concern, as they can accumulate in the body and increase toxicity, occurring during extraction or production steps such as bleaching, hydrogenation, refining, and deodorization. Determining metals in oils is challenging due to high carbon and lipid contents causing matrix interferences. Techniques such as Flame Atomic Absorption Spectrometry (FAAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are sensitive but require careful sample preparation. Green approaches, including microemulsion, miniaturized liquid–liquid extraction, supramolecular solvents (SUPRAS), and deep eutectic solvents (DES), offer safer and more sustainable alternatives. This work proposes a new methodology for cadmium determination in edible oils based on direct magnetic deep eutectic solvent sampling (DMDESS) into a flame tube in AAS, minimizing preconcentration steps and replacing conventional solvents with greener options. The MDES synthesis will be based on cobalt(II) chloride ($CoCl_2$), choline chloride (ChCl), and acetic acid (HAc) in molar ratios to be optimized using a factorial mixture design with interior and central points to evaluate component effects. After optimizing the extraction conditions using 22 and 23 factorial designs with central point, Cd2+ extraction was performed using 10.0 g of oil with 70 µL of 0.05 mol L-1 SDS solution, followed by vortex-assisted extraction with 100 µL of MDES for 2 min and centrifugation at 3000 rpm for 1 min. The rich phase was separated using an external magnetic field, collected with a micropipette, and 10 µL was directly deposited onto a custom metal rod for atomization in a flame furnace atomic absorption spectrometer. The MDES, with ChCl as the extractor, was effective for Cd2+ microextraction and characterized by 1H NMR. The method showed wide linear range (0.18–15.0 µg kg-1), high correlation (R^2 = 0.994), low detection limit (0.06 µg kg-1), and satisfactory precision (intra- and inter-day RSD 2.5–9.7%). In conclusion, the DMDESS-FAAS method is rapid, sensitive, and provides an efficient alternative for trace cadmium determination in complex oil matrices, highlighting the potential of magnetic deep eutectic solvents for analytical applications.

Acknowledgements: UEL, CAPES, CNPq and INCT-Bio.

DEVELOPMENT OF DIRECT MAGNETIC DEEP EUTECTIC SOLVENT SAMPLING (DMDESS) METHOD FOR LEAD DETERMINATION IN KEROSENE SAMPLE BY FLAME FURNACE ATOMIC ABSORTION SPECTROMETRY

Diego Prudencio dos Santos*[1], Maikon Thiago do Nascimento[1], Eduardo Costa de Figueiredo[2], Carmen Luísa Barbosa Guedes[1], Mariana Gava Segatelli[1], César Ricardo Teixeira Tarley[1]

[1]State University of Londrina
[2]Federal University of Alfenas

* Corresponding author: diego.prudencio@uel.br

The presence of lead in aviation gasoline and kerosene, poses environmental and health risks. According to the Brazilian National Agency of Petroleum, Natural Gas, and Biofuels (ANP), specific requirements for aviation kerosene are established, including its physicochemical characteristics and permitted contaminant limits. Among these, a maximum allowable lead concentration of 5 mg L^{-1} is set, highlighting the need for more effective analytical methods for its detection. Extraction methods reported in the literature for the determination of lead in such samples are based on acidic media. However, when employing highly acidic conditions in techniques such as FAAS through pneumatic aspiration, long-term damage to the equipment may occur, in addition to reduced sensitivity due to the limited nebulization efficiency of these systems. This highlights the need for the development of new technologies capable of performing this monitoring without the direct introduction of acidic media into the internal components of the equipment, while providing enhanced detectability. This work proposes the development of a new methodology for the determination of lead in aviation kerosene samples, based on the direct magnetic deep eutectic solvent sampling (DMDESS) into a flame tube in AAS. This strategy aims to reduce the number of preconcentration steps, increasing analytical efficiency, while also providing a significant sensitivity gain due to the direct injection of the enriched phase into the flame tube with the aid of a custom metal rod. MDES synthesis will be based on $CoCl_2$, ChCl, and HAc in molar ratios to be optimized, consisting of mixing these compounds and heating to 60 °C to form the MDES. The analytical methodology consists of adding 5 mL of the sample (aviation kerosene) with 5 mL of isopropyl alcohol in a 15 mL centrifuge tube. After mixing, 100 µL of MDES and 300 µL of a 0.04 mol L^{-1} SDS solution are added. The tube is then vortexed for 2 min. Rich phase is separated using an external magnetic field and collected with a micropipette. After collection, it is dropped onto the tip of a magnetic probe and directly atomized in a flame furnace atomic absorption spectrometer. The MDES will be characterized and the next experiments will focus on optimizing the parameters that influence the preconcentration process, as well as determining analytical parameters. The method aims to reduce sample preparation steps, and increase sensitivity, presenting an innovative and sustainable solution.

Acknowledgements: UEL, CAPES, CNPq and INCT-Bio.

DEVELOPMENT OF OPEN-ACCESS DATABASES OF EMERGING CONTAMINANTS AND THEIR TRANSFORMATION PRODUCTS (TPs) TO SUPPORT AUTOMATED HRMS-BASED SCREENING METHODS

Carla Sirtori*[1], Raquel Wielens Becker[1], Carla Fernanda Grasel Frois[2], Marcelo Mallmann Dias[3]

[1]Laboratório de Análises de Resíduos de Pesticidas (LARP) - Universidade Federal de Santa Maria-Brasil
[2]Instituto de Química, Universidade Federal do Rio Grande do Sul-Brasil
[3]Mallmann & Dias LTDA – ME, Porto Alegre/RS-Brasil.

* Corresponding author: carla.sirtori@ufsm.br

Contaminants of emerging concern (CECs) are frequently detected in different environmental compartments and pose serious risks to environmental and public health. To address this issue, new advanced tertiary treatment processes have been successfully applied. However, these processes are often time-consuming and costly. During such new treatments, numerous transformation products (TPs) can be formed and partially degraded, but many of them may persist and ultimately be released into the environment. Although TPs often share structural similarities with original compounds, they may exhibit greater toxicity and environmental persistence, thereby increasing the potential risks to ecosystems and human health. Monitoring TPs in wastewaters treated by new technologies or in the environment is essential but presents significant analytical challenges, primarily due to the unavailability of reference standards. In this context, chromatographic techniques coupled with high-resolution mass spectrometry (HRMS) are powerful and effective tools for the suspect screening of TPs formed during tertiary degradation processes. To improve the accuracy and efficiency of suspect screening, the use of purpose-built automated databases can significantly enhance the identification process and enable more comprehensive environmental/treatment processes monitoring. Our research group is developing, to the best of our knowledge, the first free available database focused on TPs formed through different tertiary treatment processes. The database includes information on TPs derived from a wide range of CEC classes, such as pharmaceuticals and pesticides. For each TP, molecular formula, exact mass, and fragmentation profiles (when available) are provided. All information has been curated from published literature and free databases (e.g., MassBank, mzCloud), with full traceability to the original sources. Currently, the purpose-built automated database has approximately 300 TPs and is undergoing a peer validation process with researchers in the field from different countries. This tool is intended to improve environmental and treatment quality management of water resources.

Acknowledgements: CNPq (306928/2023-0 and 171802/2023-3); CAPES – Finance Code 001.

DEVELOPMENT OF SBSE METHOD FOR FREE GLYCEROL FROM PURE BIODIESEL (B100) USING MONOLITHIC CELLULOSE AS STIR BAR COATING

Caroline Lopes da Silva*[1], Maria Aparecida Barros[1], Anizio Márcio de Faria[2]

[1]Federal University of Uberlândia, Institute of Chemistry, Uberlândia, Brazil.
[2]Federal University of Uberlândia, Institute of Chemistry, Uberlândia, Brazil / Federal University of Uberlândia, Institute of Exact and Natural Sciences of Pontal, Ituiutaba, Brazil.

* Corresponding author: caroline.lopes@ufu.br

Free glycerol in biodiesel is usually determined by gas chromatography with flame ionization detection (GC-FID), involving limiting instrumental conditions, internal standards, and derivatization reagents, leading to a low precision of the results. Alternatively, the extraction of free glycerol from biodiesel with direct extract analysis, without derivatization and the need for internal standards, by high-performance liquid chromatography with refractive index detection (HPLC-RID) has been explored. This work developed a sorptive stir bar extraction (SBSE) method using cellulose monolith-coated stir bars as the selective extractor phase for free glycerol in pure biodiesel (B100). Cellulose monolith sorptive bars (CMSB) were obtained by thermally assisted non-solvent-induced phase separation of cellulose acetate solution, followed by deacetylation by alkaline hydrolysis. The structural characterization of CMSB was performed by infrared spectroscopy and thermogravimetric analysis to obtain characteristic cellulose profiles. The morphological characterization of CMSB was obtained by macroporosity, scanning electron microscopy, and specific surface area, indicating a hierarchically porous structure with a honeycomb shape, with a total porosity of 69%. The recovery in CMSB of three dimensions (7, 10, and 18 x 4 mm o.d.) was evaluated and applied in the SBSE of methyl oleate fortified with glycerol. The SBSE conditions were optimized, with a sorption time of 40 min and 15 min of desorption using water at 70 °C as eluent, promoting an eco-friendly SBSE method. The extracts were quantified using HPLC-RID, indicating recovery between 84% and 117% (m/m) and good repeatability (RSD < 10%). Adsorption studies demonstrated the adsorptive capacity of the cellulose monolith extractor phase (10x4 mm) to adsorb glycerol at concentrations higher than the maximum content of 0.02% m/m of glycerol in biodiesel, obtaining recoveries of 105%. The developed method presents itself as an efficient, economical, and environmentally friendly alternative for monitoring biodiesel quality, contributing to the consolidation of sustainable analytical strategies in the biofuel field.

Acknowledgements: FAPEMIG (APQ-1901-22, APQ-03286-21 and PCE-00390-25), CNPq, and FINEP (01.13.0371.00).

DIATOMACEOUS EARTH-ASSISTED MSPD FOR PAH EXTRACTION IN MOSSES: A PRACTICAL AND EASY ENVIRONMENTAL BIOMONITORING TOOL

Juan José Triviño*[1], Valentina Rojas-Candia[2], Alejandra Molina-Balmaceda[2], Daniel Arismendi[2], Verónica Arancibia[3], Pablo Richter[2]

[1]Department of Inorganic and Analytical Chemistry and Department of Pharmacological and Toxicological Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, P.O. Box 233, Santiago, Chile.
[2]Department of Inorganic and Analytical Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, P.O. Box 233, Santiago, Chile.
[3]Department of Pharmacological and Toxicological Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, P.O. Box 233, Santiago, Chile.

* Corresponding author: juantrivino@ug.uchile.cl

Environmental biomonitoring corresponds to a type of passive monitoring in which organisms are used to assess exposure to different types of pollutants. Bryophytes, particularly mosses and lichens, have been widely used for the study of organic and inorganic contaminants in the environment. Although the use of these biomonitors offers analytical advantages such as ease of transport and handling, it also presents challenges, including sample preparation methods, cleaning, and analysis procedures that ensure adequate analytical performance. In this study, a matrix solid-phase dispersion (MSPD) extraction method was optimized for the extraction of polycyclic aromatic hydrocarbons (PAHs) in mosses. The type of elution solvent, solid support, clean-up procedure, as well as the amounts and volumes used, were optimized through both univariate and multivariate approaches using the model moss Sphagnum sp. The optimal conditions were 0.25 g of sample, 0.1 g of diatomaceous earth as solid support, and 0.1 g of Florisil® as clean-up sorbent, using 9 mL of methanol as the elution solvent. The 15 fluorescent PAHs (as defined by the US-EPA) were determined using HPLC-FLD, obtaining linear calibration ranges between 20 and 200 ng/g, using an acetonitrile/water gradient on a column specific for PAH separation. The limits of detection and quantification were suitable for the matrix studied, with the latter being 0.99 for the different PAHs. Repeatability and reproducibility (n = 5) were evaluated at two concentration levels, yielding values of 1.3-19.9% RSD, with absolute recoveries ranging from 15% to 98%, depending on the chemical nature of the analyte. The optimized and validated methodology was applied to moss samples collected in Santiago, Chile, revealing concentration levels dependent on the sampling area. Higher PAHs concentrations were found in urban-residential-commercial environments compared to urban parks, with Σ15 PAHs of 250 vs. 45-66 ng/g, respectively, levels comparable to those reported in other studies around the world.

Acknowledgements: National Doctoral Scholarship No. 21220946 (JJT) and Fondecyt Projects (1211637/1251804, VA), (1220225, PR), and (11240183, DA) from ANID-Chile.

DISCOVERY OF NOVEL BIOACTIVE MOLECULES FROM ANTARCTIC LICHEN (SPHAEROPHORUS GLOBOSUS) BY EFFECT-DIRECTED ANALYSIS ON HIGH-PERFORMANCE THIN-LAYER CHROMATOGRAPHY AND MASS SPECTROMETRY

Cristian Cordero[1], Gerald Zapata[2], Jaime Cabrera[3], Iván Opazo-Aballay[1], Pedro Aqueveque[4], Karem Henriquez-Aedo[3], Mario Aranda*[1]

[1]Pontificia Universidad Católica de Chile
[2]Universidad de Chile
[3]Universidad del Bío-Bío
[4]Universidad de Concepción

* Corresponding author: mario.aranda@uc.cl

The Antarctica's harsh environmental conditions force to lichens like Sphaerophorus globosus to produce a variety of bioactive molecules to survive, e.g. antioxidant with photoprotective properties. This lichen is widely distributed across the insular archipelagos of maritime Antarctica, and it could represent a promising source of bioactive metabolites with potential biomedical applications, particularly over Chronic Noncommunicable Diseases (CNCDs), which are responsible of 75% of deaths globally. The objective of this study was to identify novel bioactive molecules with inhibitory properties over cyclooxygenase (COX-2), α-glucosidase (AG), and acetylcholinesterase (AChE) enzymes, which are related to different CNCDs. Detection and identification were carried out applying effect-directed analysis on high-performance thin-layer chromatography coupled to mass spectrometry. This approach allowed the identification of two bioactive molecules, Sphaerophorin with AChE inhibitory activity associated to neuroprotective effects and Imbricaric acid, for the first time reported in S. globosus, with inhibitory properties over AChE and COX-2 enzymes, suggesting anti-inflammatory and neuroprotective activities. These findings highlight the potential of S. globosus as promising source of bioactive molecules with therapeutical potential over CNCDs

Acknowledgements: This work was funded by the Chilean Antarctic Institute, project N° RT 28-21, the Academy Installation Grant Nº85220091, and projects FONDEQUIP EQM210203 and EQY220018.

DISCRIMINATION OF CHEMOTYPES IN XYLOPIA AROMATICA AND XYLOPIA SERICEA BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY (GC-qMS)

Rosianne Pereira Silva*, Elina Bastos Caramão, Anai L. dos Santos, Laíza C. Krause

Universidade Federal de Sergipe

* Corresponding author: rosianneqmc@gmail.com

The essential oils of Xylopia aromatica and Xylopia sericea, both belonging to the Annonaceae family and native to Brazil, were obtained by hydrodistillation of aerial parts, excluding stems. The genus Xylopia is widely distributed in tropical regions and is known for its aromatic and bioactive potential. This study, part of a doctoral research project, aims to contribute to the chemical understanding of native Brazilian flora and highlight the value of its biodiversity.
Chemical analysis was performed by gas chromatography coupled to mass spectrometry (GC-MS) using a Shimadzu GC-2010 system equipped with a DB-5MS capillary column (60 m × 0.25 mm × 0.25 µm). The carrier gas flow was set to 1 mL/min, the injector temperature to 300 ºC, and the oven program consisted of a ramp from 50 to 240 ºC at 3 ºC/min, followed by 250 to 300 ºC at 10 ºC/min. The mass spectrometer operated under electron ionization at 70 eV, with a scan range of 45 to 500 Da.
GC-MS analysis enabled the identification of 81 and 62 compounds in X. aromatica and X. sericea, respectively. The objective was to perform chemical fingerprinting and compare the volatile profiles of both species, focusing on the differentiation of their chemotypes. A markedly distinct chemical profile was observed: X. aromatica showed a predominance of sesquiterpenes, while X. sericea was rich in monoterpenes. The major constituents of X. aromatica were δ-elemene (23.63%), bicyclogermacrene (12.21%), and spathulenol (8.34%), compounds associated with anti-inflammatory activity and fragrance fixation. X. sericea was characterized by high levels of β-myrcene (21.62%), β-pinene (20.58%), and D-limonene (12.63%), known for their bronchodilator and refreshing properties. Only three compounds were common to both species (linalool, terpinen-4-ol, and α-copaene), with low relative abundance, indicating orthogonal chemical profiles. These findings highlight the existence of distinct chemotypes and reinforce the potential of Brazilian biodiversity for pharmaceutical, cosmetic, and natural aroma applications.

Acknowledgements: Acknowledgements: The authors thank CAPES, CNPq, PETROBRAS, Elenito Hemes Lopes, and Solange dos Santos Cerqueira for financial support and plant material.

DISPOSITIVOS ELETRÔNICOS PARA FUMAR: CARACTERIZAÇÃO DOS E-LÍQUIDOS E SEUS PRODUTOS DE PIRÓLISE

Tarsila Dantas de Farias*[1], Andre Luiz Oliveira da Silva[2], Vinicius Tadeu Kartnaller Montalvão[1]

[1]Universidade Federal do Rio de Janeiro
[2]Agência Nacional de Vigilância Sanitária

* Corresponding author: tarsilafarias@gmail.com

Os cigarros eletrônicos, também chamados como vaporizadores ou "vapes", utilizam como insumos líquidos chamados de e-líquidos ou, popularmente, "juice". Esses líquidos são compostos principalmente por propilenoglicol, glicerina, flavorizantes e, na maioria dos casos, nicotina. Eles são aquecidos em temperaturas que variam conforme a geração do vape, o seu modelo e, mais especificamente, a voltagem da bateria. O processo ocorre em um ambiente de aquecimento fechado, sem a presença de oxigênio, visando apenas criar um aerossol com os componentes dos e-líquidos; entretanto, o aumento da temperatura pode favorecer a pirólise desses componentes. Isso pode gerar subprodutos químicos no aerossol que, ao serem inalados, representam potenciais riscos à saúde. Na literatura, estudos anteriores descrevem aparatos experimentais específicos para a simulação da geração desses vapores, que são coletados e submetidos a etapas de pré-tratamento antes da análise. No entanto, a falta de controle rigoroso da temperatura no aparato pode limitar a compreensão da relação entre as condições do processo e a formação dos subprodutos. Além disso, compostos voláteis, que são fundamentais para o estudo, podem ser perdidos durante essas etapas adicionais, comprometendo a análise.

Para superar essas limitações, o presente projeto visou utilizar um pirolisador acoplado diretamente a um cromatógrafo a gás acoplado a um espectrômetro de massas (Pi-CG/EM). O pirolisador foi utilizado na faixa de temperatura de 100ºC a 700ºC e permitiu a introdução direta de amostras de e-líquidos, sem etapas de pré-tratamento, em um cadinho de aço. Isso possibilitou uma pirólise instantânea, conhecida na literatura como “flash”, mimetizando o que ocorre dentro dos cigarros eletrônicos. Observou-se que, com o aumento da temperatura de pirólise, a área da glicerina e do propilenoglicol diminuiu, enquanto a área de subprodutos, como a água, aumenta. Essa observação confirma que ocorre a formação de subprodutos
resultantes da degradação da glicerina e do propilenoglicol. A pesquisa mostrou ainda que o aumento da temperatura intensifica a quantidade de compostos tóxicos gerados. As moléculas identificadas podem ser nocivas à saúde; o glicidol, por exemplo, é classificado como carcinogênico e mutagênico. Já a acroleína é um composto irritante e tóxico, com potencial cancerígeno, capaz de causar danos ao epitélio pulmonar e, em casos graves, levar ao óbito.

Além dessas moléculas também foi encontrado ácido fórmico, 2-Propanona-1-hidroxi, 1,4-Dioxano-2,3-diol, ácido acético, glicidol, 2-Propanol-1,1-oxibis, nicotina, furaneol, dihidroxiacetona na temperatura de 300ºC. O estudo comprova que a elevação da temperatura em vapes intensifica a formação de compostos tóxicos. A análise direta, via Pi-CG/EM, identificou substâncias carcinogênicas e irritantes, provenientes da degradação da glicerina e do propilenoglicol. Tais resultados destacam os riscos à saúde que a inalação desses subprodutos representa.

Acknowledgements: ANVISA e CAPES

Effectiveness of cassava biochar as a potential adsorbent in matrix solid-phase dispersion procedure for determination of pesticide residues in cassava flour by liquid chromatography.

Larissa de Jesus Souza*, Roseane dos Santos Nascimento, Luís Fabrício Santana Santos, Sandro Navickiene

Departamento de Química(DQI),Universidade Federal de Sergipe(UFS)

* Corresponding author: laryjesusoficial@gmail.com

Northeast is one of the main producers of cassava (Manihot esculenta Crantz) in Brazil, representing 23% of national production. Cassava is the second predominant crop in the state of Sergipe, with a production of 151,094 tons in 2022. It is also one of the most important staple food sources for low-income families in rural areas, and a primary cash crop for smallholders living in many tropical countries. However, cassava cultivation is subject to the action of different pests and the application of pesticides has been one of the forms of control. In the PARA (Food Pesticide Residue Monitoring Program) report, published by ANVISA, 38% of the presented residue concentrations were equal to or lower than the maximum residue limits established for the cassava crop, and 19% were considered unsatisfactory. A total of 470 cassava flour samples were analyzed. In total, nine different pesticides were detected, with dichlorvos (8 samples) and cypermethrin (2 samples) presenting the highest number of detections. Among the samples analyzed, 13 contained unauthorized pesticides for use in cassava crops. In this context, the present work aims to determine residues of three pesticides (diuron, vinclozolin and chlorothalonil) in cassava flour samples, using high-performance liquid chromatography with diode array detector (HPLC-DAD) and matrix solid phase dispersion (MSPD) techniques. Tests performed with standard solutions of pesticides allowed the adjustment of instrumental conditions for simultaneous determination of analytes. An elution gradient (45-100%) was made with methanol: water with a mobile phase flow-rate of 1.0 mL min-1, and C18 analytical column (40°C). Under the optimized conditions, linearity was obtained in a range from 0.01 to 1 µg g-1 with determination coefficients greater than 0.998. Fortification tests were carried out using 0.05 g of cassava biochar, 0.1 g of the cassava flour sample and elution with 2 mL of methanol: dichloromethane (50:50, v/v) in MSPD procedure. Excellent recoveries were obtained (95 ± 12.4 and 105 ± 3.3%) for the 0.5 µg g-1 fortification level (n=3). In short, it is a fast and efficient method, with low reagent consumption and minimal sample handling.

Acknowledgements: The authors are grateful to the COPES/UFS, the Multi-user Chemistry Laboratories Center (CLQM/UFS) (analytical support), and the NOVA ANALÍTICA Ltda for financial assistance.

EFFICIENT LC-MS/MS DETERMINATION OF HIGHLY POLAR PESTICIDES IN COFFEE USING TRI-MODE COLUMN AND ACETONITRILE EXTRACTION

Graziela C. R. M. Andrade, Yuri L. Freire, Luiza T. M. Shiose, Claudia M. Barbosa, Sergio H. Monteiro*

Pesticide Residue Laboratory, Reference Laboratory for Residues and Contaminants – Biological Instituto, São Paulo, Brazil

* Corresponding author: sergio.monteiro@sp.gov.br

The determination of highly polar pesticides in complex plant matrices poses significant analytical challenges due to their extreme polarity and poor retention in conventional reversed-phase chromatography. In this study, a robust LC-MS/MS method employing a Acclaim™ Trinity Q1 LC Columns was developed and validated for the simultaneous quantification of AMPA, glyphosate, ammonium glufosinate, ethephon, fosetyl, and maleic hydrazide in coffee. Sample preparation consisted of acetonitrile extraction in the same pot prior to proceeding with the subsequent QuEChERS steps, enabling efficient recovery of highly polar analytes while minimizing co-extractives, while also increasing laboratory productivity and reducing costs by allowing two analyses to be performed from the same extraction solvent. The chromatographic determinations were performed in UHPLC-MS/MS, Vanquish/TSQ Quantis Plus system - Thermo Scientific with the mobile phase starting with 100% pure water followed by a gradient of up to 4 minutes to 50 mM Ammonium Formate (pH=2.9) in Water: Acetonitrile (6+4) maintaining for another 8 min. Column cleaning with acetonitrile every 5 runs is necessary. Validation followed the SANTE 11312/2021 guidelines, meeting all performance criteria with excellent linearity ($r > 0.99$), recoveries ranging from 65% to 132% and relative standard deviations (RSD) below 20% in repeatability and in within-laboratory reproducibility. The method achieved limits of quantification (LOQs) of 0.05 mg/kg for all compounds, except fosetyl and maleic hydrazide, for which the LOQ was 0.20 mg/kg. The procedure was applied to 11 coffee samples purchased from retail supermarkets; seven glyphosate residues ranging from 0.098 to 0.495 mg/kg, and three contained ethephon residues from 0.039 to 0.720 mg/kg. The method combines simplicity, reduced solvent use, and cost savings with accurate monitoring of polar pesticides in coffee, aligning with regulatory standards, ensuring food safety, and contributing to sustainable analytical workflows.

Acknowledgements: FAPESP Processo: 2022/01101-4 ; CNPq INCT-ALIM / PIBIC

EMERGING CONTAMINANTS IN SURFACE WATER FROM RIO DE JANEIRO STATE BY HPLC-ORBITRAP HIGH RESOLUTION MASS SPECTROMETRY

Alexander Andrey Lopes da Silva*, Raquel Vieira Santana da Silva, Debora de Almeida Azevedo1

Federal University of Rio de Janeiro

* Corresponding author: alexander.silva@iq.ufrj.br

The emerging contaminant (ECs) measurement in surface waters has become essential for assessing environmental risks and supporting public policies. This research investigated the occurrence of pharmaceuticals, hormones, and metabolites in three regions of the State of Rio de Janeiro: the Macaé de Cima Environmental Protection Area (APA), the Guandu River sub-basin, and Rodrigo de Freitas and Jacarepaguá urban coastal lagoons. The samples were collected, subjected to solid-phase extraction (SPE, C18, 200mg/30um, HLB Oasis, Waters Corporation), and analyzed by high-performance chromatography with Orbitrap high-resolution mass spectrometry and electrospray ionization operated in both positive and negative modes (HPLC-ESI(±)-Orbitrap HRMS) in Selected Ion Monitoring (SIM) mode. Chromatographic separation was performed on a C18 Hypersil Gold column (100 × 2.1 mm; 3 µm), with mobile phases consisting of a water/methanol gradient containing water (A) and methanol (B), both containing 5 mM NH_4OH. The injection volume was 2 µL and a chromatographic run of 14.2 min was employed. The method showed satisfactory linearity ($R^2 > 0.99$), detection limits between 4 to 41 ng L^{-1}, and average recoveries of 70–120% for most substances. The results presented that the Guandu sub-basin surface water contained 12 EC compounds, which were quantified with concentrations above 100 ng L^{-1}, including caffeine, losartan, paracetamol, diclofenac, hydrochlorothiazide, and hormones such as estriol and estrone. In the coastal lagoons, contamination was even more widespread, with 17 EC compounds exceeding this limit, featured caffeine, losartan, clarithromycin, diclofenac, naproxen, and estrone, in addition to the presence of synthetic hormones such as 17α-ethinylestradiol. In the Macaé de Cima APA, considered a non-contaminated area, only 4 compounds reached concentrations above 100 ng L^{-1}: caffeine, acetylsalicylic acid (AAS), estriol, and paracetamol. The EC concentration values in Lagoa de Freitas urban lagoon reached up to 14 µg L^{-1} to AAS, 166 µg L^{-1} to caffeine, 11.5 µg L^{-1} to potassium losartan, 12.3 µg L^{-1} to paracetamol, and claritromycin up to 17 µg L^{-1}. In the Queimados River, Guandu area, concentration values were up to 1.1 µg L^{-1} to AAS, 24.6 µg L^{-1} to caffeine, 22.9 µg L^{-1} to potassium losartan, 9.5 µg L^{-1} to paracetamol, and no detection of claritromycin. To the APA, only reached up to 0.2 µg L^{-1} to AAS, 7.0 µg/L to caffeine, 0.1 µg L^{-1} to paracetamol. The Guandu sub-basin, although presenting fewer contaminants above 100 ng L^{-1} than the coastal lagoons, concentrates relevant compounds in its strategic water source for the supply of the Metropolitan Region of Rio de Janeiro, posing a direct risk to water security. In turn, the coastal lagoons, lentic environments and receptors of partially untreated sewage, exhibited the highest levels (e.g., caffeine, clarithromycin, and estrone), evidencing strong anthropogenic pressure. In contrast, the Macaé de Cima Environmental Protection Area showed reduced concentrations and few compounds detected, reinforcing its role as a reference site of low contamination. This study underscores the urgency of continuous monitoring, advances in effluent treatment, and an update of Brazilian legislation to include such substances.

Acknowledgements: Capes, CNPq, and FAPERJ for financial support

ENHANCED CHLOROPHYLL REMOVAL USING A AMINO/Z-SEP+® CARTRIDGE FOR IMPROVED UHPLC-MS/MS ANALYSIS OF PESTICIDES IN HIGH PIGMENTED SAMPLES

Silvestre Lucas Muiambo*, Igor F. de Souza, Renato Zanella, Osmar Damian Prestes

Laboratory of Pesticides Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900, Santa Maria-RS, Brazil

* Corresponding author: muiambosil82@gmail.com

Vegetable production is a cornerstone of global food security. However, its productivity is highly susceptible to pest attacks, necessitating the use of pesticides to prevent and reduce yield losses. Consequently, residues of these compounds are often present in foodstuffs, and their consumption can pose significant health risks to consumers. This has driven significant research interest in developing robust analytical methods for the extraction of pesticide residues from complex food matrices. This study aimed to evaluate an alternative sorbent to graphitized carbon black (GCB), which is known to strongly retain planar pesticides, often leading to poor analyte recovery. To improve extraction efficiency, two SPE cartridges were evaluated: a commercial Captiva EMR-HCF1 (Agilent Technologies) and a homemade amino/Z-Sep+® cartridge. Extracts of spinach (high chlorophyll content) were obtained with acetate-buffered QuEChERS method. After the clean-up step, visual inspection of the extracts indicated superior clean-up performance (specifically in chlorophyll removal) for the Captiva EMR-HCF1, followed by the amino/Z-Sep+®. Both strategies produced more transparent solutions when compared with GCB (d-SPE method). Analytical recovery and precision were assessed using a spiked spinach sample analyzed by UHPLC-MS/MS. Acceptable analytical recoveries (60.1–115.8%) were obtained for 121 compounds using the homemade amino/Z-Sep+® cartridge. In contrast, only 59 compounds showed good recoveries (61.6–131.5%) using the EMR-HCF1 cartridge. All methods demonstrated good precision, with relative standard deviation (%RSD) values below 30% for all recovered compounds. Based on a comprehensive evaluation of recovery, precision, and matrix effects, the homemade amino/Z-Sep+® cartridge proved to be the most effective clean-up material. Crucially, the results indicate that this cartridge can serve as a viable alternative to GCB for the clean-up of extracts in the determination of planar pesticides, effectively mitigating the strong retention and improving analyte recoveries.

Acknowledgements: Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

ENHANCING CHROMATOGRAPHIC TECHNIQUES FOR THE PURIFICATION OF AÇAÍ SEED PROCYANIDINS

Pedro Vitor de Oliveira Martins*[1], Mariana Monteiro Mattos França[1], Gabriel R. Martins[2], Ayla Sant'Ana da Silva[1]

[1]Laboratório de Biocatálise, Bioprocessos e Bioprodutos. Instituto Nacional de Tecnologia, Rio de Janeiro, Brasil.
[2]Departamento de Farmácia, Faculdade de Ciências Farmacêuticas, Universidade de São Paulo, São Paulo, Brasil.

* Corresponding author: pedro.martins@int.gov.br

In 2023, Brazil produced 1.9 million tons (Mt) of açaí. Seeds represents 85% of the fruit's mass, resulting in 1.7 Mt of seeds without proper disposal. Açaí seeds have a high concentration of oligomeric procyanidins (PCs), polyphenols with antimicrobial and antioxidant activity. Due to the structural variety and absence of analytical standards, characterization and quantification of PCs becomes challenging. This work developed a methodology to purify by degree of polymerization (DP) and quantify the PCs from the açaí seed extract. The lyophilized seed extract (0.5 g) was sequentially eluted with H2O (fraction 1 - F1), MeOH 20% (F2), 40% (F3), 60% (F4), 100% (F5), and acetone 70% (F6) through MPLC with Sephadex LH-20. F4 and F5, which expectedly contained oligomeric PCs with a DP up to 7, were collected in 5 mL aliquots, totaling 136 fractions for F4 (F4 1-136) and 70 fractions for F5 (F5 1-70). All aliquots were analyzed by UFLC-FLD (ex: 230 nm, em:321nm,) using a Torus DIOL column (100 x 3.0 mm x 1.7 µm) with gradient elution of phase A [MeCN:AcOH 98:2 (v/v)] and B [MeOH:H2O:AcOH 95:3:2 (v/v/v)], 1.0 mL/min at 50 °C. We observed PCs with DP 1-3 from fractions F4-16 up to F4-80 (a), while DP 3-4 was observed in fractions F4-81 to F4-120 (b) and F4-121 to F4-136 (c). These fractions were combined, and the oligomers were quantified using a standardized cocoa flavanol extract (NIST 8403), resulting in 3.49 mg of DP 1 (a), 5.3 mg of DP 2 (a), 9.83 mg of DP 3 (a, b and c), and 9.77 mg of DP 4 (b and c), corresponding to 0.7%, 1.1%, 1.97% and 1.95% of the initial mass of extract, respectively It was not possible to quantify PCs with DP ≥ 5, due to their low separation resolution (Rs). We attempted to improve separation varying temperature, gradient, and flow. Improvements in peaks 8–9 Rs (up to 38.2%) reduced the resolution of earlier ones. Further optimization is required to achieve consistent Rs in all retention times. This is the first study that evaluated obtaining purified fractions of açaí seeds extract to assess the degree of polymerization and quantification.

Acknowledgements: Acknowledgements: FAPERJ (SEI-260003/013232/2024), Instituto Serrapilheira (Serra-1708-15009), CNPq (440645/2022-0).

ESTILOS SENSORIAIS DE CAFÉ INTERPRETADOS PELOS COMPOSTOS VOLÁTEIS IDENTIFICADOS POR GC/MS

Letícia Gabrielly Castro dos Santos*[1], Eduardo Vicente[2], Aline de Oliveira Garcia[2]

[1]FATEC – Faculdade de Tecnologia de Campinas
[2]ITAL - Instituto de Tecnologia de Alimentos

* Corresponding author: catlaine33@gmail.com

Este estudo caracterizou 9 cafés: tradicionais, superiores, gourmets, especiais, tanto arábica como canephora. As amostras foram avaliadas sensorialmente por experts (9 atributos, 24 descritores, estilo) e submetidas ao GC-MS, utilizando extração por SPME. Os voláteis foram identificados e semiquantificados através do MassHunter e biblioteca Nist17. A mediana da triplicata foi usada para análise em conjunto com os dados da sensorial. Para interpretação dos compostos, foram levantadas as percepções olfativas de cada volátil com uso de referências como The Good Scents Company, PubChem e FlavorBase. A análise multivariada foi realizada por meio da modelagem por PLS-DA, com o objetivo de ilustrar o agrupamento dos compostos conforme o estilo de café e identificar marcadores discriminantes (critério: VIP> 0,8 para potencial discriminante) com uso do software XLSTAT. No quadrante (QD) superior direito, sensorialmente as amostras gourmet e especial (arábica e canephora) foram consideradas ácidas, encorpadas, com forte fragrância do pó, aroma/sabor da bebida, doce, frutado, fermentado, baunilha, floral e amendoado/castanhas, os compostos voláteis que as caracterizam têm correspondência com os as percepções olfativas dos descritores morango, doce, medicinal, tostado, refrescante, floral, frutado, bem como, amadeirado, pungente, picante e amargo. No QD inferior direito, o café superior foi caracterizado pelo descritor caramelizado e por compostos que conferem as percepções doce, caramelo, amendoado e amadeirado. O café fora de tipo situou-se no QD inferior esquerdo, distante de termos positivos, esta amostra apresentou amargor, adstringência, sabor de oxidado e papelão, os compostos voláteis indicam odor penetrante, solvente, picante, medicinal e rançoso. Próximo ao eixo x, à esquerda, situou-se o café Canephora Tradicional junto ao descritor sensorial de queimado/defumado e a um agrupamento de compostos voláteis que correspondem a fumaça, defumado, cravo e tostado, além de caramelo, doce, amendoado, cacau e floral. No QD superior esquerdo, situaram-se os cafés Tradicional e Gourmet Torra Escura e o sabor animálico/curral junto aos compostos voláteis que são associados a torra intensa: tostado, caramelo, frutado, queimado, amendoado, amanteigado, doce, pungente, acre, penetrante, amadeirado, amoniacal e amargo. A abordagem utilizada destacou a importância da análise química como ferramenta de apoio à análise sensorial e na avaliação cafés de diferentes estilos.

Acknowledgements: À FAPESP pelo Projeto 2020/02728-5 e ao CNPq pela bolsa PIBIC.

EVALUATING OASIS HLB® POLYMERIC CARTRIDGES FOR MULTI-RESIDUE SOLID-PHASE EXTRACTION OF DIVERSE ANTIMICROBIAL CLASSES

Mararlene Ulberg Pereira, Letícia Barros Leal, Rosana Gomes Ferreira, Amanda da Silva Rio, Lais Farias de Carvalho, Bernardete Ferraz Spisso*

Instituto Nacional de Controle de Qualidade em Saúde - Fundação Oswaldo Cruz (INCQS/Fiocruz)

* Corresponding author: bernardete.spisso@fiocruz.br

The determination of residues in food is commonly performed using liquid chromatography tandem mass spectrometry (LC-MS/MS). Given that the target analytes are often present at low concentrations within complex matrices, sample preparation becomes a critical step. In most cases, purification of the extracts is necessary to reduce or eliminate matrix effects. Solid-phase extraction (SPE) Oasis HLB® cartridges contain a universal reverse-phase polymeric sorbent compatible with water and solvents of various polarities (acidic, basic, and neutral) and are widely employed in multi-residue methods for the analysis of antimicrobial compounds from various classes in food matrices. The present study aimed to evaluate the performance of Oasis HLB® polymeric cartridges for the extraction of multi-class antimicrobial residues, based on SPE conditions, specifically for adsorption, already employed in a routine laboratory method for the determination of tetracyclines in milk. Solutions of 0.02 mol/L oxalic acid containing macrolides, quinolones, sulfonamides, tetracyclines, and β-lactams were applied to Oasis HLB® cartridges at varying pH levels (4, 6, 8, and 10). Elution was performed using different solvent compositions. For all analytes belonging to the studied antimicrobial classes, the highest recoveries were obtained in experiments using application and elution solvents under acidic pH conditions. Exceptions were observed for sulfonamides, tetracyclines, and quinolones, which also exhibited recoveries above 79% when eluted under basic pH conditions. For the simultaneous determination of tetracyclines, β-lactams, quinolones, and macrolides, the most effective method employed an aqueous application solvent at pH 4 and an elution solvent consisting of 4% formic acid in methanol:water (65:35, v/v). The Oasis HLB® sorbent demonstrated a high capacity to extract a broad range of compounds with diverse chemical properties. Experiments using 0.02 mol/L oxalic acid at pH 4 as the application solvent, combined with acidic elution conditions, yielded the highest recoveries and proved to be the most promising among the tested conditions for implementation as the SPE step in a multi-class, multi-residue analytical method for food samples of animal origin currently under development in the laboratory.

Acknowledgements: Acknowledgements: This study was supported by CAPES (Finance Code 001) and Secretaria de Gestão do Trabalho e da Educação na Saúde – SGTES/ Ministério da Saúde.

EVALUATION OF ESSENTIAL OIL EXTRACTION PARAMETERS USING MICROWAVE-ASSISTED TECHNIQUES FOR EDUCATIONAL PURPOSES

Leticia Coli Louvisse de Abreu*, Thamires Idalino da Silva, Queli Aparecida Rodrigues de Almeida, Thiago Muza Aversa

IFRJ

* Corresponding author: leticia.abreu@ifrj.edu.br

Essential oils are natural products containing various organic functions such as alcohols, ketones, and ethers, and are found in different parts of plants. They are classified as secondary metabolites and possess a complex composition that grants them a wide range of applications, including sedative, antifungal, anesthetic, antimicrobial, and repellent activities. Traditionally, essential oils are extracted using methods such as steam distillation and Soxhlet extraction, which, although effective, require long processing times. In light of this, and in accordance with the principles of Green Chemistry, this study aimed to evaluate the efficiency of using a household microwave oven as an energy source for the extraction of essential oils from different plant species (clove, star anise, cinnamon, rosemary, lemongrass, orange peel, and mint), employing renewable and non-toxic solvents (water and ethanol). The methodology involved extraction with 50% (v/v) ethanol, followed by treatment of the crude extract with hexane or octan-1-ol, and subsequent characterization by thin-layer chromatography (TLC) and gas chromatography–mass spectrometry (GC-MS). The Green Star tool was also used to assess the sustainability of the experiments. Variables such as microwave power (100–500 W), extraction time (5–15 min), and solvent type were investigated. Results indicate the feasibility of using a household microwave oven as an efficient and sustainable alternative for essential oil extraction. For all extracts, good correlations were observed between TLC and GC-MS results. The chromatographic analyses with the best peak resolution were obtained using hexane as the solvent for crude extract treatment. Although octan-1-ol is a greener, ethanol-immiscible solvent, it has low volatility, which resulted in its peaks being detected in the chromatograms. Regarding extraction conditions, reaction time had a more significant impact than microwave power, as higher power levels led to rapid heating and premature volatilization of the extraction solvent.

Acknowledgements: Authors would like to thank IFRJ for the financial support

EVALUATION OF THE CATALYTIC EFFECT OF WASTE TEXTILE SLUDGE ON THE MICROPYROLYSIS OF SUGARCANE BAGASSE THROUGH GC×GC-TOFMS AND TILE-BASED FISHER RATIO ANALYSIS

Anna Clara de Freitas Couto*[1], Marília Gabriela Araújo Pereira[2], Edson Fernandes de Morais[2], Tarcísio Martins Santos[3], Wenes Ramos da Silva[3], Alberto Wisniewski Jr[3], Jandyson Machado Santos[2], Leandro Wang Hantao[1]

[1]University of Campinas
[2]Federal Rural University of Pernambuco
[3]Federal University of Sergipe

* Corresponding author: a272412@dac.unicamp.br

The catalytic pyrolysis of lignocellulosic biomass has emerged as a promising strategy to tailor the chemical composition of bio-oil and valorize agro-industrial residues. Textile sludge is a promising potential catalyst source, as it contains considerable amounts of metallic oxides that may be able to promote deoxygenation and cracking reactions more effectively. In this study, textile sludge was investigated as a heterogeneous catalyst source in the micropyrolysis of sugarcane bagasse. Rich in oxides of calcium, aluminum, and iron, the sludge was blended with bagasse at 10%, 25%, and 50% before pyrolysis. The bio-oils were analyzed by GC×GC-TOFMS, and data were processed using tile-based Fisher ratio analysis (FRA) and PCA. Co-pyrolysis with 10% sludge increased acids and simple aromatics, such as acetic acid and guaiacol, while reducing furans and oxygenated phenolics, indicating the occurrence of secondary cracking of biopolymer fragments. At 25% sludge, the bio-oil exhibited the highest content of acids (16.5%) and alcohols (16.6%), including 2-propanol, with a concurrent decrease in aromatic content. The 50% sludge addition enhanced hydrocarbon and polycyclic aromatic contents, such as tetradecane and 2-methyl-phenanthrene, and decreased the content of phenolics, furans, and pyrans, indicating promotion of deoxygenation and hydrocarbon cyclization reactions. Fisher-ratio analysis revealed clustering by sludge content. Discriminant features included acetic acid, pentanol, and methyl hexadecanoate. Minor compounds not identified by conventional peak-table processing, such as tetradecanenitrile and C26–C35 alkenes, were determined by tile-based FRA. The results indicate that textile sludge is a viable, sustainable catalyst source for improving bio-oil energy density and reducing oxygenated content. The observed effects are similar to those of basic metal oxide catalysts like CaO, involving deoxygenation, mild cracking, and ketonization. This study supports the reuse of hazardous industrial waste for catalytic biomass pyrolysis, promoting circular economy strategies and producing bio-oils with favorable energy applications.

Acknowledgements: This study was supported by CAPES (Finance Code 001), FAPESP (Grant No. 2022/07406-1), FACEPE (Grant No. 2022/07406-1), CNPq (Grants No. 302748/2018-0 and 316202/2021-5), ANP, and Petrobras (Grants No. 2019/00209-3 and 2019/00210-1).

EXPERIMENTAL DESIGN AND CHROMATOGRAPHIC ANALYSIS IN THE OPTIMIZATION OF OBTAINING OIL FROM PLASTIC WASTE FOR GASOLINE FORMULATION

Lilian Fernandes de Oliveira*, Yasmim Eufrásio de Melo, Ana Luiza Reis Rodrigues da Cunha, Dayane Cristina da Costa, Nelson Roberto Antoniosi Filho

Laboratório de Métodos de Extração e Separação (LAMES/UFG), Instituto de Química (IQ), Universidade Federal de Goiás (UFG)

* Corresponding author: lilianfernandes@discente.ufg.br

The increase in plastic waste and the environmental impacts caused by accumulation have driven the search for sustainable alternatives for reusing these materials. In this context, one of the most promising routes is the catalytic cracking of polymers into base oils for fuel production, such as gasoline. However, to achieve high yields and suitable chemical composition of these oils, it is necessary to evaluate several variables that affect process efficiency. Thus, experimental design becomes an important tool for assessing the effects of these variables, while chromatographic analysis proves to be a valuable technique for analyzing oil composition. This study aims to use a 2^3 factorial experimental design to evaluate the significant factors in obtaining oils from the catalytic cracking of polystyrene and to assess the chemical composition via gas chromatography coupled with mass spectrometry (GC-MS). The analyses were performed using a Shimadzu GC2010 Plus coupled with a QP2010 mass spectrometer and a DB-5ms capillary column (30 m × 0.25 mm × 0.25 µm). In this work, the influence of three factors on reaction yield was evaluated, each studied at two levels: reaction time (30 and 120 minutes), atmosphere (inert and ambient), and catalyst amount (5% and 25% w/w). Cracking was carried out at a temperature of 300 ºC, stirring at 600 rpm, and mining waste as a catalyst. Based on the experimental design results, it was observed that reaction time was the most significant factor for main effects on oil yield ($p < 0.05$). Response surface plots showed that the interaction between time-catalyst had antagonistic effect on oil yield. Chromatographic analysis identified the presence of aromatic hydrocarbons with chains of 7 to 24 carbons, with toluene, ethylbenzene, styrene and α-methylstyrene being the main compounds, responsible for increasing the octane rating of gasoline, a highly desirable property of the fuel. None of the experimental factors significantly influenced the percentage area of the main compounds, which may be a positive aspect in relation to product stability, allowing parameter adjustments without compromising the octane number. Through this study, it was possible to identify the significant factors for optimizing the oil production method and evaluate the hydrocarbon profile that confers important properties to the quality of the base oil and fuel.

Acknowledgements: Acknowledgements: LAMES/UFG, IQ-UFG, FUNAPE, ANP, INCT-ALIM.

EXPERIMENTAL DESIGN-BASED OPTIMIZATION OF SAMPLE PREPARATION AND DERIVATIZATION FOR HPLC ANALYSIS OF THE PESTICIDE GLYPHOSATE AND ITS MAIN METABOLITE, AMPA, IN HUMAN LIVER MICROSOMES

Arthur Avila*, Leandro Oka-Duarte, Anderson R. M. de Oliveira

Department of Chemistry, FFCLRP, University of São Paulo

* Corresponding author: arthuravila86@usp.br

Glyphosate (GLYP) is the most widely used herbicide worldwide. Numerous studies have raised concerns regarding the contamination of water bodies, atmospheric air, and food. Consequently, there is significant concern regarding human exposure, as both this herbicide and its metabolite, aminomethylphosphonic acid (AMPA), have been detected in human biological fluids. Understanding the metabolic behavior of xenobiotics in humans is essential, particularly for pesticides, whose metabolism data remain scarce. In the human body, these compounds can be metabolized by cytochrome P450 enzymes and/or inhibit their enzymatic activity, potentially leading to pesticide-drug interactions. In this context, the objective of this study was to optimize a sample preparation method utilizing human liver microsomes (HLM) to further assess the in vitro behavior of GLYP and AMPA with respect to these enzymes. To achieve this, an LC-UV method was optimized, incorporating pre-column derivatization with 9-fluorenylmethyl chloroformate (FMOC-Cl). Analysis was carried out by using an Ascentis® Express C18 column (100 mm × 4.6 mm; 2.7 µm), and a gradient elution consisted of an aqueous buffer at pH 8.0 containing 0.3% (v/v) NH_4OH and 0.1% (v/v) CH_3COOH and acetonitrile as mobile phase at a flow rate of 1.0 ml min^{-1}. The sample preparation was performed by using HLM as sample matrix and began with protein precipitation using cold acetonitrile. Next, the derivatization of GLYP and AMPA was carried out, and subsequently, backwashing the aqueous phase via liquid-liquid extraction (LLE). Subsequently, a univariate screening was conducted to optimize the vortex time after the addition of FMOC-Cl and to select the best extraction solvent, with 0 s and dichloromethane identified as the optimal conditions. Two-level factorial design with 3 factors (23) was then performed twice: the first one to optimize the LLE step and the second one the derivatization reaction. This approach successfully reduced the agitation time, the borate buffer concentration, and the reaction time to 5 min, 10 mmol L^{-1}, and 20 min, respectively. Finally, the relative recovery was evaluated, yielding values of 105 ± 6% for GLYP, and 111 ± 5% for AMPA.

Acknowledgements: FAPESP (grant numbers 2025/04629-8; 2024/20783-4) and CNPq (grant number 304319/2024-4).

Exploring the Versatility of the Velox Column: Method Development for the Determination of Cannabinoids and Aflatoxins

Marilia Santoro Cardoso*, Monique Fabiane dos Santos, Marcos A Pudenzi, Ichiro Hirano

Shimadzu do Brasil

* Corresponding author: marilia.cardoso@shimadzu.com.br

Introduction: In recent years, medical cannabis has gained increasing relevance in Brazil. ANVISA (National Health Surveillance Agency) is responsible for regulating the therapeutic use of cannabis-based products. To ensure the safety, efficacy, and quality control of these medications, precise analytical methods—such as quantitative cannabinoid analysis, and contaminant analysis (e.g., aflatoxins)—are essential. The Shim-pack Velox column, developed by Shimadzu, stands out as a fast and precise analytical tool for these compounds. Featuring core-shell particle technology, Shim-pack Velox offers high separation efficiency, low system pressure, and shorter analysis times compared to traditional fully porous columns. In this context, we explored how the Shim-pack Velox optimizes the analysis of 10 cannabinoids and 4 aflatoxins. Methods: In both methods (cannabinoids and aflatoxins) were used the analytical column Shim-pack Velox C18 held at 20 °C and 40 °C and linearity range of 2-100 µg/mL and 0.1-20 µg/mL, respectively. In cannabinoids method were used a diode array detector, quantifying at 228 nm, injecting five microliters. The mobile phase flow was 1.2 mL/min and consisted of formic acid (0.1%) in water and in acetonitrile. The elution gradient was established as follows: 75% B (0,0 – 1,5 min), 80% B (1,5 – 1,71 min), 80% B (1,71 – 7,70 min), 75% B (7,70 – 7,71 min), with a total running time of 10 minutes. In aflatoxins method were used a fluorescence detector and a Kobra® Cell for derivatization post column, emission at 455 nm and excitation at 362 nm, injecting three microliters. The mobile phase flow was 1.0 mL/min and consisted of water:methanol (60:40), potassium bromide and nitric acid, in isocratic mode with a total running time of 6 minutes. Results: Linearity was evaluated for both methods, with calibration curves generated in triplicate ($R^2 > 0.99$) using seven different concentrations. The chromatographic peaks showed appropriate shapes and good resolution. Conclusion: The use of the Nexera XR system combined with the Shim-pack Velox column enabled the development of efficient and versatile methodologies for the analysis of cannabinoids and aflatoxins. The results obtained demonstrate the feasibility of robust methods capable of accurately and reproducibly quantifying different classes of compounds using the same analytical column.

Acknowledgements: The speaker would like to acknowledge this present work to Shimadzu Corporation and Shimadzu do Brasil.

EXTRACTION AND CHARACTERIZATION OF VOCS IN CONCENTRATE JUICES VIA HS/GC-MS

Lucas de Sousa Rodrigues*, Rhyan César Santos Dias, Dayane Cristina da Costa, Nelson Roberto Antoniosi Filho

Laboratório de Métodos de Extração e Separação (LAMES/UFG), Instituto de Química Universidade Federal de Goiás (IQ-UFG)

* Corresponding author: lucasquimicafacul@gmail.com

D-limonene, γ-terpinene, and β-pinene are volatile organic compounds (VOCs) found in concentrate juice samples. Juices are widely consumed by the population due to their refreshing flavor and associated health benefits. The global juice market generates billions of dollars annually, with orange juice ranking among the most consumed. Volatile substances consist of monoterpenic and sesquiterpenic hydrocarbons, oxygenated derivatives, aldehydes, alcohols, and aliphatic esters, which may occur in small amounts but are largely responsible for the odor and flavor profiles of fruits, thereby enhancing consumers' olfactory preference. The non-volatile fraction of juice may contain sterols, fatty acids, waxes, carotenoids, coumarins, psoralens, and flavonoids. This non-volatile and/or semi-volatile fraction is complex and can influence the vapor pressure and diffusion of terpenes during extraction and analysis, thereby affecting the quality control of these products. Therefore, the aim of this study is to investigate the optimal extraction conditions of the terpenes d-limonene, γ-terpinene, and β-pinene using headspace GC-MS in different matrices, and to characterize the volatile compounds present in commercial concentrate juices. For each assay, 1 µL of standard and 1000 µL of matrix were transferred into 10 mL vials, prepared in triplicate. The matrices tested included hexane, ethyl acetate, water, and concentrate cashew juice. Extractions were carried out at 50, 80, and 150 °C with agitation times of 5, 10, and 20 minutes. Thirteen juice samples of various flavors (grape, tangerine, orange, cashew, acerola, pineapple, lemon, and passion fruit) were analyzed using 3 mL aliquots in 10 mL vials at 80 °C for minutes. Analyses were conducted on an Agilent 7890B GC coupled to a 7000D MS using a DB-5ms capillary column (30 m 0.25 mm × 0.25 µm). Terpene peak intensities were low in hexane and ethyl acetate matrices, likely due to headspace saturation by solvent molecules volatilizing at room temperature via London dispersion forces. Moreover, the solubility of terpenes is favored in nonpolar solvents, mediated by these weak forces. In juice and water matrices, terpene peaks exhibited higher intensities, with the optimal extraction condition being 10 minutes at 80 °C. Analysis of the commercial samples led to the identification of 28 VOCs, including α-pinene, terpinolene, o-cimene, (−)-β-pinene, ethyl acetate, 3-carene, γ-terpinene, 1R-α-pinene, ethyl butanoate, β-myrcene, ethanol, and d-limonene. Principal component analysis (PCA) of the data revealed greater distinction for passion fruit, tangerine, and pineapple samples, and similarity among orange, cashew, lemon, acerola, and grape samples. The pineapple sample exhibited the highest number of esters, with at least five unique compounds compared to the other samples. The extraction time for juice samples was maintained at 20 minutes to ensure complete extraction of terpenes not investigated in this study. This study identified key headspace parameters for optimizing analytical response and demonstrated the chromatographic application for VOC quality control in commercial concentrate juices, enabling characterization of the volatile sensory profile underlying their distinctive flavors and aromas.

Acknowledgements: LAMES/UFG, IQ-UFG, CAPES, INCT-ALIM, ANP, FUNAPE.

EXTRACTION, CHEMICAL CHARACTERITION, ANTIMICROBIAL ACTIVITY AND TOXICOLOGICAL BIOASSAY OF NEEM OIL (AZADIRACHTA INDICA A. JUSS)

Andressa Danieli Araujo Cavalcante*, Flamys Lena do Nascimento Silva

Universidade Federal do Norte do Tocantins

* Corresponding author: andressa.cavalcante@ufnt.edu.br

The use of plant extracts as an alternative to synthetic compounds has gained prominence in scientific research, particularly in the development of antimicrobial agents and bioinsecticides. Neem oil, obtained in greatest abundance from the seeds and leaves of the Azadirachta indica plant, is known for its rich composition of limonoids and other secondary metabolites with broad biological activity. This study aimed to evaluate the toxicity and microbial activity of oil extracted from neem seeds using the Soxhlet technique, as well as chemical characterization through gas chromatography-mass spectrometry (GC-MS) and Fourier transform infrared spectroscopy (FTIR). Toxicity bioassays were evaluated using Artemia salina nauplii, according to Meyer criteria, at different concentrations of neem oil. Microbial activity followed the methodology described by the Clinical and Laboratory Standards Institute (CLSI) using the agar diffusion method to assess neem oil's activity against Bacillus subtilis, Escherichia coli, Staphylococcus aureus, Candida albicans, Candida krusei, Candida tropicalis, and Candida parapsilosis, with these microorganisms suspended on the 0.5 McFarland scale. Bioassays indicated that more dilute concentrations cause greater mortality. Microbial analysis did not observe neem oil's efficacy against the tested strains, with significant results only in the positive controls. The results of chemical characterization by FTIR indicate that the oil is composed of several substances belonging to different chemical classes, such as alcohols, esters, ketones, and aromatics. Among the compounds identified by GC-MS are: hydroperoxides, pyrazines, esters, trisulfanes, thianes and aldehydes, supposedly responsible for the characteristic aroma of the oil, as well as for its toxicological and microbial action.

Acknowledgements: I thank UFNT for supporting the research, IFTO for the analyses carried out, and professors Daniel Barra, Paiva, and Hebert for their valuable contributions.

FATTY ACID AND TOCOPHEROL PROFILES OF MONOVARIETAL EXTRA VIRGIN OLIVE OILS PRODUCED IN RIO GRANDE DO SUL

Natalia Caroline da Silva Reis[1], Allan Eduardo Wilhelm[2], Rosemar Antoniassi[3], Humberto Ribeiro Bizzo*[2]

[1]Programa de Pós-Graduação em Ciência de Alimentos, Universidade Federal do Rio de Janeiro
[2]Programa de Pós-Graduação em Ciência de Alimentos, Universidade Federal do Rio de Janeiro e Embrapa Agroindústria de Alimentos
[3]Embrapa Agroindústria de Alimentos

* Corresponding author: humberto.bizzo@embrapa.br

The chemical composition of olive oil differentiates it from other vegetable oils, and the characterization of its fatty acids and tocopherol profiles is fundamental to attest its quality. The objective of this work was to determine the fatty acid and tocopherol profiles of Brazilian extra virgin olive oils (EVOO) of three different varieties, Koroneiki, Arbequina, and Picual, all produced in Rio Grande do Sul, and to verify the conformity of these parameters with those from both the Brazilian legislation. Fatty acids profiles were determined by GC-FID, while tocopherols were analyzed by HPLC-Fluorescence, according to methodologies described by the AOCS – American Oil Chemists' Society. Analysis of variance (ANOVA) and Tukey's test were performed for comparison of means with a significance level (p

Acknowledgements: INCT da Olivicultura e do Azeite Brasileiros (CNPq 406921/2022-9), CNPq 303475/2025-0 and CAPES Proex 88887.951257/2024-00.

Fatty Acid Profile of Quixaba (Sideroxylon obtusifolium) Pulp and Seed

Luisa dos Santos Conceição[1], Deborah Murowaniecki Otero[1], Pedro Minasi Brandão[2], Fernanda Bedinoto Guerra[2], Luiz Henrique Han[2], Gabriele Avila Costa[2], Anelise Christ-Ribeiro*[2]

[1]Universidade Federal da Bahia
[2]Universidade Federal do Rio Grande

* Corresponding author: anelise.christ@hotmail.com

Quixaba (Sideroxylon obtusifolium), a native fruit of the Brazilian semi-arid region, represents an underutilized source of nutrients with potential for the food and nutraceutical industries, with its fatty acid composition being crucial for its nutritional and technological valorization. This study aimed to determine and compare the fatty acid profile of Quixaba pulp and seed. The methodology for determining the fatty acid profile involved lipid extraction according to Folch, Lees, and Stanley (1957). The oils were esterified following Hartman and Lago (1973): approximately 30 mg of oil were treated with 500 µL of 0.1 mol/L KOH and 1.5 mL of 1 M H_2SO_4 in a water bath (60 °C, 1.5 h for each step), followed by the addition of 2 mL of n-hexane for the extraction of methyl esters. For analysis, a gas chromatograph (Shimadzu, model – 2010 Plus), equipped with a split/splitless injector, a Zebron ZB-FAME capillary column (20 m x 0.18 mm ID x 0.15 µm), and a flame ionization detector (FID) was used. The injector temperature was 250 °C and the detector temperature was 260 °C. Nitrogen (N_2) was used as the carrier gas. The chromatographic conditions for the column were an initial temperature of 80 °C for 1.5 min, then raised to 160 °C at a heating rate of 40 °C min^{-1}, followed by an increase to 185 °C at a rate of 5 °C min^{-1}, and finally to 260 °C at a rate of 30 °C min^{-1}, totaling 11 min of run time. Peak identification was performed by comparing the retention times of the samples with fatty acid methyl ester standards (Supelco 37 components FAME MIX – Sigma-Aldrich Products), and quantification was achieved using peak areas. GC-FID analysis revealed very similar fatty acid profiles between Quixaba pulp and seed. Both showed a predominance of unsaturated fatty acids. The main ones were oleic (C18:1 C, ~40.7%), linoleic (C18:2 C, ~24.4%), and palmitic (C16:0, ~21.7%). The monounsaturated (MUFA) and polyunsaturated (PUFA) fractions were high (~41.1% and ~24.5%, respectively), while the saturated (SFA) fraction was ~34.3% in both parts. This similarity and the high content of MUFA and PUFA indicate a lipid profile of high nutritional value. In conclusion, Quixaba (Sideroxylon obtusifolium) pulp and seed have very similar fatty acid profiles, with a predominance of oleic and linoleic acids.

Acknowledgements: CAPES and CNPq.

Fecal Lipid Profiling Using UPLC–qTOF–MS to Identify Biomarkers of Cattle Phenotype

Ousmane Diarra[1], Renato Cardoso Leal Netto[2], Luciana Correia de Almeida Regitano[3], Daniel Rodrigues Cardoso*[2]

[1]Laboratory of Research in Microbiology and Microbial Biotechnology (LaboREM-Biotech), Faculty of Sciences and Techniques, University of Sciences, Techniques and Technologies of Bamako, Mali BP E3206 and Chemistry Institute of Sao Carlos, University of Sao Paulo, Sao Carlos, SP 13560-970, Brazil
[2]Chemistry Institute of Sao Carlos, University of Sao Paulo, Sao Carlos, SP 13560-970, Brazil
[3]Embrapa Pecuária Sudeste, Empresa Brazileira de Pesquisa Agropecuária, São Carlos, Brazil

* Corresponding author: drcardoso@usp.br

Ultra-performance liquid chromatography coupled with high-resolution accurate mass spectrometry (UPLC-QqTOF-MS) is a cornerstone in lipidomics, enabling large-scale lipid profiling and biomarker discovery related to disease, diet, and phenotype. In this study, we employ two high-resolution UPLC-MS/MS acquisition strategies—data-dependent acquisition (DDA; Full-MS and Auto-MS2) and data-independent acquisition (DIA; bbCID MS/MS2)—on a UPLC-VIP-HESI-QqTOF system (Bruker Impact II TargetScreener). Fecal samples were collected from 93 Nelore bulls (18–30 months old) participating in the PNAT 2020 (National Young Sires Evaluation Test, ABCZ, Brazil). Samples were obtained directly from the rectal ampulla, flash-frozen in liquid nitrogen, and stored at –80 °C. Lipid extraction was performed from 50 mg of feces using a commercial cell disruptor (FastPrep, MPBio; matrix type D) with 1.75 mL of methyl tert-butyl ether (MTBE)/methanol/water (1:0.25:0.5, v/v/v). After ultracentrifugation, the organic phase was collected, dried in a vacuum centrifugal evaporator (Savant Speedvac), and reconstituted in 1 mL of UPLC mobile phase B (isopropanol/acetonitrile, 90:10 v/v). Analyses were conducted in positive ionization mode under both DDA and DIA conditions. Quality control samples were prepared by pooling daily sample batches and spiking with an internal standard (16:0-18:1 D5 PG, CAS 1246298-34-9). Data processing and ion annotation are being performed with MS-DIAL (v4.92) and MS-FINDER (v3.52). Multivariate statistical analysis (PCA) revealed two distinct sample clusters, with annotated lipids identified as key discriminating features. Relevant lipid biomarkers were further integrated with characteristic phenotypic markers using the mixOmics R package, providing insights into their associations with performance and feed efficiency. This study advances the characterization of ruminal bacterial lipid metabolites and their potential role as biomarkers in cattle phenotype.

Acknowledgements: FAPESP, CAPES, and CNPq.

Forensic Chemical Profiling of Ecstasy Tablets: A Simple and Rapid GC/MS Method

Gabriel Pardini Coelho*, Murilo M. R. Oliveira, Nayara Silva Fraga, Josimar M. Batista, Clésia Cristina Nascentes, Zenilda de Lourdes Cardeal, Helvécio Costa Menezes

UFMG

* Corresponding author: gabrielpardinicoelho@hotmail.com

Chemical profiling of seized ecstasy tablets provides essential data for forensic investigations and public health monitoring, yet regional studies focusing specifically on the chemical profiling of ecstasy in Minas Gerais remain limited. This study evaluates a simplified sample preparation method for gas chromatography-mass spectrometry (GC/MS) analysis of ecstasy tablets seized in this region. The ecstasy tablets seized in Minas Gerais were analyzed using a simple and rapid extraction approach. Each tablet was homogenized, and a 10.0 mg sample was extracted with 1.0 mL of methanol by vortex agitation for 2 min. After centrifugation at 14,000 rpm (1,9x10^4g) for 2 min, 0.7 µL of the supernatant injected into a Shimadzu GCMS-TQ8040 NX system. Chromatographic separation was performed using an SH-I-5Sil MS capillary column (30 m × 0.25 mm i.d., 0.25 µm film thickness) with helium as carrier gas. Mass spectra were acquired in the scan mode (m/z 40-450). The single-step extraction protocol enabled identification of multiple chemical compounds across the sample set. MDMA was identified as the primary active substance in 22.2% of samples, and synthetic cathinones, particularly N-ethylpentylone, served as the main psychoactive component in multiple samples. Additional substances included other stimulants (cocaine, caffeine), anesthetics (lidocaine, ketamine), and an anabolic steroid (mesterolone). Synthesis markers were also found, including precursors (piperonal, MDP2P), and manufacturing by-product. Tableting excipients such as fatty acids and phthalates were consistently identified. The single-step methanol extraction procedure provided effective sample preparation for GC/MS analysis of ecstasy tablets. The method offers advantages in simplicity, reduced solvent consumption, and analysis time. The results demonstrate the prevalence of adulterated products in the Minas Gerais ecstasy market, with synthetic cathinones frequently substituting for MDMA. The methodology represents a practical approach for routine analysis in forensic laboratories.

Acknowledgements: Instituto Nacional de Ciências e Tecnologia sobre Substâncias Psicoativas (INCT-SP/CNPq), FAPEMIG/INCT-SP, CAPES/INCT-SP, and CEI-DQ-UFMG.

FROM LIPIDOMICS TO MEMBRANE PROPERTIES: IMPACT OF OLEIC ACID SUPPLEMENTATION ON THE LIPID COMPOSITION AND BIOPHYSICAL BEHAVIOR OF Staphylococcus aureus UNVEILED BY HPLC-QTOF-MS, FLUORESCENCE SPECTROSCOPY AND FTIR

Juan E. González*, Santiago Mongua, Elizabeth Suesca, Chad Leidy, Chiara Carazzone

Universidad de los Andes

* Corresponding author: je.gonzalezm123@uniandes.edu.co

Staphylococcus aureus is an opportunistic pathogen whose pathogenicity and resistance are strongly influenced by its membrane lipid composition. Modulation of lipid profiles through supplementation with unsaturated fatty acids, such as oleic acid, can significantly alter membrane structure and function, thereby impacting bacterial physiology and susceptibility to external stress. Understanding these lipidomic and biophysical changes is crucial to unravel bacterial adaptation mechanisms.

In this study, S. aureus was cultured under standard conditions and supplemented with oleic acid. Lipidomic profiling by LC-qTOF-MS in dual ESI modes enabled characterization of global lipid composition and annotation of species modulated by supplementation. In parallel, membrane biophysical properties were assessed through fluorescence spectroscopy with DPH and Laurdan probes, as well as FTIR spectroscopy, in order to correlate lipidomic changes with alterations in membrane order and dynamics.

Results revealed the presence of diverse lipid classes, including free fatty acids, phosphatidylglycerols (PG), cardiolipins (CL), lysyl-phosphatidylglycerols (Lysyl-PG), diacylglycerols (DG), monogalactosyldiacylglycerols (MGDG), and digalactosyldiacylglycerols (DGDG). Notably, supplementation with oleic acid led to the incorporation of C18:1 into the membrane lipidome, along with the unexpected detection of C20:1 and lipid species containing acyl chains with two double bonds. Membranes from supplemented strains showed increased fluidity, particularly in the gel phase at low temperatures (FTIR). Fluorescence data from DPH and Laurdan confirmed reduced anisotropy and generalized polarization, consistent with looser lipid packing. This suggests a complex remodeling of the lipid biosynthetic pathways and elongation/desaturation processes, reflecting a high degree of metabolic plasticity and adaptive capacity in response to exogenous fatty acid availability

This integrative lipidomic-biophysical approach reveals how unsaturated fatty acids reshape S. aureus membrane architecture, promoting adaptability and offering potential targets for antimicrobial strategies.

FRUTOS DE Genipa americana L. NA INVESTIGAÇÃO DA ATIVIDADE ANTIOXIDANTE

Lariza Leisla Leandro Nascimento, José Galberto Martins da Costa*, Débora Odília Duarte Leite, Gerson Javier Torres Salazar, Ana Cecília Calixto Donelardy, Mariana Pereira da Silva, Fabíola Fernandes Galvão Rodrigues

UNIVERSIDADE REGIONAL DO CARIRI

A procura por compostos biologicamente ativos vem estimulando a busca por métodos de extração sustentáveis, eficientes e que favoreçam a composição química e atividades biológicas. Esse estudo investiga a eficácia dos métodos extrativos QuEChERS e maceração no potencial antioxidante dos frutos da Genipa americana L. Os frutos verdes foram submetidos a maceração a frio com etanol, por 72 h, e ao métodos QuEChERS, com etanol, seguido por limpeza para retirar coextrativos. Os ensaios antioxidantes foram realizados pelos métodos de DPPH•, captura do cátion radical ABTS•+, quelação de Fe2+ e redução de Fe3+. Os resultados demostraram maior rendimento da extração por maceração com 5,4 % em comparação a QuEChERS que apresentou 3,84 %, além da diferença de coloração nos produtos extraidos, amarelo pálido (maceração) e azul límpido (QuEChERS). No ensaio por DPPH• o produto da maceração apresentou IC50 488.24 µg/mL e por QuEChERS não apresentou atividade, enquanto que na captura do cátion radical ABTS•+ os resultados foram de 276.96 µg/mL e 363.86 µg/mL, respectivamente. Para a quelação de Fe2+ e redução de Fe3+, os extratos não apresentaram atividade dose dependente. Na quelação de Fe2+ a maior porcentagem para a maceração foi de 35 % na concentração de 500 µg/mL e para QuEChERS 83,82 % na concentração de 10 µg/mL. Para redução de Fe3+ a concentração de 100 µg/mL apresentou porcentagens máximas de 90.17 % e 97.06 %, nas respectivas extrações. Portanto, a maceração permitiu maior recuperação de compostos fenólicos relacionados a doação de hidrogênio ou de elétrons, tornando radicais livres em substâncias estáveis, mecanismo que ocorre no DPPH• e captura do cátion radical ABTS•+. Em contrapartida, no método QuEChERS, as etapas de extração/partição eliminam interferentes, o que pode ter favorecido os resultados na quelação de Fe2+ e redução de Fe3+. O método extrativo interfere nas concentrações de metabólitos secundários, rendimento e atividades biológicas, como antioxidante, por exemplo. Os resultados mostram que o método antioxidante que envolve radicais livres apresentou melhores resultados para o extrato obtido por maceração, enquanto que nos métodos de quelação de Fe2+ e redução de Fe3+, esse fato foi observado na extração por QuEChERS, evidenciando a importância de se avaliar a atividade antioxidante por diferentes métodos de extração.

Acknowledgements: CNPq, CAPES, FUNCAP, FINEP e INCT-ALIM.

Fusion Splicing Techniques of Capillaries with Capillaries and Others: Imagination Seems to be the Limit.

Tarso B Ledur Kist*

Laboratory of Instrumentation and Automation in Analytical Chemistry. Institute of Chemistry, Federal University of Rio Grande do Sul, Porto Alegre, RS, Brazil, 91501-970.

* Corresponding author: tarso.kist@gmail.com

Fusion splicing of quartz microtubes allows the fabrication of all quartz made joints, connections, and “Ts” using cylindrical, elliptical, square, or rectangular microtubes. This is now a mature technology that allows new set-ups to be fabricated and applied in great diversity of fields, such as GC, HPLC, capillary electrophoresis, microchip electrophoresis, flow cytometry, cell sorters, and many other fields. In this presentation a variety of such set-ups using fusion splicing are demonstrated. The results are all quartz made set-ups with smooth inner surfaces, and unlike polymer or adhesive mediated connections, they withstand high temperatures, strong alkali solutions, strong acid solutions, high pressures, and strong electric fields. In addition to this, the internal surfaces can be chemically modified using the known properties of the silanol group, resulting in a physically and chemically homogeneous coating.

Geochemical evaluation of crude oils from the Santos Basin pre-salt using light hydrocarbon parameters by GC×GC-TOFMS

Thales Nideck Rodrigues*[1], Clarisse Lacerda Torres[1], Dayane Magalhães Coutinho[1], Felipe Raposo Passos Mansoldo[1], Daniel Silva Dubois[2], Joelma Pimentel Lopes[2], Gabriela Vanini[1], Débora de Almeida Azevedo[1]

[1]Universidade Federal do Rio de Janeiro
[2]CENPES/Petrobras

* Corresponding author: thalesnideck@gmail.com

Light hydrocarbons (up to C13) comprise a significant portion of most crude oils, particularly in light oils such as those from the pre-salt of the Santos Basin, which are known for their high quality and API gravity of around 28. Therefore, interpreting molecular parameters based on light hydrocarbons is critical for assessing information regarding source rock, thermal maturity levels, and potential secondary alteration processes. This study aimed to evaluate the application of light hydrocarbons, analyzed via comprehensive two-dimensional gas chromatography coupled to time-of-flight mass spectrometry (GC×GC-TOFMS), in geochemical characterization of 32 crude oils from a field located at the pre-salt of the Santos Basin. The samples, provided by Petrobras, were prepared by weighing approximately 2.00 mg of each crude oil and then dissolving it in 200 µL of carbon disulfide containing an internal standard mixture. The analyses were performed using a GC×GC-TOFMS Pegasus 4D system (Leco, St. Joseph, MI, USA). The chromatographic columns consisted of a DB−5ms (30 m, 0.25 mm ID, 0.25 µm) in the first dimension and a DB−17ht (1.0 m, 0.25 mm ID, 0.15 µm) in the second dimension (Agilent Technologies). The analytical conditions were set according to Coutinho et al. (2025). GC×GC data were processed using ChromaTOF software version 4.51, with a signal-to-noise ratio of 50:1. A peak table approach was employed to extract the analytical data. Classical geochemical parameters were then evaluated, such as those proposed by Mango (1997) and Thompson (1983). The Mango K1 parameter, based on C7 hydrocarbons, is often used to differentiate oil families. This parameter was calculated for all samples, and the linear correlation indicated that the oils likely originated from the same petroleum system. The Thompson H–I diagram (heptane vs isoheptane ratio) indicated that the oils predominantly exhibit a normal maturity level. The B–F diagram (paraffinicity vs. aromaticity) showed no evidence of secondary alteration processes (Zhang et al., 2025), reflecting the preservation of the original geochemical signature of the oils and contributing to the understanding of the petroleum system in the Santos Basin. This approach is a promising analytical tool due to its high-resolution capacity, which effectively separates low molecular hydrocarbons that coelute in conventional GC, providing more accurate information. Additional studies are ongoing to strengthen the geochemical interpretation of these oils.

Acknowledgements: PIBIC−CNPq−UFRJ, FAPERJ, CNPq, Capes, Petrobras

GRAPHENE-BASED HYBRID SORBENTS IN SAMPLE PREPARATION: 1. SYNTHESIS AND CHARACTERIZATION

Maria Flávia Assunção Magalhães*, Rafael Oliveira Martins, Alessandra Timóteo Cardoso, Jussara da Silva Alves, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brasil

* Corresponding author: mfamag@usp.br

In the last decades, graphene-derived sorbents have been widely applied in sample preparation techniques, mainly due to their characteristics such as high surface area, delocalized π electrons, and single-layer structure. The Hummers method (1958), with slight modifications, has been used to obtain graphene oxide (GO) from graphite. Graphite powder is oxidized using H_2SO_4, $NaNO_3$, $KMnO_4$, and H_2O_2, and graphite oxide undergoes physical exfoliation through ultrasonication to provide GO. After obtaining GO, it can be anchored onto silica for use in dispersive or packed sample preparation techniques, without stacking of graphene sheets, thereby avoiding clogging. For this purpose, GO is treated with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) in aqueous solution, and then anchored onto aminopropyl silica. In addition, the surface of the nanomaterial can be functionalized with several compounds, including octadecylsilane (C18), ionic liquids (ILs), and polysaccharides such as chitosan (CS) and β-cyclodextrin (β-CD). For C18 functionalization, SiGO is refluxed under an inert atmosphere with toluene, imidazole, and chlorodimethyl-n-octadecylsilane (ODS). Endcapping of this material is carried out using trimethylchlorosilane (TMS). For functionalization with ionic liquids, the modification of the oxygenated groups of GO with thiol groups is required. For this, 3-mercaptopropyltrimethoxysilane (MPTMS) is used under N_2 atmosphere, followed by heating under alkaline conditions. The ionic liquids themselves are prepared separately by mixing imidazoles with alkyl halides or sultones. The functionalization of GO is then performed under an inert atmosphere in the presence of 2,2′-azobis(2-methylpropionitrile) (AIBN). For the synthesis of biosorbents, CS is heated together with SiGO in an acetic acid solution in the presence of the crosslinker glutaraldehyde. For functionalization with β-CD, (3-aminopropyl)triethoxysilane (APTES) was used in DMF to couple the polysaccharide to the GOSi. The synthesized sorbent materials are characterized by several techniques, including Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), and Thermogravimetric Analysis (TGA).

Acknowledgements: FAPESP [Grants 2017/02147-0; 2017/21984-0; EMU; 2017/21985-6 – EMU; 2023/06258-1; 2023/15675-5]; CNPq [Grants 308843/2019-3 and INCT-ALIM Grant 406760/2022-5]; CAPES [Grant: 88887.005608/2024-00; 88887.999341/2024-00] financed this study.

GRAPHENE-BASED HYBRID SORBENTS IN SAMPLE PREPARATION: 2. STRATEGIES AND ANALYTICAL ALTERNATIVES FOR CHALLENGING SCENARIOS

Rafael Oliveira Martins, Maria Flávia Assunção Magalhães*, Alessandra Timóteo Cardoso, Jussara da Silva Alves, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brasil

* Corresponding author: mfamag@usp.br

The continuous advancement of sample preparation techniques, both conventional and miniaturized, has driven the development of new selective sorbents with distinct properties for applications in complex matrices. Although conventional commercial silica-based sorbents such as C8 and C18 remain among the most viable strategies in many scenarios, the creation of new materials has provided not only novel phases but also modified versions of existing sorbents, resulting in hybrid materials with physicochemical properties that surpass traditional options. Among these materials, graphene derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) stand out for their high surface area, mechanical strength, and thermal stability, characteristics that favor their use across various sample preparation methodologies. These materials also offer broad potential for modification, allowing functionalization to be aligned with the chosen preparation approach and enabling the production of hybrid sorbents with a more environmentally friendly profile. Silica modified with graphene oxide (SiGO) has been utilized in microextraction by packed sorbent (MEPS) to extract parabens from water, thereby mitigating the backpressure commonly associated with graphene sorbents in packed formats. SiGO, functionalized with chitosan, stabilizes graphene sheets and has been applied in MEPS for the analysis of food contaminants. Where backpressure is not limiting in packed formats, other routes have been explored for graphene-based sorbents. Ionic liquids combined with GO have been used in stir bar sorptive extraction (SBSE) via thiol insertion with application to grape juice. Furthermore, SiGO modified with cyclodextrin has enabled the determination of isoflavones in soy-based juices, using host-guest inclusion to add size and shape selectivity and reduce nonspecific adsorption. Overall, such modifications both address method-specific drawbacks and support more sustainable sample preparation.

Acknowledgements: São Paulo Research Foundation, FAPESP [Grants 2017/02147-0; 2017/21984-0 – EMU; 2017/21985-6 – EMU]; the National Council for Scientific and Technological Development, CNPq [Grants 308843/ 2019-3 and INCT-ALIM Grant 406760/2022-5]; Coordenação de Aperfeiçoamento de Pessoal de Nível Superior [Grant: 88887.005608/2024-00] financed this study.

GRAPHENE-BASED HYBRID SORBENTS IN SAMPLE PREPARATION: 3. MINIATURIZED SAMPLE PREPARATION DEVICES

Alessandra Timóteo Cardoso*, Jussara da Silva Alves, Maria Flávia Assunção Magalhães, Rafael Oliveira Martins, Fernando Mauro Lanças

São Carlos Institute of Chemistry, Universidade de São Paulo

* Corresponding author: alessandracardoso@usp.br

Graphene oxide (GO), in addition to typical graphene-based properties such as π–π interactions, abundant binding sites, and remarkable thermal and mechanical stability, contains oxygenated groups that enable functionalization with diverse materials, including magnetic nanoparticles, aminopropyl silica, C18, chitosan, ionic liquids, and cyclodextrins, broadening its applicability toward compounds with different characteristics [1]. GO-based materials have been widely employed in sorbent-based miniaturized sample preparation techniques due to their environmentally friendly features. In dispersive pipette extraction (DPX) for pesticide analysis in sugarcane-derived samples [2], a device was assembled using 1000 µL tips, 5 mg of glass wool, and 10 mg of Si@GO-C18. Anchoring GO onto silica provided structural support, prevented particle agglomeration and backpressure, and maintained sorbent dispersion over repeated cycles. A zwitterionic ionic liquid anchored on GO ([VIm+C4SO3−]@GO) was applied in dispersive and non-dispersive techniques, such as dispersive solid-phase microextraction (DSPME) and stir bar sorptive extraction (SBSE). In DSPME, 15 mg of sorbent was vortexed with 1.5 mL of cosmetic sample containing parabens, allowing high sample–sorbent contact and up to six device reuses. In SBSE, 10 mg of [VIm+C4SO3−]@GO was immobilized on glass-encapsulated magnets using epoxy resin, outperforming conventional polydimethylsiloxane (PDMS) bars for triazine herbicides in environmental water and grape juice, with up to six reuses [3–4]. Additionally, two microextraction by packed sorbent (MEPS) configurations were evaluated for pesticide extraction from wine and vegetable samples. The first method utilized a 1 mL polypropylene syringe packed with GO@Si-[VHIm]+PF_6^- (3 mg), resulting in more uniform sorbent beds, lower backpressure, and minimal analyte loss, and could be reused up to six times. The second configuration employed a mini-repackable cartridge coupled to a 500 µL Hamilton syringe, packed with 7 mg of silica anchored to GO and functionalized with chitosan (SiGO@CS). This device showed superior performance compared to traditional silica-GO sorbents for pesticide extraction in tomato and corn samples and could be reused up to 15 times [5]. These results, along with others obtained in our laboratory, demonstrate that GO-based hybrid sorbents can be applied in both dispersive and non-dispersive techniques, and that sorbents can be tailored according to the principles of each extraction method, eliminating the need for complex device.

References

[1] Q. Jiang et al. TrAC, Trends Anal. Chem., 2023, doi:10.1016/j.trac.2023.117283.
[2] T.C. Oliveira, F.M. Lanças, J. Chromatogr. A, 2023, doi:org/10.1016/j.chroma.2022.463690.
[3] A.T. Cardoso, F.M. Lanças, Anal. Chim. Acta, 2025 doi:10.1016/j.aca.2025.343691.
[4] A.T. Cardoso, F.M. Lanças, Michrochem. J., 2025 doi:10.1016/j.microc.2025.114270.
[5] R.O. Martins, F.M Lanças, Adv. Sample Prep., 2024 doi:10.1016/j.sampre.2024.100134

Acknowledgements: This study was financed, in part, by the São Paulo Research Foundation (FAPESP), Brasil (Process Numbers: 2023/06258-1, 2023/07159-7, and 2024/12325-6) CNPq (INCT-ALIM, 406760/2022-5) and CAPES (88887.005608/2024-00, 88887.999341/2024-00).

GRAPHENE-BASED HYBRID SORBENTS IN SAMPLE PREPARATION: 4. DEVELOPMENT AND APPLICATIONS IN ENVIRONMENTAL AND FOOD ANALYSIS

Jussara da Silva Alves*, Alessandra Timóteo Cardoso, Rafael Oliveira Martins, Maria Flávia Assunção Magalhães, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: jussaraalves@usp.br

Graphene-based hybrid sorbents are promising materials for use in microextraction techniques during sample preparation. Their surface modifications can improve selectivity, stability, and compatibility with different matrices. In this study, we summarize selected applications developed by the CROMA group, which utilize graphene-based hybrid sorbents in various microextraction techniques, for a range of analytes and complex matrices. Applications involving graphene oxide-based hybrid sorbents, such as [VHIm]Br, [VIm+C4SO3−], and thiol-functionalized GO (GO-SH), were conducted to extract triazine herbicides from environmental waters and grape juice using stir bar sorptive extraction (SBSE). Graphene oxide–silica functionalized with 1-vinyl-3-hexylimidazolium octane sulfonate (GO@Sil-[VHIm]+OS−) was employed to extract tebuconazole from orange juice by dispersive solid-phase microextraction (DSPME). Multiclass pesticides in Spanish wines were extracted using silica–graphene grafted with ionic liquids through microextraction by packed sorbent (MEPS). Using silica-supported ionic liquids (ILz/Si@GO), selected pesticides were extracted from coffee samples, also with MEPS. Pesticides from sugarcane crops and derived foods were extracted with octadecylsilane endcapped phases using disposable pipette extraction (DPX). Chitosan-based biosorbents (SiGO@CS) were utilized to extract triazoles from fruits using DPX, as well as pesticides (thiamethoxam, atrazine) and antibiotics (ceftiofur, sulfonamide) from food matrices such as corn, tomato, and milk using MEPS. β-Lactam antibiotics in water samples were determined using graphene oxide supported on silica (GO@SiO2) combined with MEPS. In addition, isoflavones from human urine samples were extracted using a β-CD–graphene oxide composite supported on aminopropyl silica (Si@GO@βCD) coupled to a needle-sleeve extraction device for automated SPME. Overall, the applied modifications, including imidazolium ionic liquids, chitosan-based biosorbents, functionalized silica supports, and endcapped phases, as will be shown in the poster, demonstrate the versatility of graphene-based materials. They also highlight the potential of the phases developed by the group to expand sample preparation capabilities.

Acknowledgements: FAPESP [Grants 2017/02147-0; 2017/21984-0; EMU; 2017/21985-6 – EMU; 2023/06258-1; 2023/15675-5]; CNPq [Grants 308843/2019-3 and INCT-ALIM Grant 406760/2022-5]; CAPES [Grant: 88887.999341/2024-00; 88887.005608/2024-00] financed this study.

GRAPHENE-CHITOSAN BIOSORBENT: AN ENVIRONMENTAL MICROEXTRACTION APPROACH FOR THE ASSESSMENT OF PESTICIDES AND ANTIBIOTICS IN FOOD MATRICES

Rafael Oliveira Martins, Maria Flávia Assunção Magalhães*, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brasil

* Corresponding author: mfamag@usp.br

Advances in agricultural and veterinary practices have introduced pesticides and antibiotics into food commodities, raising concerns about their harmful effects on human health. Consequently, innovative microextraction protocols have been developed to enable accurate trace-level analysis through effective clean-up and preconcentration. In this context, microextraction by packed sorbent (MEPS) has demonstrated great potential for the analysis of challenging matrices. Moreover, with the advent of automation, researchers have overcome the limitations of previous laborious MEPS procedures, expanding its applicability. Additionally, the development of bio-based sorbents aligns with the principles of green analytical chemistry (GAC) by promoting the use of enhanced biodegradable materials as alternatives to conventional sorbent phases. In this study, silica-graphene oxide@chitosan (SiGO@CS) was synthesized via an in-situ reaction and employed for MEPS extraction of atrazine and thiamethoxam from corn and tomato samples, respectively, as well as ceftiofur and sulfonamide from milk samples. Characterization assays confirmed the successful modification of the SiGO@CS. Method optimization identified draw/eject and washing cycles as the most significant parameters for pesticide extraction from corn and tomato, while washing cycles were critical for sulfonamide extraction from milk. The method achieved limits of detection (LOD) and quantification (LOQ) ranging from 0.020 to 0.045 μg L^{-1} and 0.045 to 1.0 μg L^{-1} for pesticides, and from 5 to 15 μg L^{-1} and 15 to 20 μg L^{-1} for antibiotics, respectively, with recoveries between 82% and 109%. The manual MEPS protocol was successfully adapted to an automated lab-made platform, offering insights into the balance between analytical performance and environmental impact. Application to regional samples revealed thiamethoxam and atrazine at levels exceeding the recommended daily intake in one tomato and one corn sample. Overall, the use of the novel SiGO@CS biosorbent demonstrated a green, high-performance strategy, reinforcing the potential of bio-based sorbents for both manual and automated microextraction.

Acknowledgements: FAPESP [Grants 2017/02147-0; 2017/21984-0 – EMU; 2017/21985-6 – EMU]; CNPq [Grants 308843/ 2019-3 and INCT-ALIM Grant 406760/2022-5]; CAPES [Grant: 88887.005608/2024-00] financed this study.

GREEN ANALYTICAL CHEMISTRY IN ION CHROMATOGRAPHY: SUSTAINABLE ADVANCES

Jhonatan Faria Costa*[1], José Roberto Miranda Júnior[2], Camila Rodrigues Carneiro[2], Muhammad Alhaji Adamu[2], Moysés Naves Moraes[2], César Augusto Sodré da Silva[2], Eduardo Basílio de Oliveira[2], Jane Sélia Dos Reis Coimbra[2]

[1]Universidade Federal de Viçosa - UFV, Department of Food Technology - MG, Brazil; Instituto Federal do Sudeste de Minas Gerais, Campus Rio Pomba – MG, Brazil

[2]Universidade Federal de Viçosa - UFV, Department of Food Technology - MG, Brazil

* Corresponding author: jhonatan.f.costa@ufv.br

Green analytical chemistry requires methods that promote waste reduction and cost-effectiveness, minimize the use of polluting reagents, and enable simultaneous detection of multiple compounds. Ion chromatography (IC) stands out as a sustainable method, benefiting from advances in the design of efficient suppressors and the miniaturization of equipment. IC uses safe and economical eluents, ensuring reproducibility and waste reduction. In contrast, conventional organic solvents (acetonitrile, methanol, hexane, tetrahydrofuran, phosphate buffers, and acids) demonstrate chromatographic efficiency but are widely avoided due to their high toxicity. Alternative solvents, such as ionic liquids, cyclodextrins, and surfactants, enable the partial replacement of organic solvents with micellar water or aqueous systems; however, they face challenges related to cost and biodegradability. Ion chromatography demonstrates intrinsic alignment with some of the 12 principles of Green Chemistry: (1-2) elimination of waste and optimization of atom economy through direct ion analysis, avoiding derivatization steps; (3-5) replacement of toxic solvents with aqueous eluents and elimination of risks through in situ eluent generation via electrolysis; (6-7) reduction of energy consumption via automation and miniaturization, coupled with the use of renewable resources (deionized water); (11-12) pollution and accident prevention through real-time monitoring and operation in automated closed systems. Therefore, ion chromatography establishes itself as a fundamental pillar of green analytical chemistry, integrating technological innovations that harmonize analytical performance, sustainability, and laboratory safety. Its advances not only meet international green chemistry principles but also set a new paradigm for eco-efficient analyses, particularly in complex matrices. Future perspectives on IC include overcoming the economic and environmental limitations of emerging alternatives and expanding its applications in environmental monitoring and food quality control.

Acknowledgements: CAPES (001), CNPq, and FAPEMIG

HIGH-PERFORMANCE THIN-LAYER CHROMATOGRAPHY WITH EFFECT-DIRECTED ANALYSIS AND MASS SPECTROMETRY FOR THE IDENTIFICATION OF BIOACTIVE METABOLITES IN ANTARCTIC LICHENS

Valentina Parada Haquin[1], Cristian Cordero Pinto[2], Mario Aranda[2], Karem Henríquez-Aedo*[1]

[1]Laboratorio de Biotecnología y Genética de los Alimentos, Departamento de Ciencias Básicas, Facultad de Ciencias, Universidad del Bío-Bío, Chillán, Chile
[2]Laboratorio de Investigación en Fármacos y Alimentos, Departamento de Farmacia, Facultad de Química y Farmacia, Pontificia Universidad Católica de Chile, Santiago, Chile

* Corresponding author: kahenriquez@ubiobio.cl

Antarctic lichens represent a predominant component of the vegetation in the Antarctic region and are unique symbiotic organisms formed by a filamentous fungus (mycobiont) and a photosynthetic partner (photobiont: microalga, cyanobacterium, or both). Their remarkable ability to synthesize exclusive secondary metabolites as an adaptive strategy to extreme environments makes them a valuable reservoir of bioactive compounds with biotechnological relevance. Recent studies have highlighted their antimicrobial, cytotoxic, antioxidant, and antiproliferative properties, suggesting promising applications in the search for therapeutic agents against non-communicable diseases (NCDs), which include cardiovascular, respiratory, neurodegenerative diseases, cancer, and diabetes.

This study aimed to identify bioactive compounds from Antarctic lichens with potential therapeutic activity against NCDs. Five lichen species collected in Antarctica were extracted using solvents of different polarity and analyzed by high-performance thin-layer chromatography combined with effect-directed analysis (HPTLC-EDA). Antioxidant activity and inhibitory effects on acetylcholinesterase, α-glucosidase, and cyclooxygenase-2 were evaluated. Bioactive zones detected on chromatograms were further analyzed and identified by mass spectrometry.

The results revealed that Himantormia lugubris contains hematommic acid, a metabolite exhibiting significant antioxidant activity and inhibitory effects on α-glucosidase and cyclooxygenase-2. These findings highlight Antarctic lichens as a promising source of novel bioactive molecules, providing valuable insights into their potential use in the development of therapeutic strategies against NCDs.

Acknowledgements: This work was supported by project INACH RT28-01, the National Agency of Research and Development (ANID) projects Academy Installation Grant Nº85220091 and FONDEQUIP EQY220018.

HIGH-THROUGHPUT µSPE METHOD FOR THE DETERMINATION OF 131 PESTICIDE RESIDUES IN HUMAN URINE BY UHPLC-MS/MS

Juliana Diniz de Barros Kuntz*[1], Franciele Fátima Machado[1], Igor Franceschi de Souza[1], Gabriel Alexsander Barboza Prates[1], Douglas Andrade[2], Renato Zanella[1], Osmar Damian Prestes[1]

[1]Universidade Federal de Santa Maria
[2]Especialista em Aplicações de Campo, Sciex Brasil

* Corresponding author: juukuntz30@gmail.com

Human biomonitoring (HBM) is a critical tool for assessing exposure to environmental contaminants, particularly pesticides, whose intensive use poses significant risks to public health. Urine is the matrix of choice in HBM studies due to its non-invasive collection, ease of handling, and suitability for determining residues at low concentrations. In this study, a multiresidue method was developed for the determination of pesticide residues in urine samples. Sample preparation was performed using the supported liquid extraction (SLE) technique with Chem Elut S (Agilent Technologies) well plates, followed by LC-MS/MS analysis. The sample preparation protocol involved dilution of 200 µL of urine with ultrapure water, followed by vortexing, and percolation through a Chem Elut S well plate. Analytes were eluted with 2 × 400 µL of ethyl acetate. The eluate was then evaporated under a gentle nitrogen stream, reconstituted in 1 mL of mobile phase, and filtered through a PVDF filter (0.22 µm). Chromatographic separation was achieved using a Kinetex Biphenyl column (100 × 3 mm, 2.6 µm) on a QTRAP® 6500+ LC-MS/MS system (Sciex). The mobile phase consisted of (A) water:methanol (98:2, v/v) and (B) methanol:water (98:2, v/v), both containing 5 mmol L-1 ammonium formate and 0.1% (v/v) formic acid. The injection volume was 5 µL. The method was validated at the spike levels 0.125, 0.250, and 0.500 ng/mL. Analytical curves were linear over the range of 0.025 to 1.0 ng/mL. A total of 131 compounds were validated with limits of quantification (LOQs) of 0.125 ng/mL for 42 compounds, 0.250 ng/mL for 69 compounds, and 0.500 ng/mL for 20 compounds. The method demonstrated satisfactory precision, with relative standard deviation (RSD) values ≤ 30%, and accuracy, with recoveries ranging from 40 to 120%. These results demonstrate that the use of Chem Elut S for sample preparation, combined with the high sensitivity and selectivity of the QTRAP® 6500+ system, effectively minimizes matrix interference and ensures adequate reproducibility, even at very low concentrations. Consequently, this method represents a reliable and robust tool for human biomonitoring studies, enabling the comprehensive assessment of exposure to multi-class pesticides across various environmental and occupational settings.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS e UFSM.

HS-GC-MS AND PLS-DA TO ASSESS VOCS FROM CERRADO PLANTS AND QUALITY OF COMMERCIAL PERFUMES

DAYANE CRISTINA DA COSTA*[1], Nelson Roberto Antoniosi FIlho[2]

[1]Universidade Federal de Goiás
[2]Universidade Federal de Goias

* Corresponding author: dayanecristina_3@hotmail.com

The fragrance and flavor market constitutes a rapidly expanding multibillion-dollar sector and a continuous source of scientific development and innovation. Nevertheless, products derived from Brazilian biodiversity remain scarce within this industry. Moreover, no standardized analytical framework currently exists for assessing the quality and aromatic families of commercial perfumes and essences. This study aimed to characterize the volatile organic compounds (VOCs) of leaves, flowers, and fruits from endemic Cerrado species - Handroanthus impetiginosus (purple ipê), Handroanthus heptaphyllus (pink ipê), Dipteryx alata (barú), Spondias dulcis (cajá-manga), and Eugenia dysenterica (cagaita) - using HS-GC-MS, and to evaluate the quality of commercial perfume and essence formulations. Gas chromatography coupled with mass spectrometry was applied to formulation ingredients. At the same time, PLS-DA served as a chemometric tool to discriminate between aromatic classes and differentiate between expired and non-expired products. Leaves of cagaita (E. dysenterica) and leaves and bark of barú (D. alata) exhibited VOCs commonly found in commercial perfume ingredients, such as limonene, linalool, eucalyptol, benzaldehyde, and pinene. All analyzed plants contained terpenoid compounds, including elemene, carene, copaene, muurolene, germacrene, bicyclogermacrene, aromadendrene, styrene, farnesene, and humulene, as well as aldehydes such as nonanal and hexanal. The fruit of cajá-manga (S. dulcis) also presented esters such as ethyl acetate, ethyl butanoate, ethyl sorbate, ethyl tiglate, and ethyl butenoate, in addition to aldehydes (heptanal, 2-octenal, 2-hexenal), terpenes (pinene, terpinene), and acetoin. Commercial perfumes were found to contain compounds of toxicological concern, including diethyl phthalate (DEP), musk 36A, and musk xylene. Notably, commercial essences labeled as “ipê,” “cajá flower,” and “pequi flower” exhibited high DEP contents (37.47%, 67.92%, and 36.84%, respectively). Perfumes classified as herbal, floral, woody, oriental, as well as expired and non-expired, were satisfactorily discriminated with positive Q^2 values. Overall, the findings highlight the urgent need for stricter quality control in commercial perfumes and essences to ensure that their formulations contain only ingredients deemed fully safe for topical application.

Acknowledgements: IQ-UFG, ANP, FUNAPE e INCT-ALIM

IDENTIFICAÇÃO DO PERFIL VOLÁTIL DE KOMBUCHAS COMERCIAIS SABORIZADAS POR SPME/GC-MS

Maria Aparecida Liberato Milhome*[1], Maria Edlane Almeida da Silva[1], Hilton César Rodrigues Magalhães[2], Fernando Mauro Lanças[2]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará-IFCE
[2]Instituto de Química de São Carlos, Universidade de São Paulo, IQSC-USP

* Corresponding author: maria.milhome@ifce.edu.br

A kombucha consiste em uma bebida fermentada produzida a partir da infusão das folhas da planta Camellia sinensis adoçada e pela ação da cultura simbiótica de bactérias e leveduras (SCOBY). Este processo é responsável pela conversão dos açúcares e outros elementos em ácidos orgânicos, álcoois, ésteres e aldeídos, relacionados ao perfil volátil característico da bebida. A kombucha pode ser saborizada com diversos substratos, como as frutas. O objetivo do trabalho foi caracterizar o perfil de compostos voláteis (CVs) em kombuchas comerciais saborizadas com hibisco e maracujá (KHMA) e hibisco com morango (KHMO). Os CVs foram extraídos usando a técnica de microextração em fase sólida (SPME) com fibra CAR-PDMS (85 µm), durante 15 min equilíbrio e 30 min exposição (à 60 ºC, sob agitação,). Em seguida, os CVs foram dessorvidos (250 °C, 10 min) no sistema de injeção do GC-MS (Shimadzu Q2010 Ultra). A identificação dos CVs foi realizada através das bibliotecas NIST e WILEY. O Índice de Retenção de Kovats (IRkovats) foi calculado, a partir de uma mistura padrão de n-alcanos, considerando a concordância entre valores experimentais e de referência. Os resultados mostraram a identificação de 65 CVs em KHMA e 35 CVs em KHMO, sendo 20 picos comum entre as amostras. Os grupos químicos predominantes em KHMA, foram: terpenos (40%), ésteres (≈33,85%) e álcoois (≈16,92%). Enquanto em KHMO foram: ésteres (≈51,43%), álcoois (20%) e terpenos (≈11,43%). Em relação aos componentes majoritários (área do pico >1%) para KHMA foram: 2-isopropil-5-metilcicloexano (≈11,48%), responsável pelo odor mentolado; acetato de 1-feniletila (≈10,34%), que atribui o odor fresco, com notas florais suaves e ácidos e um fundo terroso; hexanoato de etila (≈7,70%), responsável pelo odor do maracujá amarelo e butanoato de etila (≈4,65%), associado ao odor frutado. Já em KHMO os CVs majoritários foram: octanoato de etila (≈13,77%), responsável por atribuir notas frutadas e doces a bebida; decanoato de etila (≈6,14%), conferindo notas frutadas e alcoólicas; álcool isoamílico (≈5,53%), atribuído ao odor fermentativo e álcool fenetílico (≈5,30%), contribuindo para o odor floral. Os resultados indicam que, apesar de possuírem uma base fermentativa semelhante e apresentarem 20 CVs em comum, os perfis voláteis se diferenciam pela predominância dos compostos associados à saborização.

Acknowledgements: INCT-ALIM (CNPQ), PRAPG (CAPES), FUNCAP

IDENTIFICAÇÃO E MONITORAMENTO DE COMPOSTOS ORGÂNICOS VOLÁTEIS EM BEBIDA PROBIÓTICA DE FRUTA TROPICAL DURANTE O ARMAZENAMENTO POR CROMATOGRAFIA GASOSA ACOPLADA À ESPECTROMETRIA DE MASSAS

Amélia Ruth Nascimento Lima*[1], Antônia Carlota de Souza Lima[1], Elisabeth Mariano Batista[1], Hélio Oliveira do Nascimento[2], Ronaldo Ferreira do Nascimento[3], Luciana de Siqueira Oliveira[1]

[1]Departamento de Engenharia de Alimentos, Universidade Federal do Ceará
[2]Instituto Federal de Educação, Ciência e Tecnologia do Ceará, IFCE Campus Crateús
[3]Departamento de Química Analítica e Físico-Química, Universidade Federal do Ceará

* Corresponding author: ameliaruth.lima@gmail.com

Bebidas de frutas apresentam perfis aromáticos complexos devido a diversos compostos orgânicos voláteis (COVs) que influenciam diretamente na sua aceitação sensorial. Este estudo objetivou identificar e monitorar o perfil de compostos voláteis de uma bebida mista probiótica durante o armazenamento sob refrigeração. As bebidas foram elaboradas homogeneizando em água potável as polpas de caju, cajá-umbu e manga (11 °Brix), sendo pasteurizadas e envasadas em garrafas de vidro esterilizadas. Em seguida, Lactobacillus rhamnosus GG (10^{10} UFC/g) foram inoculados e as amostras armazenadas a 4 °C por 30 dias. O perfil dos voláteis foi analisado aos 0, 15 e 30 dias, realizando microextração em fase sólida no modo headspace, e analisado por cromatografia gasosa acoplada à espectrometria de massas (HS-SPME/GC–MS). Foram identificados 19 compostos voláteis majoritários, incluindo álcoois, terpenos, terpenoides, ácidos, ésteres, cetonas e hidrocarbonetos. Ácido benzóico, assim como, etanol e linalol estiveram presentes durante todo o armazenamento, os quais conferem aromas alcoólico e floral. A presença de terpenos (β-mirceno, 3-careno, α-pineno e cariofileno) atribuíram notas cítricas, herbais e amadeiradas. Os compostos limoneno-6-ol pivalato, hidrocarbonetos e benzofenona foram detectados apenas no início do armazenamento, enquanto os ésteres acetato de etila e butanoato de etila nos dias 15 e 30, os quais contribuem com aromas picante e frutado. Conclui-se que a diversidade dos compostos voláteis observadas ao longo do tempo, provavelmente devido a atividade metabólica residual, sugere potencial para desenvolvimento de bebidas funcionais com perfis aromáticos diferenciados.

Acknowledgements: Os autores expressam sua gratidão à Universidade Federal do Ceará e ao Instituto Nacional de Ciência e Tecnologia em Química Analítica de Alimentos.

IDENTIFICAÇÃO E QUANTIFICAÇÃO DE ÁCIDOS GRAXOS (AG) EM AMOSTRAS DE ÓLEO VEGETAL COMESTÍVEL (OVC) COMERCIALIZADAS NO ESTADO DE MINAS GERAIS ENTRE OS ANOS DE 2018 E 2023

Shirley S. S. Chaves*, Mariem R. R. Cunha, Fabiano Narciso Paschoal, Maria de Fátima Gomides

Fundação Ezequiel Dias

* Corresponding author: shirley.chaves@funed.mg.gov.br

Estudos demonstram que a ingestão de gorduras insaturadas exerce um efeito positivo sobre a incidência de certos agravos à saúde enquanto efeitos negativos são observados pela ingestão de gorduras saturadas. Esses conhecimentos motivaram uma evolução nas recomendações e normas sobre o consumo de AG. Parte dessas normas relaciona-se ao perfil de AG presentes nos OVC. O cumprimento da regulamentação dos OVC se faz necessário com vistas a identificar e quantificar os AG presentes no alimento, dificultando, principalmente, as fraudes. O objetivo deste trabalho foi avaliar, identificar e quantificar AG em amostras de OVC comercializadas no estado de Minas Gerais (MG) entre os anos de 2018 e 2023. Foram coletadas 32 amostras fiscais de OVC pela VISA de MG no período citado, das quais 25 foram azeites de oliva e 07, os óleos de uso culinário, dentre eles, os de soja, canola, milho e girassol. Em relação à identificação e quantificação dos AG, o método de preparação e extração dos ésteres metílicos adotado foi uma adaptação daquele proposto por Hartman e Lago. Os padrões de referência utilizados foram o F.A.M.E. MIX 37 e o padrão interno (PI) do ácido nonadecanóico que foram, posteriormente, analisados por cromatografia gasosa acoplada ao detector de ionização por chama (CG/DIC). Das amostras avaliadas, apenas 07 apresentaram teores adequados de AG recomendados pelas legislações vigentes e 25 apresentaram inconformidades em relação ao perfil de AG, o que representa 78 % desse total. Dentre os resultados insatisfatórios, 100 % dos óleos de uso culinário estavam em desacordo em relação aos seus principais constituintes de ω-3, ω-6 e ω-9, cujos teores estavam abaixo daqueles recomendados pela IN 49/2006 (BRASIL, 2006). Para o mesmo período avaliado, as outras 18 amostras inconformes representam 72 % em relação ao total de amostras de azeite, estando os resultados em desacordo com a IN 01/2012 (BRASIL, 2012). Os resultados apresentados demonstram a importância do monitoramento constante e contínuo da composição de AG nos OVC, impedindo adulterações que possam lesar o consumidor, tornando-se necessário, por parte dos fabricantes, a observância dos dispostos nas legislações vigentes, fazendo-se cumprir a lei. Além disso, esses nutrientes são de extrema importância para a saúde, tendo em vista suas funções metabólicas relacionadas à prevenção de doenças crônicas não transmissíveis.

IMPACT OF SAMPLE PREPARATION IN GC-MS ANALYSIS OF EARWAX COMPOUNDS AND ITS IMPLICATIONS FOR METABOLOMIC STUDIES

Ana Luiza Reis Rodrigues da Cunha*, Dayane Cristina da Costa, Nelson Roberto Antoniosi Filho

Universidade Federal de Goiás - UFG

* Corresponding author: analuizarrcunha@gmail.com

Clinical metabolomics is a research area with high growth in recent years. Despite intrinsic and extrinsic aspects of the individual influencing the metabolome chemical composition, other factors such as biological sample type, sample preparation process, and analytical platform can drastically alter the chemical fraction investigated in a metabolomic study. Therefore, including aspects that are few described in literature, for instance, the use of non-conventional biomatrices, is a promising approach to improving the knowledge about how a pathological process alters an organism. In this sense, earwax or cerumen, a non-conventional biomatrix with a complex chemical composition, has shown great potential in clinical metabolomics research for the discovery of pathological biomarkers for disease process in humans and other animals. However, despite this potential, there are few studies focused on the importance of experimental aspects on the chemical coverage analyzed by chromatographic techniques. Thus, this study aimed to investigate factors in the earwax sample preparation process and their influence on the chemical composition analyzed by GC-MS. The experimental steps included the solvent addition in the sample, vortex agitation, extract centrifugation, extract filtration, internal standard addition, and chromatographic analysis. The experiments were conducted on a GC-MS QP-2010 ultra (Shimadzu, Japan), with a DB-5MS column (25m×0,25mm×0,25µm). The optimization of the number of extracted compounds was carried out by a fractional factorial design 23-1 with a simplex-centroid design. The factors optimized were the sample agitation time in the solvent, the incubation temperature, the number of extraction cycles, and the solvent composition (methanol, acetone, and dichloromethane). Through the Analysis of Variance (ANOVA, p-value < 0.05), we estimate that the only significant factor for all compositions of solvent was the number of extraction cycles, except for the experiments conducted in methanol. Moreover, it was determined that all compositions of solvents were significant for the response. In general, in the earwax extracts we found metabolites from different chemical class, such as fatty acids, alcohols, steroids, and esters, in which integrate biochemical pathways such as steroids and fatty acids biosynthesis, and glycerolipids metabolism, highlighting the importance of investigate the influence of the sample preparation process on the chemical profiling analyzed by GC-MS for a non-conventional biomatrix like earwax.

Acknowledgements: CAPES, PPGQ-UFG, ANP, FUNAPE, and INCT-ALIM

IMPACTO DO ULTRASSOM DE ALTA INTENSIDADE NOS COMPOSTOS FENÓLICOS DA POLPA DE Passiflora edulis Sims QUANTIFICADOS POR HPLC-DAD

Lorena Santos de Almeida[1], Luciano de Almeida Albuquerque*[1], Fernanda Pitta Teixeira[1], Alini Tinoco Fricks[1], Fábio de Souza Dias3[2], Jefferson da Silva Santos[1], Marcelo Silva Bomfim Júnior[1], João Victor Ferreira Lima[1], Larissa da Silveira Ferreira[1], Bruna Louise de Moura Pita[1], Camila de Almeida Moreira[1]

[1]Faculdade de Farmácia, Universidade Federal da Bahia (UFBA)
[2]Faculdade de Química, Universidade Federal da Bahia (UFBA)

* Corresponding author: bioalbuquerque@gmail.com

O maracujá-amarelo (Passiflora edulis Sims), fruta nativa do Brasil, é amplamente valorizado por suas propriedades antioxidantes, atribuídas principalmente à presença de compostos fenólicos em sua composição. Assim, a adoção de estratégias inovadoras de processamento, como o uso de ultrassom, é relevante para a agroindústria, uma vez que pode contribuir para a preservação da estabilidade físico-química e funcional da polpa. Portanto, o objetivo desse estudo foi avaliar a influência do processamento ultrassom no perfil de compostos fenólicos da polpa de maracujá-amarelo. Amostras de polpa foram submetidas ao US (SONICS VIBRA-CELL, VCX 500), durante 5 minutos, de forma pulsada (30s on/off), em amplitude de 50%. Foram conduzidos tratamento com amostras em banho de gelo (US-20) e sem banho de gelo (US-60). Para efeito de comparação, amostras foram pasteurizadas a 63°C/30 minutos (PS-63). Amostras não-tratadas (controle) e pós-tratamento foram imediatamente avaliadas quanto aos compostos fenólicos. Para a determinação dos compostos fenólicos, foi preparado um extrato hidroetanólico, o qual foi posteriormente submetido à separação e quantificação por cromatografia líquida de alta eficiência acoplada a detector de arranjo de diodos (HPLC-DAD), seguindo metodologias previamente validadas. As médias foram expressas em µg 100g−1 de peso seco (DW). A comparação entre as médias dos compostos fenólicos quantificados evidenciou alterações dinâmicas. O teor de catequina na polpa não tratada foi de 428,91 ± 0,11 µg 100g−1, conteúdo que aumentou 5,90% e 6,84% após os tratamentos US-60 e US-20, respectivamente, e diminuiu 11,55% após PS-63. Os níveis de ácido vanílico aumentaram em média 5,89% após os tratamentos US-60 e US-20. O nível de ácido siríngico manteve-se após o tratamento US-60, e a média foi 45,43 µg 100g−1. Contudo, diminuiu 72,12% após PS-63. O ácido cafeico apresentou estabilidade entre os tratamentos, com em média 9,63 µg 100g−1. O ácido clorogênico diminuiu de 29,78 µg 100g−1 na polpa não tratada para 25,33 µg 100g−1 após o tratamento PS-63, refletindo uma diminuição de 14,94%. O ácido ferúlico manteve-se estável após os tratamentos US-60 e US-20, e a média foi de 104,43 µg 100g−1, no entanto, houve uma diminuição de 8,24% após PS-63. Conclui-se que o ultrassom foi eficaz na manutenção e extração de compostos fenólicos da polpa, com destaque para o tratamento US-60. Dessa forma, a tecnologia apresenta potencial promissor e, portanto, pode ser uma alternativa sustentável e viável para aplicação na cadeia produtiva da polpa de maracujá.

Acknowledgements: Capes, FAPESB e CNPq

IMPLEMENTAÇÃO DO PROGRAMA DE ENSAIO DE PROFICIÊNCIA EM COMPRIMIDOS DE HIDROCLOROTIAZIDA VISANDO A CONSOLIDAÇÃO DE PRÁTICAS DE QUALIDADE QUE APOIAM A VIGILÂNCIA SANITÁRIA

Maria Luiza Raimundo Azevedo de Oliveira*, Bianca Santos de Oliveira, Tawany Sandy Moraes, Larissa Valentina Teixeira de Almeida, Valery Martinez Jean, Patrícia de Castro Moreira Dias, Soraya de Mendonça Ochs, Mychelle Alves Monteiro

Instituto Nacional de Controle de Qualidade em Saúde (INCQS) – Fundação Oswaldo Cruz (FIOCRUZ)

* Corresponding author: luiza.azevedo@fiocruz.br

O ensaio de proficiência é uma importante ferramenta da qualidade que permite a avaliação da habilidade de diferentes laboratórios em obter resultados analíticos precisos. Esse ensaio possibilita a comparação interlaboratorial na identificação de analitos específicos, através de parâmetros estabelecidos, sendo essencial para programas de controle de qualidade. Além de assegurar a confiabilidade dos resultados, o ensaio de proficiência contribui para o cálculo da incerteza de medição e agrega credibilidade às análises, especialmente no setor farmacêutico no Brasil. A hidroclorotiazida (HCTZ) é um diurético tiazídico amplamente utilizado como tratamento de primeira linha para hipertensão leve a moderada, atuando por meio da inibição da reabsorção de sódio no túbulo contorcido distal. Este estudo objetivou determinar o teor e verificar a uniformidade de massa de comprimidos de HCTZ 25 mg, conforme a monografia da Farmacopeia Brasileira 7ª edição, utilizando HPLC-DAD para quantificação e a norma ISO 13528 para avaliação da homogeneidade. O teste de homogeneidade da massa apresentou média de 130,32 mg, desvio-padrão analítico (□□□□) de 0,62 mg e médias (□□ₓ) de 0,44 mg. Apesar de □□ₓ ultrapassar o limite de 0,39 mg, a baixa variabilidade entre os itens e a incerteza de homogeneidade de 0,036 mg (0,028%) permitiu classificá-lo como suficientemente homogêneo. Para o teor, a média foi 99,92%, com □□ₓ de 1,19%, acima do limite de 0,30%, e incerteza de 1,05%, indicando homogeneidade insuficiente, embora a repetitividade analítica (□□□□ = 0,79%) fosse satisfatória. Conclui-se que o estudo evidenciou que, embora a uniformidade de massa dos comprimidos de hidroclorotiazida 25 mg tenha se mostrado adequada, a variabilidade observada no teor do fármaco indica a necessidade de melhorias nos processos de fabricação, especialmente nas etapas de mistura e compressão. Dessa forma, a implementação do ensaio de proficiência reforça seu papel estratégico na detecção de não conformidades, promovendo maior confiabilidade nos resultados analíticos e contribuindo para a consolidação de práticas de qualidade que apoiam a vigilância sanitária e a segurança em saúde pública.
.

Acknowledgements: Os autores gostariam de agradecer ao INCQS e a ANVISA pelo apoio financeiro e acesso às instalações necessárias para a realização deste projeto.

IMPORTANCIA DO CURSO À DISTÂNCIA “CROMATOGRAFIA – CONCEITOS BÁSICOS” PARA PROFISSIONAIS E ESTUDANTES

Maria de Lourdes Mendes de Souza*, Monalisa Santana Coelho de Jesus

Embrapa Agroindústria de Alimentos

* Corresponding author: marialourdes.m.souza@embrapa.br

O curso “Cromatografia – Conceitos Básicos”, da Embrapa Agroindústria de Alimentos, evidencia a relevância do ensino a distância (EAD) para a democratização do conhecimento científico e técnico. Com mais de 24 mil inscritos e 8 mil concluintes, ampliou o alcance geográfico e a diversidade do público, favoreceu a atualização profissional e estimulou a aplicação dos conteúdos em atividades teóricas e práticas, beneficiando a pesquisa científica e a indústria. Entre os impactos relatados em pesquisa de satisfação destacaram-se: maior segurança técnica, motivação pelo tema e autoconfiança no desenvolvimento de atividades de laboratório e ensino. Os pontos fortes foram: didática, clareza, objetividade, organização do conteúdo e relevância para diferentes áreas. As sugestões foram: inclusão de aulas práticas em vídeo, exemplos de análises cromatográficas e oferta de módulos mais aprofundados. Entre os participantes 80% aplicaram os conhecimentos adquiridos; 70,6% relataram maior segurança no desenvolvimento de atividades; 81,8% registraram aumento da motivação pelo tema; 73% declararam ganho de autoconfiança; 98,9% recomendariam o curso. O curso despertou interesse pela cromatografia e incentivou a busca por formações avançadas. Embora tenha ficado evidente a necessidade de maior aprofundamento, como vídeos demonstrativos e módulos avançados, a avaliação geral foi positiva: mais de 97% dos participantes recomendariam o curso e reconheceram sua relevância para a atuação profissional. O sucesso da iniciativa proporcionou uma capacitação online para pesquisadores de Angola e a publicação de um artigo no 28º Congresso Internacional ABED de Educação a Distância (2023). Conclui-se que cursos como este são ferramentas estratégicas na qualificação de recursos humanos, na integração entre a ciência e o setor produtivo e no estímulo à inovação. Ainda, reforçam a importância da educação digital no desenvolvimento científico e tecnológico. O curso cumpriu seu objetivo de disseminar conceitos básicos de cromatografia, impactando a formação e a prática profissional dos participantes e despertando interesse por capacitações mais aprofundadas. Baseado na demanda a Embrapa produziu outro curso mais aprofundado, acompanhado de um livro para 2025 sobre preparo de amostras para cromatografia.

Acknowledgements: EMBRAPA

IMPORTÂNCIA DO PREPARO DE AMOSTRAS PARA CROMATOGRAFIA

Maria de Lourdes Mendes de Souza*, Monalisa Santana Coelho de Jesus, Marianna Ramos dos Anjos, Paola Ervatti Gama

Embrapa Agroindústria de Alimentos

* Corresponding author: marialourdes.m.souza@embrapa.br

Os alimentos apresentam matrizes complexas, com grande diversidade de componentes (proteínas, lipídios, carboidratos, pigmentos, sais minerais), que podem interferir na separação, detecção e quantificação de analitos como contaminantes, aditivos, resíduos de agrotóxicos ou compostos bioativos. Um preparo adequado permite a extração seletiva dos analitos, a eliminação de interferentes e a concentração das substâncias, tornando a análise mais eficiente e precisa. Além disso, reduz riscos de danos aos equipamentos cromatográficos, melhora a vida útil das colunas cromatográficas e favorece a comparabilidade entre diferentes laboratórios. As técnicas de preparo variam conforme a matriz, o analito e a instrumentação. Assim, o preparo de amostras não deve ser visto apenas como um passo preliminar, mas como etapa determinante para a qualidade, confiabilidade e aplicabilidade dos dados analíticos. No contexto da análise de alimentos, ele possibilita identificar contaminantes, nutrientes e compostos bioativos com maior rigor científico, impactando diretamente a pesquisa, a inovação tecnológica e a segurança alimentar. Atendendo às demandas da avaliação final do curso EAD Cromatografia - Conceitos básicos, onde a necessidade de material mais aprofundado e prático sobre cromatografia foi identificada, a Embrapa iniciou a produção de um novo curso: Preparo de amostras para cromatografia, com lançamento previsto para 2025, acompanhado de um livro de apoio para ampliar e consolidar o aprendizado. Este curso apresentará de forma prática várias técnicas de preparo de amostras para a análise de alimentos por cromatografia líquida de alta eficiência (CLAE) e por cromatografia gasosa (CG). Serão demonstrados métodos clássicos amplamente conhecidos como a extração líquido-líquido e hidrodestilação de óleos essenciais e também abordagens mais recentes, como extração em fase sólida (EFS), microextração em fase sólida (MEFS) e QuEChERS (Quick- rápido, Easy - fácil, Cheap - barato, effective - Eficiente, rugged - robusto e Safety - seguro). Serão demonstradas as vantagens e desvantagens em termos de seletividade, rapidez, menor consumo de solventes e compatibilidade com análises cromatográficas modernas.

Acknowledgements: EMBRAPA

IMPUREZAS CARCINOGÊNICAS DE N-NITROSAMINAS EM MEDICAMENTOS DE PIOGLITAZONA DO BRASIL: DESENVOLVIMENTO E VALIDAÇÃO DE MÉTODO DE QUANTIFICAÇÃO POR CLAE-EM/EM

Soraya de Mendonça Ochs*, Bianca dos Santos de Oliveira, Matheus Nicolau de Souza, Patrícia Condé de Lima, Jayane Valente Meirelles da Silva, André Colonese, Sthefany Maria Libonati Cury, Sibele Guimarães, Mychelle Alves Monteiro

Fundação Oswaldo Cruz

* Corresponding author: soraya.ochs@fiocruz.br

As N-nitrosaminas (NA) são impurezas de elevado potencial carcinogênico e teratogênico, têm sido motivo de preocupação para a indústria farmacêutica e agências reguladoras em vários países nos últimos anos. Elas podem ser formadas em diversas etapas do processo de produção de um medicamento, principalmente se existem precursores amina ou nitrito envolvidos. Diante deste cenário, a ANVISA estabeleceu limites de ingestão aceitáveis de NA em medicamentos e criou o Programa de Monitoramento de N-Nitrosaminas em Medicamentos em parceria com o Instituto Nacional de Controle de Qualidade em Saúde da Fiocruz para possibilitar a adoção de medidas sanitárias. A pioglitazona é um sensibilizador de insulina amplamente utilizado no que já se considera uma epidemia de diabetes mellitus, e que também requer monitoramento quanto à presença dessas impurezas. Por esta razão, pioglitazona foi selecionado para participar do Programa de Monitoramento. Este trabalho tem o objetivo de desenvolver e validar método de quantificação de seis NA (NDMA, NDEA, NDIPA, NDBA, NEIPA e NMBA) por CLAE-EM/EM em medicamentos de Pioglitazona. O espectrômetro de massas com interface APCI em modo de ionização positiva foi empregado em modo de monitoramento de reações múltiplas. Metanol e água foram usados para extração de NA dos comprimidos de pioglitazona, etapas de agitação por ultrassom e centrifugação foram empregados no método. O método apresentou boa linearidade, recuperações de 90,6–98,6% e limites de quantificação de 556 $\mu g \cdot kg^{-1}$ (NDMA e NMBA) e 222 $\mu g \cdot kg^{-1}$ (demais NA), em conformidade com a RDC nº 677/2022. O método analítico foi aplicado com confiabilidade na determinação de impurezas de NA como parte do Programa de Monitoramento da Anvisa em 2 insumos farmacêuticos ativos e 8 medicamentos de pioglitazona de diferentes marcas comercializadas no Brasil. Com base nos critérios de limite de aceitação de NA em medicamentos, todas as amostras atenderam aos níveis aceitáveis de N-nitrosaminas. Esses resultados reforçam a importância de Programas de Monitoramento como estratégia de proteção à Saúde Pública e garantia da qualidade, eficácia e segurança de medicamentos.

Acknowledgements: Anvisa, Fiocruz.

Increased Productivity of Chiral Separation in Semi-preparative Scale by SFC and Application to Structural Analysis of Fractionated Samples by CD Spectrometer

Renato Orsino*[1], Satoe Iijima[2], Keijin Iwaya[2], Takuya Nakamura[2], Yoshiro Kondo[2], Satoko Suzuki[2], Kengo Yoshida[2]

[1]JASCO do Brasil
[2]JASCO Corporation

* Corresponding author: rorsino@jasco.com.br

The means of generating enantiomers in chiral substances can be broadly classified into asymmetric synthesis, crystallization, enzymatic reactions, and optical resolution by chromatography. Among these, optical resolution by normal-phase HPLC using a chiral stationary phase has long been used in a wide range of fields, such as pharmaceuticals, agrochemicals, natural products, biomolecules, and functional materials, because it is cost-effective. Recently, chiral preparative chromatography using supercritical fluid chromatography (SFC), which is capable of higher speed and separation than LC, has also attracted attention as an efficient enantiomer generation method, especially in the pharmaceutical field. In SFC, supercritical carbon dioxide (CO2) is mainly used as the mobile phase, and since it has a similar solvent polarity as hexane, it can be easily transferred from normal-phase HPLC conditions. Preparative SFC also has advantages in the post-handling of the fractionation. Removal of mobile phase from fractions is easy because the main solvent, which is CO2, evaporates by itself under atmospheric pressure and room temperature.

On the other hand, nuclear magnetic resonance (NMR), X-ray diffraction (XRD), electron circular dichroism (ECD), and vibrational circular dichroism (VCD) are commonly used for the qualitative and structural analysis of enantiomers in chiral substances. These analyses typically require sample amounts from a few mg to 100 mg.

In this study, bromuconazole, a pesticide with two asymmetric carbons, was separated into four isomeric peaks on a 20 mmI.D. chiral column and fractionated using a semi-preparative SFC system. This system has been equipped with a stacked injection function that can improve the yield per hour and a fraction unit that can handle large volume collection by repeated injection.

The fractionation results by semi-preparative SFC were compared with those of a semi-preparative LC system using the same column in terms of analysis time, solvent consumption, etc. Once the solvent in fractionated isomeric peaks was removed, they were applied to ECD and VCD spectral measurements. These experimental spectra were compared with theoretical spectra obtained by computational chemistry to finally determine the absolute configuration of each isomer. This work was previously presented as a poster at the Chirality 2025, held in New York, July 2025.

Influence of extraction method on the fatty acid profile of co-products from the olive oil chain

Cristierry Salort Ferreira, Isabel de Oliveira Silva, Pedro Minasi Brandão, Carla Pereira Wenderroschs Gomes, Maria Vitoria Fonseca, Yuri Conte, Luiz Henrique Han, Marcelo de Paula Campos, Anelise Christ-Ribeiro

Universidade Federal do Rio Grande

The olive oil value chain generates co-products such as olive pomace and olive leaves (Olea europaea L.). Traditionally underutilized, these materials represent a strategic opportunity within the circular bioeconomy. Valorizing these side streams through compositional characterization makes it possible to transform residues into functional ingredients, reducing waste, diversifying raw material sources, and adding value to the olive sector. In this context, the fatty acid profile is a core analytical axis. Beyond “how much,” the “how” of measurement matters: different lipid extraction methods can bias the apparent profile of the oil fraction by differentially recovering lipid classes and fatty acids with greater or lesser polarity/volatility. Therefore, comparing classic extraction protocols—Bligh & Dyer, Folch, and Soxhlet—combined with methyl ester analysis by gas chromatography with flame ionization detection (GC-FID) provides a robust and comparable view of the system. The fatty acid profiles of olive leaves and pomace show a predominance of monounsaturated fatty acids (MUFA), with oleic acid (C18:1) as the major component. In leaves, C18:1 ranged from 60.51% (Soxhlet) to 66.38% (Folch), with Bligh & Dyer at 62.84%, whereas in pomace Folch and Soxhlet yielded values close to 58% (58.05–58.25%). Pomace exhibited higher saturated fatty acids (SFA), especially palmitic acid (C16:0), reaching 22.28% (Folch) and 21.00% (Soxhlet), compared with 16.27–19.69% in leaves; stearic acid (C18:0) was also higher in pomace (2.49–3.00%) than in leaves (1.68–2.30%). Among the polyunsaturated fatty acids (PUFA), linoleic acid (C18:2, n-6) remained stable in leaves (~11.92–12.33%) regardless of method but was lower in pomace (~9.81–10.12% in Folch/Soxhlet). Linolenic acid (C18:3, n-3) appeared at low levels in both matrices (~0.47–0.62%). Detection of long-chain PUFA (LC-PUFA) was sporadic: in leaves, EPA and DHA appeared in trace amounts, with Soxhlet indicating slightly higher values (EPA 0.794%; DHA 1.032%) than Bligh and Folch; in pomace, DHA ranged from 0.598% to 0.702%, with no EPA reported, in addition to C20:2 between 1.116% and 3.384%. In summary, Folch provides a consistent, more oleic snapshot for leaves; Soxhlet tends to enhance detection of minor components (including long-chain PUFA); and in pomace, the higher palmitic levels suggest greater oxidative stability.

Acknowledgements: CAPES and CNPq

INFLUENCE OF FAT REMOVAL ON THE QUANTIFICATION OF BIOACTIVE AMINES IN DARK CHOCOLATE BY HPLC-FLD

Maria Beatriz Abreu Gloria*[1], Valterney L. Deus[1], Ederlan S. Ferreira[2]

[1]UFMG
[2]UFBA

* Corresponding author: mbeatriz.gloria@gmail.com

Chocolate is rich in bioactive amines. Some amines are neurotransmitters (tryptamine, serotonin, phenylethylamine, agmatine), and others are antioxidants (spermidine, spermine, tryptamine). Therefore, their presence can warrant functional potential and add value to chocolate. On the other hand, some amines are indices of quality (putrescine, cadaverine, histamine, tyramine), reflecting the quality and safety of the chocolate. In this context, reliable methods for the analysis of amines in chocolate are needed. The method of choice for the analysis of amines in food is ion-pair HPLC separation, post-column derivatization with o-phthalaldehyde, and fluorimetric detection. Amines are extracted from the matrix with 5% trichloroacetic acid (TCA). As chocolate is rich in fat, the objective of this study was to investigate whether fat removal is needed prior to amine extraction. Fat was removed with petroleum ether (30 mL/10 g): the mixture was shaken for 5 min in a vortex, centrifuged at 6000 × g for 15 min, and the supernatant was removed. Afterward, amines were extracted from samples with and without fat removal with 5% TCA. The experiments were undertaken in triplicate. Overall, five amines were detected in the samples: spermidine, putrescine, tryptamine, tyramine, and phenylethylamine. The defatted sample had a cleaner and more stable chromatography baseline. However, total amines were significantly lower in the samples with fat removal (Tukey test, p

Acknowledgements: Acknowledgements: We acknowledge the support from INCT-Alim (CNPq 406760/2022-5), CAPES (001), FAPEMIG, and CNPq (306124/2025-4).

INFLUÊNCIA DO CARBONATO DE CÁLCIO NO PERFIL DE PIRÓLISE DE MICROPLÁSTICOS ANALISADOS POR PY-GC/MS

Maria Rosa de Moraes*, Rafaela Prata, Naiara Mariana Fiori Monteiro Sampaio, Matheus Coutinho Gazolla

CNPEM – Centro Nacional de Pesquisa em Energia e Materiais

* Corresponding author: maria.moraes@lnbr.cnpem.br

A poluição por microplásticos representa um dos principais desafios ambientais da atualidade, dada a sua ampla dispersão em ecossistemas e potenciais riscos à saúde humana e ambiental. Essa problemática tem impulsionado o desenvolvimento de metodologias analíticas robustas e minimamente confiáveis para a identificação e quantificação desses contaminantes. Nesse contexto, a pirólise acoplada à cromatografia gasosa e espectrometria de massas (Py-CG/MS) tem se consolidado como uma ferramenta de destaque, ao possibilitar a decomposição térmica dos polímeros e a detecção de fragmentos característicos de cada tipo de microplástico. Entre os polímeros mais recorrentes destacam-se o politereftalato de etileno (PET), o polipropileno (PP), o policloreto de vinila (PVC) e os polietilenos de alta (HDPE) e baixa densidade (LDPE), amplamente utilizados em embalagens e produtos de consumo. Como parte do desenvolvimento analítico, foi avaliada a aplicação do carbonato de cálcio (CaCO3) como diluente, estratégia que se mostrou vantajosa por minimizar erros associados à pesagem de pequenas massas e consequentemente reduzir erros sistemáticos na preparação das curvas de calibração. No entanto, por não ser um material inerte, o $CaCO_3$ pode exercer efeito catalítico, resultando em modificações significativas no perfil de pirólise. Essa dualidade reforça a necessidade de uma avaliação experimental criteriosa de sua influência nos resultados obtidos. As análises evidenciaram que, para os polímeros PP, PVC, HDPE e LDPE não houve mudanças significativas na presença ou ausência do diluente. Entretanto, para o polímero PET verificou-se um perfil de pirólise diferente, com a formação da benzofenona na presença de CaCO3, atribuída ao seu efeito catalítico. Assim, embora o uso do CaCO3 como diluente possa contribuir para maior precisão na preparação das curvas de calibração, sua aplicação requer cautela, uma vez que pode induzir modificações no perfil de pirólise de determinados polímeros.

Acknowledgements: CNPEM

INNOVATIVE APPROACH FOR QUANTIFYING HORMONE RELEASE FROM SLUDGE BY ROTATING DISK EXTRACTION AND SOLID-PHASE MICROEXTRACTION

Jhon Jairo Rios Acevedo*[1], Danna Buitrago Hoyos[1], Mateo Martinez Valencia[2], Milton Rosero Moreano[3]

[1]Universidad Santiago de Cali
[2]Universidad Santiago de cali
[3]Universidad de Caldas

* Corresponding author: jhon.rios04@usc.edu.co

The hormones have been shown high disruption endocrine activity. Nowadays these compounds are considered an emergent pollutants due to high use and abuse as controlling for pregnancy the first one and as preservative and antimicrobial agents the second one.
In the wastewater treatment plant (WWTP) some of these low polar emergent compounds are settled with the sludge due to it high porosity and well known sorption capacity. These properties are verified when these analytes are released to environment, by requesting a hard evaluation about their toxicity in the aqueous media. For this reason are high important issue to known in this kind of sample about the leaching fraction of these pollutants.
Some works in our group have been leading to analyze the leaching fraction in the sludge of WWTP with special interesting in polychlorinated biphenyls PCBs4, and triclosan. In the first one case the developed method has implicated the accomplish of RDSE in reverse mode and the SPME for sludge of WWTP, and the second one was modified for analyze the triclosan in sludge of hospital WWTP by using the assembly RDSE in reverse mode with SDME.
Actually, the method used for analysis of the toxicity characteristic leaching procedure for micro-pollutants (organic and inorganic) in waste and solid samples require more time, more reagents, more steps and the processes related with sampling and analysis are separately. For to develop this study, the first step was the sampling sludge from hospital WWTP in dry bed sludge stage, then the sample was dried to 100 ºC during 45 min. Then the sludge sample was grounded to mesh 50 for it homogenization. From sieved sample was weighted 40 mg and packed into the rotating disk cavity. the rotating disk with the waste sample has been leached during 2 hours, allowing release the four (4) target compounds (17-β-Estradiol, 17-α-Ethinylestradiol, Estrone, Estriol, was extracted by direct immersion SPME microextraction with in-drop derivatization (MSTFA) followed by GC - MS analysis.
This work has been proposed a good approach related to Fiber derivatization, and a novel, simple, eco-efficient method for the leaching fraction analysis of hormones in waste samples.

Acknowledgements: The authors would like to thank the General Directorate of Research (Dirección General de Investigaciones, DGI) of Universidad Santiago de Cali for the support provided during the development of this work. This study was made possible thanks to the funding from DGI under project 939-621122-051.

Integrated LPGC-MS/MS and UHPLC-MS/MS Approaches for Pesticide Multiresidue Detection in Citrus - Impact on Huanglongbing Management

Yuri Limeira Freire, Luiza Tiemi Morikawa Shiose, Graziela Cristina Rossi Moura Andrade, Claudia Maria Barbosa, Kleber Ribeiro Dutra, Sergio Henrique Monteiro*

Pesticide Residue Laboratory, Reference Laboratory for Residues and Contaminants – Instituto Biológico, São Paulo, Brazil

* Corresponding author: sergio.monteiro@sp.gov.br

Greening, also known as Huanglongbing (HLB), is one of the most destructive diseases affecting citrus production, especially oranges. This bacterial disease is transmitted by insect vectors, mainly Diaphorina citri, and has proven to be a significant threat to the global citrus industry. Since chemical control is the primary method used for managing the insect vector, constant monitoring is required to ensure safe food and compliance with regulations. During the study, 74 citrus samples, mainly oranges, were analyzed. Sample preparation was performed using the QuEChERS method and analyzed by ultra-performance liquid chromatography (UPLC-MS/MS) using the Vanquish/TSQ Quantis Plus system, and by low-pressure gas chromatography (LPGC-MS/MS) with the Agilent 6890 A GC / 7000 system, both coupled to triple quadrupole mass spectrometers. In UPLC-MS/MS, a Thermo Accucor aQ C18 column (2.1 × 100 mm, 6 µm) was used. The mobile phase consisted of 2% methanol in water (A) and 2% water in methanol (B), both with 5 mM ammonium formate and 0.1% formic acid. The elution program was as follows: 0–1 min with 2% B, 1–2 min gradient to 50% B, 2–9 min gradient to 98% B, 9–12 min held at 98% B, and 12.1–15 min re-equilibrated to 2% B, with a flow rate of 0.3 mL/min and an injection volume of 10 µL. The column oven was maintained at 25 °C. Ionization was performed by electrospray in both MRM positive and negative modes. In LPGC-MS/MS, low-pressure columns were used (Rtx-5ms 15 m × 0.53 mm ID × 1.00 µm analytical column, 1 m × 0.53 mm ID integrated transfer line, and 5 m × 0.18 mm ID Hydroguard restrictor). The oven program started at 75 °C, held for 0.5 minutes, followed by an increase to 250 °C at 30 °C/min, and then by 10 °C/min until reaching 310 °C, maintained for 1.67 minutes. The total run time was only 14 minutes. Detection was carried out with a triple quadrupole mass spectrometer operated in dMRM mode with electron impact at 70 eV. Both liquid and gas chromatography systems were optimized for maximum sensitivity and selectivity, allowing for a scope of 272 analytes. Among the total analyzed, 25 samples (32.8%) were considered non-compliant, with three exceeding the MRLs for the pyrethroid insecticides permethrin and bifenthrin. Furthermore, 81% of the samples showed the presence of at least five different analytes. Our data was compared with previous monitoring results, and a significant increase in the amount of residues in the samples was observed, most likely related to HLB control.

Acknowledgements: FAPESP Processo: 2022/01101-4; CNPq INCT – ALIM / PIBIC

ION CHROMATOGRAPHY COUPLES WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (IC-ICP-MS): A POWERFUL TOOL FOR CHROMIUM SPECIATION IN DIFFERENT TYPES OF WATER

Gabriel Gosling Stollar, Naomi Akiba, Valeska Meirelles, Marcos Alves dos Santos*

Nova Analítica Importação e Exportação LTDA

* Corresponding author: marcos.santos@novanalitica.com.br

Chromium can be found in six different oxidation states, with trivalent chromium (Cr^{3+}) and hexavalent chromium (Cr^{6+}) being the two main valence states present in the environment. Cr^{3+} exhibits low toxicity and, at low concentrations, can act as an essential micronutrient for certain biota, whereas Cr^{6+} is extremely toxic due to its high solubility, which allows it to penetrate human cell membranes, leading to mutagenic and carcinogenic effects. Brazilian legislation, such as CONAMA Resolutions No. 357/2005 and 430/2010, and Ordinance GM/MS No. 888/2021, establish maximum limits for different types of water, ranging from 0.05 ppm for freshwater and drinking water to 1.10 ppm for saline, brackish, and effluent waters. Performing speciation is of utmost importance to understand the toxicological impacts on the environment and on human health. The most efficient method for chromium speciation is the hyphenation of ion chromatography (IC) with inductively coupled plasma mass spectrometry (ICP-MS), and to evaluate these two chromium species, three groups of water samples were investigated: three drinking water samples (Group 1) and three seawater samples (Group 2) from different regions of Brazil, as well as three bottled mineral water samples (Group 3) from different brands. For the analyses, an INUVION IC system and an iCAP RQplus ICP-MS, both from Thermo Scientific, were used with the following conditions: mobile phase of 0.40 M nitric acid at a flow rate of 0.40 $mL \cdot min^{-1}$; an IonPac AG7 column (50.0 × 4.00 mm); an injection volume of 25.0 µL; and detection by ICP-MS equipped with a Micromist nebulizer, a quartz spray chamber, and an injector center tube (ID 2.50 mm), connected to a sampling and skimmer cone interface. Plasma power was set at 1550 W, with nebulizer and auxiliary gas flow rates of 1.02 and 0.80 $L \cdot min^{-1}$, respectively. Data acquisition was performed with a dwell time of 0.01 s and a total analysis time of 200 s. The calibration curve ranged from 0.05 to 10.0 ppb for Cr^{3+} and Cr^{6+}, and the samples were analyzed in triplicate for the entire set. In the evaluated samples, Cr^{3+} was not detected. Cr^{6+}, on the other hand, was detected in only one sample from Group 1, with an average concentration of 0.30 ppb, while in Group 2, two samples showed average concentrations of 0.23 and 1.04 ppb. All three samples from Group 3 presented concentrations of approximately 0.12 ppb for Cr^{6+}. The results obtained are following Brazilian regulations, as they are below the established limits, and the IC-ICP-MS hyphenation proved effective in separating chromium species while achieving values well below those stipulated by legislation.

ION CHROMATOGRAPHY FOR LACTOSE QUANTIFICATION IN WHOLE, CONCENTRATED, SPRAY-DRIED, AND FREEZE-DRIED MILK

Jhonatan Faria Costa*[1], José Roberto Miranda Júnior[2], Camila Rodrigues Carneiro[2], Muhammad Alhaji Adamu[2], Moysés Naves Moraes[2], Eduardo Basílio de Oliveira[2], Jane Sélia Dos Reis Coimbra[2]

[1]Universidade Federal de Viçosa - UFV, Department of Food Technology - MG, Brazil; Instituto Federal do Sudeste de Minas Gerais, Campus Rio Pomba – MG, Brazil

[2]Universidade Federal de Viçosa - UFV, Department of Food Technology - MG, Brazil

* Corresponding author: jhonatan.f.costa@ufv.br

Accurate quantification of lactose in dairy products is crucial for quality control and nutritional labeling. This study compared three analytical methods: (1) indirect gravimetric calculation (by difference between moisture, protein, fat, and ash content relative to the total sample weight); (2) sample weighing, dilution, extraction with 0.1 N HCl (50 °C/15 min), centrifugation, supernatant removal, and filtration (PVDF membrane, 0.22 µm); and (3) sample weighing, dilution, and direct filtration (PVDF membrane, 0.22 µm). Twenty-one dairy samples were analyzed in triplicate, including spray-dried milk (130 °C and 180 °C), freeze-dried milk, pasteurized whole milk, and concentrated milk. Shapiro–Wilk tests indicated non-normal data distribution (p 3.1 ± 0.32%). No significant differences were found between freeze-dried and concentrated milk. The study shows that the choice of analytical method should consider the product type, with acid-extraction chromatography being more suitable for milk powder and pasteurized milk, while all three methods are equally effective for freeze-dried and concentrated dairy products.

Acknowledgements: CAPES (00-1), CNPq, and FAPEMIG

LC-MS/MS METHOD DEVELOPMENT FOR THE DETERMINATION OF PARAQUAT AND DIQUAT IN URINE FOR OCCUPATIONAL EXPOSURE ASSESSMENT

Ana Carolina Paschoarelli do Nascimento*[1], Willian Garcia Birolli[2], Álvaro José dos Santos Neto[3]

[1]Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil; Center for Biological and Health Sciences, Federal University of São Carlos, São Paulo, Brazil
[2]Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil; Molecular Oncology Research Center, Barretos Cancer Hospital, Barretos, São Paulo, Brazil
[3]Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: acpnascimento@estudante.ufscar.br

The importance and high productivity of Brazilian agriculture are unquestionable and has been achieved for the Brazilian farmers relying not only on technological innovations but also on the extensive use of pesticides, which can pose risks to human health and the environment. In this context, the herbicide paraquat, widely used in Brazil until its ban in 2020, and its replacement, diquat, are of particular concern due to their high toxicity and lethality. Monitoring these compounds is therefore essential to safeguard the health of rural workers and ensure food safety. The main objective of this study was to develop and validate an analytical method based on liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS, Waters Acquity UPLC/Xevo™ TQ MS) for the determination of paraquat and diquat in urine samples from rural workers. The method development involved the evaluation of ACQUITY UPLC BEH Amide 1.7 µm and ACQUITY UPLC BEH HILIC 1.7 µm chromatographic columns, different mobile phase compositions, and sample preparation by the use of solid-phase extraction (SPE). Optimization of the mass spectrometric parameters was performed by adjusting cone voltage and collision energy for the transitions 183 > 157 and 183 > 168 for diquat and 171 > 77 and 171 > 155 for paraquat, ensuring high sensitivity, selectivity, and analytical reproducibility of the method. The chromatographic results demonstrated efficient separation of paraquat and diquat, with sharp and well-defined peaks. The proposed method represents a reliable strategy for monitoring occupational exposure to highly toxic herbicides in different populations. Beyond its analytical relevance, this study reinforces the importance of strengthening surveillance systems and provides scientific evidence that may guide public health policies aimed at mitigating the risks associated with pesticide exposure.

Acknowledgements: FAPESP, n° 2025/12187-5 and 17/02147-0; CNPq, n° 309282/2025-0; Brazilian Ministry of Health n° 881187/2018, 879335/2018, 894586/2019, and 894588/2019.

LC-MS/MS METHOD FOR THE QUANTIFICATION OF TETRACYCLINES, AMINOGLYCOSIDES, AND FLUOROQUINOLONES RESIDUES IN MILK

Maria de Fátima Gomides[1], Mariem Ribeiro Cunha[1], Christian Fernandes[2], Maria Beatriz A. Gloria*[3]

[1]Funed, MG
[2]UFMG
[3]UFMG, UFBA

* Corresponding author: mbeatriz.gloria@gmail.com

The presence of antibiotic residues in milk involves public health risks. Antibiotic residues may cause toxic or allergic reactions in susceptible individuals, an imbalance of the intestinal microbiota, and teratogenic effects. In addition, they may increase bacterial resistance, selecting resistant bacterial strains. The aim of this study was to develop and validate a fast and straightforward HPLC method coupled to LC-MS/MS for the analysis of aminoglycosides (gentamycin, neomycin), fluoroquinolones (ciprofloxacin, norfloxacin, enrofloxacin), and tetracyclines (tetracycline, oxytetracycline, chlortetracycline, doxycycline) residues in milk. Sulfaphenazole was used as an internal standard. Extraction of the antibiotic residues was carried out with 5% trichloroacetic acid (TCA), followed by centrifugation. The compounds eluted in a single run of 17 min using C18 Nucleodur MN column at 40 °C, with 0.1% pentafluoropropionic acid, and acetonitrile: methanol (9:1), in a gradient elution. The performance of the method was evaluated by an intra-laboratory procedure with reference standard solutions, blank samples (antibiotic-free milk), and samples spiked with standards. The validation parameters were linearity, matrix effect, selectivity, accuracy, precision, limits of quantification (LOQ), decision limit (CCα), and detection capability (CCβ). Matrix-matched analytical curves were used, with linear regression coefficients (R2) ranging from 0.8930 to 0.9999. Recoveries ranged from 87.7 to 119% for tetracyclines, 83.3 to 110.3% for fluoroquinolones, and 71.9 to 103.8% for aminoglycosides. Lower LOQs were observed for fluoroquinolones and tetracyclines (1.5 – 2.5 µg/L) compared to aminoglycosides (12.5 – 27.0 µg/L). The decision limit and detection capability (µg/L) of the method, respectively, varied from 7.27 to 113.99 and 12.66 to 133.99 for fluoroquinolones; from 4.42 to 107.52 and 8.50 to 116.60 for tetracyclines, and from 229.63 to 550.28 and 290.69 to 612.53. The validated method was suitable for the intended use.

Acknowledgements: We acknowledge the support from INCT-Alim, CAPES, FAPEMIG, and CNPq.

Lipid Potential of Vegetable Oils from the Brazilian Cerrado: Chromatographic Analysis of FAME and Triacylglycerides

Tatiana de Oliveira Zuppa Neto*[1], Nelson Roberto Antoniosi Filho[2]

[1]Federal Institute of Goias
[2]Federal University of Goias

* Corresponding author: tatiana.neto@ifg.edu.br

Vegetable fats and oils are strategic inputs used on a large scale in the food, pharmaceutical, cosmetic, and biofuel industries. Considering the importance of the search for new lipid sources, this study aimed to evaluate ten native species from the Brazilian Cerrado in terms of total lipid yield and fatty acid and triacylglyceride composition, with a view to identifying potential nutritional and industrial applications. The oils were extracted by Soxhlet with hexane, and for FAME analysis, micro-scale transesterification was performed using a mixture of ammonium chloride and sulfuric acid in methanol. Gas chromatography (GC) was used to analyze fatty acid methyl esters (FAME), and high-temperature gas chromatography (HT-GC) was used for triacylglycerides (TAG). The species amburana, araticum, baru, buriti, pequi (almond and pulp), pimenta-de-macaco, and tinguí showed high lipid yields, with pequi reaching 58.6%. The fatty acid profiles showed that oils such as murici, araticum, and lobeira have unsaturated proportions similar to commercial oils such as soybean, corn, and olive, while buriti had an oleic acid content similar to olive oil (71.6%). The other oils showed no similarity to commercially known oils, but pequi (almond and pulp) and monkey pepper oil were similar to each other. Triacylglyceride analysis identified OOO, POO, OLO, PLO, POP, OLL, and LLL as the predominant constituents, with a marked presence of polyunsaturated fatty acids in several species. The predominant composition in triacylglycerides in the oils studied was polyunsaturated (T 52:2, T 52:3, T 52:4, T 54:3, T 54:4, T 54:5, T 54:6, T 56:2, T 56:3, and T 58:4), in addition to the monounsaturated T 50:1. Compositional similarities with soybean, sunflower, peanut, and corn oils were also observed. Similar to palm oil, which has saturated fatty acids in the center of the TAG, such as PPP, POO, and POP, amburana, buriti, and pequi (almond and pulp) oils were detected as possibly similar in terms of their high thermal and oxidative stability and plasticity at room temperature. The results highlight the economic and nutritional potential of Cerrado oilseeds, emphasizing their relevance for sustainable development and the preservation of this biome.

Acknowledgements: We would like to thank the funding agencies CNPq, INCT-Alim and IFG for their institutional support in the development of this research.

LIPIDOMIC PROFILING OF BIODIESEL OXIDATION PRODUCTS BY UHPLC-HRMS AND MULTIVARIATE ANALYSIS

Renan de Oliveira Muniz*[1], João Vitor Barros Mendes[2], Cristiane Gimenes de Souza[3], Vinícius Tadeu Kartnaller Montalvão[4], Monica Costa Padilha[4], Débora França de Andrade[4], Luiz Antonio d`Avila[1]

[1]Program in Chemical and Biochemical Process Engineering, School of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil
[2]School of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil
[3]Petroleum and Biofuels Chemical Program, PRH 20.1, Institute of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil
[4]Institute of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil

* Corresponding author: rendo.muniz@gmail.com

Biodiesel is inherently unstable and degrades when exposed to oxygen, heat, moisture and trace metals, conditions that accelerate the oxidation of its unsaturated fatty-acid esters and generate degradation products that impair performance. To monitor this process, six commercial B100 samples from different Brazilian distribution bases and one laboratory-made transesterification product were oxidised by two standard tests: RapidOxy (140 °C/700 kPa O_2, ASTM D7545) and Rancimat (110 °C/10 L h^{-1} compressed air, EN 14112) followed by analysis of the oxidised oil residues by ultra-high-performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC-HRMS) in full-scan/dd-MS^2 mode and subsequent multivariate statistics. Non-oxidised samples served as controls. The untargeted workflow yielded 7,722 signals that a Python script consolidated into 3,131 unique variables. After log_2 and z-score normalisation, supervised partial least-squares discriminant analysis (PLS-DA) and its orthogonal variant (OPLS-DA) were applied; both models were validated by 200 permutations and returned coefficients of determination (R^2) close to 1.0 and cross-validation coefficients (Q^2) above 0.8. Features with a variable-importance-in-projection (VIP) value greater than 2.0 in PLS-DA or greater than 1.5 in OPLS-DA were subjected to the Wilcoxon–Mann-Whitney test, and p-values were adjusted by the Benjamini–Hochberg method and filtered with |log_2-fold-change| greater than 2.0, yielding 12 statistically robust candidate markers. Individual receiver-operating-characteristic (ROC) curves displayed areas under the curve (AUC) from 0.80 to 1.00, confirming the high discriminatory power of these molecules. The chemical profile clearly distinguishes the degradation routes: RapidOxy generates hydroperoxy-epoxy-dienoates and furan-fatty acids, products favoured by heat and pressure, whereas Rancimat produces hydroxy-stearates, dihydroxypalmitates and the lactone curvulalide, formed during prolonged oxidation in the presence of air. The results enable rapid diagnosis of both the presence of oxidation and the predominant oxidation mechanism in biodiesel.

Acknowledgements: The authors thank FUJB for the financial support and LBCD and LAGEQUIM for the partnership.

LOW PRESSURE GAS CHROMATOGRAPHY: FAST AND SUSTAINABLE PESTICIDE RESIDUE ANALYSIS

Claudia M. Barbosa[1], Graziela C. R. M. Moura-Andrade[1], Eliane Vieira[2], Sergio H. Monteiro*[1]

[1]Instituto Biológico - Laboratório de Resíduos de Pesticidas
[2]Instituto Biológico - Laboratório de Ecologia de Agroquímicos

* Corresponding author: sergio.monteiro@sp.gov.br

Low-Pressure Gas Chromatography (LPGC) provides a powerful and innovative platform for multi-residue pesticide analysis, achieving high-resolution separations in a fraction of the time required by conventional GC. By employing short, wide-bore capillary columns operated at reduced inlet pressures, LPGC increases carrier gas velocity while maintaining chromatographic efficiency, enabling the complete separation of 198 pesticides in just 14 minutes, almost three times faster than the 40-minute runtime of a traditional setup. In addition to its remarkable speed, LPGC dramatically reduces helium consumption, delivering significant cost savings and aligning with green chemistry principles by promoting more sustainable laboratory operations. In this study, an LPGC-MS/MS method was developed and validated in accordance with SANTE 11312/2021 guidelines. Gas chromatographic separation employed a low-pressure configuration column (Rtx-5ms 15 m × 0.53 mm ID × 1.00 µm analytical column, 1 m × 0.53 mm ID integrated transfer line, and 5 m × 0.18 mm ID Hydroguard restrictor). The oven temperature program started at 75 °C for 0.5 min, ramped to 250 °C at 30 °C/min, then increased at 10 °C/min to 310 °C, held for 1.67 min, resulting in a total run time of only 14 min. Injection mode: pulsed splitless; pulse pressure 35 psi until 0.5 min; injection volume: 1.5 µL; inlet liner: low-pressure drop inlet with wool. Sample preparation followed the QuEChERS EN 15662 method and was applied to a diverse range of challenging food matrices, including high-acid (pineapple), high-water (tomato), high-oil (soybean), and high-sugar (sugar) plant products, as well as animal-derived samples (egg, milk, meat, and bees). Method performance fulfilled all regulatory requirements, achieving excellent linearity ($r > 0.99$), recoveries of 60–130%, precision with RSD < 20%, and LOQs between 0.001 and 0.1 mg/kg, while substantially increasing sample throughput without compromising robustness. LPGC stands out as a high-impact chromatographic alternative that combines analytical performance, operational efficiency, and sustainability, offering an optimal solution for modern pesticide residue monitoring in complex food matrices, saving both time and costs.

Acknowledgements: FAPESP (Processo: 2022/01101-4); CNPq INCT-ALIM

MAGNETIC PARTICLE SPRAY MASS SPECTROMETRY: A NEW AMBIENT IONIZATION TECHNIQUE

Mariana Azevedo Rosa*, Ana Clara Dias Figueredo, Vanessa dos Santos Fernandes Corrêa, Elizângela Maria de Castilho Alves Morais, Estela Domingos Arnoni, Amanda Maria de Vasconcellos, Tássia Venga Mendes, Eduardo Costa de Figueiredo

Universidade Federal de Alfenas

* Corresponding author: mariana.rosa@unifal-mg.edu.br

Magnetic particle spray mass spectrometry (MPS-MS) is an ambient ionization technique recently developed by our research group that enables sample preparation in just two steps: extraction of the analytes by magnetic solid-phase extraction, followed by their direct desorption and ionization into the MS. This approach offers significant advantages by reducing the sample preparation time, costs, waste, and sample handling. Different magnetic materials were employed in our works: restricted access carbon nanotube (M-RACNT), molecularly imprinted polymer (M-MIP), restricted access copolymer (M-RACP), and biosorbent based on orange peel (M-OPP). In the analysis, the sample is agitated with the materials for an established time (defined by the adsorption kinetics), then the material is collected at the tip of a magnetized metal probe and inserted into the MS inlet. A solvent is dispensed onto the material, and a high voltage is applied, enabling the desorption/ionization of the analyte. Using MPS-MS, we successfully developed methods to determine (i) antidepressants in human plasma for therapeutic monitoring, (ii) β-blockers in human plasma for doping control, (iii) tetracyclines in milk for food quality assessment, and (iv) antidepressants in water for environmental monitoring, employing M-CNT, M-MIP, M-RACP, and M-OPP, respectively. Since its first application, MPS-MS has been upgraded. For instance, the probe angle was optimized from 45° (first application) to 90°, improving reproducibility. Additionally, the insertion of a pipette tip at the probe (in the applications using M-RACP and M-OPP) facilitated cleaning, as the tip was replaced after each analysis, while minimizing potential interference from the metal probe. All developed methods enabled the simultaneous determination of multiple analytes (ranging from 3 to 8) without chromatographic separation, achieving satisfactory precision and accuracy, as well as adequate limits of quantification: 10.0 (i), 3.0 (ii), 50.0 (iii), and 0.1-0.5 (iv) µg L-1. In all cases, MPS-MS proved to be highly time-efficient (1.2 min), requiring minimal amounts of sample (0.75–2.00 mL), solvent (34–180 µL), and sorbent (0.5–0.8 mg) per analysis. These results make MPS-MS highly suitable for routine analysis and fully aligned with green chemistry principles. Furthermore, its application across different matrices demonstrates its versatility and robustness.

Acknowledgements: Federal University of Alfenas. CNPq (150777/2024-8). CAPES (Finance code 001). Fapemig (APQ-01287-24, APQ-00544-23, APQ-00043-21, APQ-01287-24).

METABOLIC PROFILES OF CASHEW APPLE JUICE AND BAGASSE AFTER IN VITRO SIMULATED GASTROINTESTINAL DIGESTION

Camila Tomé da Cunha*[1], Thatyane Vidal Fonteles[1], Sueli Rodrigues[1], Humberto Henrique de Carvalho[1], Carlos Farley Herbster Moura[2], Maria Raquel Alcântara de Miranda[1]

[1]Universidade Federal do Ceará
[2]Empresa Brasileira de Pesquisa Agropecuária

* Corresponding author: camila_tome@outlook.com

Cashew apple contains nutrients and bioactive compounds with antioxidant activity; however, during digestion, these substances undergo changes that may inactivate them or increase their bioaccessibility. Therefore, this study aimed to evaluate how digestion influences the metabolic profile of compounds in the juice and bagasse of the cashew apple varieties CCP 06, CCP 76, and BRS 189. The juice and bagasse of each variety were subjected to in vitro digestion simulation using the INFOGEST 2.0 method and the samples were analyzed before and after digestion. Metabolic profiles were obtained by gas chromatography coupled with mass spectrometry. To demonstrate the differences in metabolic profiles between treatments, a principal component analysis (PCA) was performed. For the juices, the first two principal components explained 91.2% of the total variance (PC1 = 79.3% and PC2 = 11.9%). The separation of samples along PC1 was primarily influenced by metabolites phenylalanine, valine, maltotriose, glycine, and threonine, while PC2 was determined by dehydroascorbic acid, melezitose, fructose, turanose, and alanine. There was an overlap between the digested and non-digested juice samples of the BRS 189 and CCP 76; however, the digested juice of the CCP 06 overlapped with the non-digested BRS 189 and CCP 76 groups, indicating similarities among them. In contrast, the undigested juice of the CCP 06 was separated from all other samples, demonstrating that this variety exhibits a distinct metabolic profile compared to the other varieties. For bagasse, PCA also demonstrated strong discrimination with PC1 explaining 77.8% and PC2 10.6% of the total variance. The metabolites that most contributed to the separation along PC1 were phenylalanine, glutamic acid, valine, maltotriose, and threonine, whereas PC2 was influenced by lyxose, kestose, fructose, glucose, and leucine. Bagasses from the three cashew apple varieties showed clear separation before digestion, highlighting differences most likely due to genetic background. However, after digestion, there was an overlap among the digested bagasse samples from all three varieties, indicating that the digestive process promoted the release of a common set of metabolites. This finding suggests that digestion reduced the variability among the varieties and increased the relative abundance of amino acids. Therefore, the PCA results confirm that simulated digestion significantly alters metabolic profiles and promoting greater homogeneity among samples.

METABOLOMICS-BASED UPLC-HRMS FOR IDENTIFYING POTENTIAL MARKERS OF CYTOTOXICITY IN SCHINOPSIS BRASILIENSIS LEAVES IN DIFFERENT SEASONS UNDER THREE CONTRASTING MICROENVIRONMENTS

Licia dos Reis Luz[1], Jhonyson Arruda Carvalho Guedes*[2], Maria Francilene Souza Silva[3], Maria Madalena da Silva Soares[4], Tamyris de Aquino Gondim[2], Claudia do Ó Pessoa[3], Diogo Denardi Porto[4], Guilherme Julião Zocolo[5]

[1]1Departamento de Química Analítica e Físico-Química, Campus do Pici, Universidade Federal do Ceará (UFC), Fortaleza - CE, CEP 60440-900, Brasil
[2]Departamento de Química Analítica e Físico-Química, Campus do Pici, Universidade Federal do Ceará (UFC), Fortaleza - CE, CEP 60440-900, Brasil
[3]Núcleo de Pesquisa e Desenvolvimento de Medicamentos, Campus Porangabuçu, Universidade Federal do Ceará (UFC), Fortaleza - CE, CEP 60430-275 - Brasil
[4]Embrapa Semiárido, Rodovia BR-428, Km 152, Zona Rural, Petrolina, PE CEP 56302-970, Brazil
[5]Embrapa Soja, Londrina - PR, CEP 86001-970, Brasil

* Corresponding author: jhonyson@ufc.br

Schinopsis brasiliensis Engl. (baraúna) is a plant species widely distributed in areas of the dry tropical forest of Caatinga (Northeastern Brazil) and Cerrado (Central-Western Brazil). Its leaves have recognized antimicrobial, anti-inflammatory, antiseptic, antifungal and anticancer potential. Therefore, the investigation of the chemical profile and phenotypic diversity of baraúna leaves, considering different microenvironments and collection periods, is essential to identify the conditions that maximize their cytotoxic activity. In this study, leaves collected in different seasons and microenvironments over consecutive years were analyzed. The samples were subjected to analysis by liquid chromatography coupled to high-resolution mass spectrometry, where the data obtained were evaluated through multivariate statistical analysis. In addition, the cytotoxic potential of leaves extracts against a breast cancer cell line was evaluated, with the aim of relating chemical variability to biological response. Ultra-performance liquid chromatography coupled with high-resolution mass spectrometry (UPLC-HRMS) enabled the annotation of 45 compounds from different leaves samples. Principal component analysis (PCA) allowed efficient distinction of the chemical profiles of leaves collected in different seasons of the year. Additionally, orthogonal partial least squares discriminant analysis (OPLS-DA), combined with the variable importance in the projection (VIP) and S-Plot tools, enabled the identification of 23 potential marker compounds associated with the best IC_{50} values, especially in samples collected in June from plants from the reserve microenvironment.

Acknowledgements: This work was supported by INCT-ALIM (CNPq (406760/2022-5: INCT - CHAMADA Nº 58/2022), Embrapa (03.14.01.012.00.00), INCT BioNat (465637/2014-0).

Method development for pesticide residues determination in urine, assessing occupational exposure in agricultural communities

Willian Garcia Birolli*[1], Henrique Cesar Santejo Silveira[2], Álvaro José dos Santos Neto[3]

[1]1-Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil. 2-Molecular Oncology Research Center, Barretos Cancer Hospital, Barretos, São Paulo, Brazil.
[2]2-Molecular Oncology Research Center, Barretos Cancer Hospital, Barretos, São Paulo, Brazil.
[3]1-Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil.

* Corresponding author: willianbirolli@gmail.com

Occupational exposure to pesticides represents an increasing public health concern, primarily due to its association with adverse health outcomes. This study aimed to develop and validate an analytical method for the determination of pesticide residues from multiple chemical classes in human urine. A total of 35 analytes were targeted, including 20 parent compounds and 15 urinary metabolites. Sample preparation involved the extraction of 1.0 mL of urine with isotopically labeled internal standards. Enzymatic hydrolysis was performed using a glucuronidase mix, followed by solid-phase extraction using Oasis HLB cartridges (30 mg sorbent). Analyses were conducted using LC-MS/MS on an Acquity Premier M-Class system equipped with an Acquity UPLC BEH C18 microbore column (1.7 µm, 1.0 mm × 100 mm), coupled to a Waters Xevo TQ-S micro mass spectrometer. The mobile phases consisted of (A) water with 5 mM ammonium formate and 0.1% formic acid, and (B) methanol containing 5 mM ammonium formate and 0.1% formic acid. The method achieved limits of quantification ranging from 0.3 to 3.0 $ng \cdot mL^{-1}$, with accuracy between 83% and 112%, and precision varying from 1% to 22%. This method was applied in urine samples from 23 agricultural workers (occupationally exposed group, OE) and 23 individuals without known occupational exposure (non-occupationally exposed group, NOE), collected in 2021. The results revealed the presence of desdimethyldiuron (a diuron metabolite; 0.0 $ng \cdot mL^{-1}$ in NOE; 0.6 $ng \cdot mL^{-1}$ in OE), 2,4-D (0.0 $ng \cdot mL^{-1}$ in NOE; 4.8 $ng \cdot mL^{-1}$ in OE), 6-chloropyridine-3-carboxylic acid (imidacloprid metabolite; 0.0 $ng \cdot mL^{-1}$ in NOE; 4.8 $ng \cdot mL^{-1}$ in OE), 2-aminobenzimidazole (carbendazim metabolite; 0.6 $ng \cdot mL^{-1}$ in NOE; 1.0 $ng \cdot mL^{-1}$ in OE), 3,5,6-trichloro-2-pyridinol (chlorpyrifos metabolite; 0.5 $ng \cdot mL^{-1}$ in NOE; 1.7 $ng \cdot mL^{-1}$ in OE), among others. These findings demonstrate the presence of pesticide residues in $ng.mL^{-1}$ levels, consistent with international biomonitoring data. The results highlight the importance of continuous surveillance, particularly in vulnerable populations such as agricultural workers.

Acknowledgements: Ministry of Health of Brazil (881187/2018, 879335/2018, 894586/2019 and 894588/2019); Brazilian National Council for Scientific and Technological Development, CNPq (314247/2021–1 and 314731/2021–0); São Paulo Research Foundation, FAPESP (2018/23105–6 and 2017/02147–0).

METHOD DEVELOPMENT FOR THE DETERMINATION OF MULTIPLE ANTIBIOTICS RESIDUES IN SURFACE WATER BY HPLC-MS/MS

Almir Custodio Batista Junior*[1], Pedro Henrique de Oliveira Carvalho[2], Gisele Augusto Rodrigues de Oliveira[2], Andrea Rodrigues Chaves[1]

[1]Instituto de Química, Universidade Federal de Goiás
[2]Faculdade de Farmácia, Universidade Federal de Goiás

* Corresponding author: custodioalmir16@gmail.com

The widespread use and environmental persistence of antibiotics have led to their classification as emerging contaminants, frequently detected at trace levels in water, soil, and sediments. Their presence in aquatic environments poses serious risks to ecosystems and public health, particularly by promoting the development of antibiotic-resistant bacteria. In this context, the present study aimed to develop an analytical protocol for the determination of ten of the most used antibiotics worldwide in surface water, employing high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS) analysis. The developed method evaluated ten antibiotics: amoxicillin, azithromycin, ceftriaxone, ciprofloxacin, cefazolin, cefoxitin, chloramphenicol, metronidazole, sulfamethoxazole and tetracycline. Eight real surface water samples were collected in a river and four water samples were collected after water treatment (Goiânia, Brazil). For preconcentration of the analytes prior HPLC-MS/MS analysis, a solid-phase extraction protocol was employed, using STRATA-X cartridge and methanol as elution solvent. HPLC-MS/MS analysis was performed using an Agilent 1290 Infinity II system coupled with an Agilent 6495D triple quadrupole mass spectrometer. Chromatographic separation was achieved on a C18 column, injecting 10 µL of sample. The mobile phase employed a flow rate of 0.300 $mL \cdot min^{-1}$, consisting of (A) an aqueous solution of 0.10% (v/v) formic acid and 5 mM ammonium formate, and (B) methanol in a gradient elution mode. The total chromatographic run time was 8 minutes. Mass spectrometric analysis was carried out using an electrospray ionization source. Data acquisition was performed using a dynamic multiple reaction monitoring (dMRM) mode, monitoring 20 specific transitions (a quantifier and a qualifier transition for each analyte). The method provided suitable limits of detection for each compound, ranging from 0.019 to 0.78 ng.mL-1. Thus, calibration curves were constructed for all analytes over the concentration range of 0.019 to 50 ng.mL-1, demonstrating linearity ($r^2 > 0.99$) and high accuracy. The samples were analyzed, allowing the detection of amoxicillin, azithromycin, metronidazole, sulfamethoxazole, and tetracycline at trace levels. Thus, the proposed protocol proved effective for assessing the occurrence of antibiotics in aquatic environments, even at very low concentrations.

Acknowledgements: CAPES, CNPQ, FAPEG, PPGQ-IQ-UFG, LaCEM, FF-UFG, INCT-ALIM

Method Development in LC-MS/MS Focused on Derivatization and Sample Pre-treatment for Determination of Glyphosate, Glufosinate, and AMPA at Low Concentration in Urine for Chronic Exposure Assessment

Matheus Barraca*[1], Willian Garcia Birolli[2], Álvaro José dos Santos Neto[1]

[1]1-Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil.
[2]1-Chromatography Group, São Carlos Institute of Chemistry, University of São Paulo, São Carlos, São Paulo, Brazil. 2-Molecular Oncology Research Center, Barretos Cancer Hospital, Barretos, São Paulo, Brazil.

* Corresponding author: matheusbarraca@usp.br

Since its classification as probably carcinogenic by IARC in 2015, concerns have grown over agricultural and general population exposure to glyphosate, the world's most widely used pesticide since the advent of herbicide-resistant genetically modified crops. Exposure to pesticides can be assessed in various ways, including through biomarkers and pesticides residues such as AMPA, the co-formulated glufosinate and glyphosate itself. Urine is an excellent matrix for glyphosate biomonitoring, as it is easy to collect, store, and reflects excretion of the compound largely as the parent active ingredient. Urine analysis for glyphosate detection and quantification can be effectively performed using liquid chromatography coupled with mass spectrometry, due to its high detectability and sensitivity; however, optimized performance is required for population assessment of chronic exposure at ng/mL. This study presents an LC-MS/MS method to detect glyphosate, glufosinate, and AMPA in urine, using FMOC-Cl derivatization to improve sensitivity. In addition to derivatization, a solid-phase extraction (SPE) step will be optimized using Supelco Supelclean LC-SAX cartridges. The chromatographic system includes a microbore Acquity UPLC BEH C18 column, in an Acquity UPLC M-CLASS/Xevo™ TQ-S Micro system from Waters, coupled to a Waters Xevo TQ-S Micro mass spectrometer. The selected mobile phases are ammonium acetate in water with 0.1% acetic acid (mobile phase A) and pure methanol (mobile phase B). The method aims to achieve a high detection frequency in human samples with low limits of quantification (between 0.1 and 1 ng/mL) and is expected to provide a reliable tool for large-scale biomonitoring of chronic pesticide exposure in human populations.

Acknowledgements: CAPES Nº 88887.102980/2025-00; FAPESP, n° 17/02147-0; CNPq, n° 314731/2021-0; Brazilian Ministry of Health n° 881187/2018, 879335/2018, 894586/2019, and 894588/2019.

MICRO-QUECHERS AND GC-MS APPROACH FOR THE DETERMINATION OF PARABENS IN PHARMACEUTICAL SYRUPS

Sergiane Caldas Barbosa*, Paula de Souza Garcia, Maria Luiza Soares Trindade, Sthefanie Lopes do Valle, Julia Bitencourt Cunha, Jean Lucas de Oliveira Arias, Ednei Gilberto Primel

Universidade Federal do Rio Grande - FURG

* Corresponding author: sergianecaldas@furg.br

Parabens (PBs) are widely used as preservatives in cosmetics, pharmaceuticals, beverages, and foods, being simple and inexpensive to synthesize, which increases their popularity in industry. In the pharmaceutical context, syrups stand out due to their widespread consumption, especially among the pediatric population, and they are often formulated with parabens as preservatives. However, PBs are endocrine disruptors and may exhibit estrogenic and antiandrogenic activity, representing a risk. For the determination of parabens in syrups, sample preparation is a crucial step. This pharmaceutical matrix is highly complex due to the presence of sugars, dyes, flavoring agents, and other excipients that may interfere with the detection and quantification of the analytes. Without proper preparation, these components can cause matrix effects, compromising the results and the equipment. For sample preparation, the QuEChERS method and its miniaturized version (micro-QuEChERS) have gained prominence for their speed, low cost, high extraction efficiency, reduced solvent consumption, and lower waste generation. Therefore, the aim of this study was to propose the use of the Micro-QuEChERS technique for the extraction of 9 PBs in syrup samples. Validation was carried out according to INMETRO guidelines. The instrumental LOQ values for all parabens were 0.005 mg L−1, while the LOD values were 0.001 mg L−1. Analytical curves showed correlation coefficients higher than 0.99, ensuring good linearity. Recoveries ranged from 70 to 117%, and RSDs below 17% confirmed the precision and accuracy of the procedure. The method was applied to six widely consumed syrup samples, in which methylparaben, propylparaben, and butylparaben were detected. The application of Micro-QuEChERS using five times less solvent volume (2 mL acetone) and salt masses (0.8 g MgSO4 and 0.2 g NaCl) represented an improvement over conventional QuEChERS, maintaining extraction efficiency while substantially reducing the use of reagents and sample, making the process more sustainable and economical. This miniaturization proved to be relevant for the analysis of PBs in pharmaceutical syrups, representing a viable alternative for routine quality control analyses of liquid medicines, ensuring the compliance of liquid medicines with safety and regulatory standards.

Acknowledgements: CNPq, FAPERGS, FINEP, FURG

MINIATURIZATION OF THE MSPD METHOD FOR THE DETECTION OF MULTI-RESIDUE PESTICIDES IN FRUIT-, VEGETABLE-, AND CEREAL-BASED BABY FOODS USING LIQUID CHROMATOGRAPHY

Roseane dos Santos Nascimento*, Larissa de Jesus Souza, Luís Fabrício Santana Santos, Sandro Navickiene

Universidade Federal de Sergipe

* Corresponding author: roseanny@academico.ufs.br

The application of pesticides in agricultural activities is known. A part of these pesticides can reach the environment and then end up in the food consummation. Contamination of plant production with pesticide residues is a source of risk for human health. Special attention should be focused on the health protection of infants and young children as they represent the most vulnerable group of the population. Infants and young children have been shown to be very sensitive to certain toxic effects. As a consequence, monitoring of their residue levels in the baby food is a necessity. This work explored the feasilibity of miniaturizing the matrix solid-phase dispersion (MSPD) method followed by high-performance liquid chromatography diode array detector (HPLC-DAD) for pesticide residue analysis in baby food samples. The pesticides were enriched in a sorbent material (60 mg) packed into a pipette tip to selectively isolate and concentrate pesticides from a sample matrix (40 mg). Then the pesticides were eluted with methanol, and the eluent was analyzed by HPLC-DAD. The separation was accomplished on a C18 column with the mobile phase consisting of methanol and water at 1.0 mL min-1 in gradient elution. Calibration conditions of HPLC-DAD showed excellent linearity for the pesticides studied (abamectin, acetamiprid, azoxystrobin, bifenthrin, clothianidin, difenoconazole, epoxiconazole, lufenuron, malathion, pyraclostrobin, teflubenzuron, thiacloprid, thiamethoxam, thiophanate-methyl, imidacloprid, and dimethoate) in the range from 10 to 1000 µg L-1, with correlation coefficients ranged from 0.9986 to 0.9992. Good average recoveries of the analytes were obtained from spiked baby food matrix at one concentration level 10 µg L-1, ranged from 79 to 99 %, with relative standard deviations (RSD) values below 20%. The method is easy, with low consumption of reagents, is characterized by reliability, sensitivity and therefore is suitable for the monitoring the levels of pesticide residues in baby food samples.

Acknowledgements: The authors are grateful to the CAPES, the Multi-user Chemistry Laboratories Center (CLQM) (analytical support), and the NOVA ANALÍTICA Ltda for financial assistance.

MINIATURIZED DIRECT MATRIX SOLID-PHASE DISPERSION FOR MULTIRESIDUE DETERMINATION OF PESTICIDE RESIDUES IN RICE BY UHPLC-MS/MS

Igor Franceschi de Souza*, Dylan Mehler Hoffmann, Luana Floriano, Osmar Damian Prestes, Renato Zanella

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria -RS, Brazil

* Corresponding author: igor.souza@acad.ufsm.br

Rice is one of the most widely consumed cereals globally, making the continuous monitoring of its food safety essential to ensure quality and compliance with national and international regulations. This study aimed to develop and validate a miniaturized and simplified sample preparation method based on matrix solid-phase dispersion (MSPD) for the multiresidue determination of pesticides in rice by ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS). In contrast to the conventional MSPD technique, the proposed sample preparation is performed entirely in a single tube, eliminating the need for transfer to a solid-phase extraction cartridge. Several parameters were optimized, including the extraction solvent, type and mass of sorbent, sonication time, and dilution solvent. The optimized procedure employed a small sample portion blended with diatomaceous earth as the sorbent, homogenized using ceramic homogenizers, and extracted with acetonitrile containing 1% (v/v) acetic acid under ultrasonication. The extracts were diluted 1:1 (v/v) with ultrapure water prior to analysis by UHPLC-MS/MS with electrospray ionization in positive and negative modes (ESI±). Chromatographic separation was achieved on an Acquity BEH C18 column (50 × 2.1 mm, 1.7 µm) using a gradient elution with mobile phase (A) water:methanol (98:2, v/v) and (B) methanol:water (98:2, v/v), both containing 0.1% (v/v) formic acid and 5 mmol L^{-1} ammonium formate. The method was validated for 60 pesticides, demonstrating linearity within the range of 4 to 160 µg kg^{-1}, recoveries between 70 and 120%, and relative standard deviations (RSD) ≤ 20%. The method limits of quantification (LOQs) were established at 4 µg kg^{-1} for 48 compounds and 8 µg kg^{-1} for 12 compounds. Application of the method to 24 commercial rice samples revealed pesticide residues in 11 samples, with concentrations ranging from

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

Monitoramento de multiresíduos de agrotóxicos em pimentões verdes por Cromatografia Gasosa acoplada à Espectrometria de Massas (CG-EM)

Mairlane Silva de Alencar*[1], Maria Vitória Lima Ramos[2], Cleidiane Gomes Lima[3], Denilson Gonçalves Queiroz[3], Renata de Oliveira Silva[3], Ruth Maria Bonfim Vidal[2]

[1]Universidade Federal do Ceará; Núcleo de Tecnologia e Qualidade Industrial do Ceará
[2]Universidade Federal do Ceará
[3]Núcleo de Tecnologia e Qualidade Industrial do Ceará

* Corresponding author: alencarmairlane@gmail.com

O pimentão é rico em vitaminas, minerais e antioxidantes, é também uma das hortaliças mais consumidas no Brasil, apresentando grande importância econômica para o país. Entretanto, relatórios do Programa de Análise de Resíduos de Agrotóxicos em Alimentos (PARA) tem apontado o pimentão como uma das culturas mais críticas em relação a irregularidades no uso de agrotóxicos, tanto pela presença de substâncias não autorizadas, como também por concentrações acima dos Limites Máximos de Resíduos (LMR) estabelecidos pela legislação. Diante disso, o objetivo do presente trabalho foi analisar 13 agrotóxicos em amostras de pimentões verdes convencionais e orgânicos comercializados em Fortaleza – CE, utilizando o método QuEChERS citrato para a extração dos resíduos de agrotóxicos e cromatografia acoplada a espectrometria de massas para identificação e quantificação dos compostos. Todas as amostras de pimentões convencionais apresentaram resíduos de agrotóxicos e uma amostra de pimentão orgânico apresentou um agrotóxico. Foram identificados e quantificados os agrotóxicos clorotalonil, difenoconazol e clorpirifós nas amostras de pimentões convencionais e clorotalonil em uma amostra de pimentão orgânico. As concentrações encontradas de clorotalonil e difenozonazol ficaram dentro dos limites estabelecidos pela monografia da ANVISA para a cultura do pimentão, porém o clorpirifós é um agrotóxico não autorizado para essa cultura, o que demonstra irregularidade, assim como foi relatado nos relatórios do PARA e isso levanta preocupações quanto a segurança alimentar. A presença de resíduos de agrotóxicos em amostras de pimentão orgânico evidencia possíveis falhas na cadeia produtiva ou contaminação cruzada e necessita de uma maior fiscalização. O estudo contribuiu para reforçar a importância da cromatografia aplicada a segurança alimentar, além de apontar a necessidade de ações regulatórias mais rigorosas para proteger o consumidor.

Acknowledgements: Agradecemos à Universidade Federal do Ceará (UFC) e ao Núcleo de Tecnologia e Qualidade Industrial do Ceará (NUTEC) pelo suporte e infraestrutura disponibilizados para a realização deste trabalho.

MONITORAMENTO DE SUBPRODUTOS DA DESINFECÇÃO EM ÁGUA PARA CONSUMO HUMANO: UMA ABORDAGEM ANALÍTICA E INSTITUCIONAL COM LC-MS/MS EM LABORATÓRIO PÚBLICO

Suellen Gordiano de Oliveira Cunha*, Luciano Menezes Maia, Ana Paula Tojal Nicanor Ferreira, Júlio Cesar Mato Grosso de Sousa, Jorge Tadeu de Freitas, Sandra Regina Novaes de Oliveira Luz

Empresa Baiana de Águas e Saneamento S.A - EMBASA

* Corresponding author: suellen.cunha@embasa.ba.gov.br

A água é um recurso essencial à vida, e o controle de sua qualidade é fundamental para a proteção da saúde pública. Entre os subprodutos formados durante o tratamento da água, os ácidos haloacéticos (HAA) se destacam por seu potencial tóxico e carcinogênico, resultante da reação entre matéria orgânica natural e agentes oxidantes utilizados na desinfecção. No Brasil, a Portaria GM/MS nº 888/2021 atualizou os parâmetros de potabilidade, ampliando a lista de compostos monitorados e estabelecendo limites mais rigorosos, o que demandou maior sensibilidade analítica por parte dos laboratórios. Neste contexto, este estudo relata a experiência de um laboratório público na implementação e validação de um método baseado em cromatografia líquida acoplada à espectrometria de massas em tandem (LC-MS/MS) para determinação simultânea de nove HAA em amostras de água potável. O método, operando no modo MRM, apresentou ampla faixa de linearidade (5–250 $\mu g \cdot L^{-1}$), altos coeficientes de determinação ($R^2 \geq 0,992$) e baixos limites de detecção (2–5 $\mu g \cdot L^{-1}$) e quantificação (5–20 $\mu g \cdot L^{-1}$), atendendo plenamente às exigências da nova regulamentação. A inclusão dos compostos tribromoacético (TBAA) e dibromocloroacético (DBCAA) exigiu ajustes nos parâmetros cromatográficos e transições MRM, sem comprometer a robustez do método. A aplicação da metodologia permite o monitoramento eficaz dos HAA, assegurando conformidade com os valores máximos permitidos e contribuindo para a melhoria dos programas de vigilância da qualidade da água e para a proteção da saúde da população.

Acknowledgements: Agradecemos à EMBASA pelo suporte técnico e ao laboratório público de controle ambiental pela infraestrutura disponibilizada.

MONITORING OF CAFFEINE IN ENVIRONMENTAL SAMPLES FROM THE TRAMANDAÍ RIVER ESTUARY

Julia da Silva Souza[1], Lenise Guimarães de Oliveira[1], Antônio Miguel Gomes Lima[1], Marcia Helena Scherer Kurz[1], Anna Carolina Nickel Meireles[1], Fabio Ferreira Gonçalves[1], Mariana Scheffer Formagio[1], Cacinele Mariana da Rocha[2]

[1]FURG-SAP
[2]Ceclimar-UFRGS

Keywords: Caffeine; emerging contaminants; SPE; HPLC-DAD; Rio Tramandaí

Emerging compounds have increasingly become the focus of environmental monitoring, as even at low concentrations they can indicate significant anthropogenic pressures on aquatic ecosystems (DAS et al., 2024; ROCHA; FÉLIX; FARIAS, 2024). Among these, caffeine stands out as a reliable environmental marker due to its predominantly human origin and its direct association with untreated domestic sewage discharges. The use of caffeine as a tracer underscores its utility in environmental impact assessments and in informing water quality management strategies in coastal and estuarine systems, particularly in areas subjected to intense anthropogenic stress. In this context, this study aims to monitor caffeine in the Tramandaí estuary as an indicator of anthropogenic contamination and to support the understanding of local water quality dynamics. The sample preparation procedure was based on solid-phase extraction (SPE) using Hypersep Retain PEP cartridges. The cartridge was conditioned with 3 mL of MeOH and 3 mL of ultra pure water, after which 250 mL of sample (pH 7) was percolated. It was washed with 3 mL of ultra pure water and then left to dry for approximately 15 minutes. The elution was performed in two steps of 0.5 mL of MeOH. Quantification was carried out by HPLC-DAD using an Inertsil C18 column (150 × 4.6 mm, 5 µm). The mobile phase consisted of ultra pure water and methanol, delivered at a 0.8 mL/min flow rate. Detection was monitored at 220 and 272 nm. The method validation demonstrated linearity over the range of 0.1–5.0 mg L^{-1} ($R^2 > 0.99$), limit of quantification (LOQ) of 1.0 µg L^{-1}, and recoveries within recommended parameters, confirming the robustness of the analytical procedure. Monitoring will be carried out every two months over a period of one year (from August 2025 to July 2026). Nine monitoring points were established along the estuary, encompassing urban, rural, transitional, and coastal marine zones to assess diverse environmental pressures. The initial monitoring revealed caffeine concentrations below the LOQ at one site located in the coastal marine zone, indicating potential anthropogenic inputs in this area.

DAS, Shubhasikha; PARIDA, Vishal Kumar; TIWARY, Chandra Sekhar; GUPTA, Ashok Kumar; CHOWDHURY, Shamik. Emerging Contaminants in the Aquatic Environment: Fate, Occurrence, Impacts, and Toxicity. In: ACS Symposium Series. Washington, DC: American Chemical Society, 2024. DOI: https://doi.org/10.1021/bk-2024-1475.ch001
ROCHA, Thiago Lopes; FÉLIX, Luís Manuel; FARIAS, Davi. Ecotoxicological Effects of Emerging Contaminants on Aquatic Species. Toxics, v. 12, n. 8, p. 567, 2024. DOI: https://doi.org/10.3390/toxics12080567

MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS IN MARGINAL LAGOONS USING A NOVEL PASSIVE THERMAL DESORPTION SAMPLER AND GCXGC/MS

Caroliny Gonzaga*[1], Victor Eduardo Almeida Pereira Silva[1], Jhonatan Bispo de Oliveira[2], Patterson Patricio de Souza[1], Ildefonso Binatti[1], Patrícia Sueli de Rezende[1]

[1]Centro Federal de Educação Tecnológica de Minas Gerais
[2]Universidade Federal de Minas Gerais

* Corresponding author: gonzaga.caroliny@yahoo.com.br

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds composed of two or more fused aromatic rings, known for their environmental persistence and toxicity. Classified by the United States Environmental Protection Agency (USEPA) as persistent organic pollutants (POPs), these compounds can accumulate in living organisms, causing adverse effects such as DNA mutations[1]. This study used the Intra-tube Flux Extraction (IT-FEx) device as a passive thermal desorption sampler to monitor PAHs in marginal lagoons. IT-FEx is the inlet liner internally coated with polydimethylsiloxane (PDMS), the device adsorbs and pre-concentrates compounds directly at the site of exposure, allowing for subsequent analysis by thermal desorption. This eliminates the use of solvents, reduces preparation steps, and favors clean, rapid, and reproducible analyses[2],[3]. Combined with comprehensive two-dimensional gas chromatography (GC×GC), the IT-FEx allows the identification and quantification of PAHs at trace levels, even in complex environmental matrices. Twenty devices were fabricated, from the spincoating process by 2 h and 2800 rpm, and the PDMS film was characterized by TG and FTIR. The average mass of sorbent deposited in the devices was 5,45 ± 0,005 mg. Statistical tests demonstrated similarity between the devices. The system, which uses the passive sampler, was calibrated in a laboratory process during 15 days of passive sampling at 25 °C and 250 L h-1. The determined sampling time was 5 days, with passive sampling rates ranging from 0.008-0.068 mL d-1 and partition coefficients (Kpdms-water) ranging from 1.260-7.810. Three different flow rates (50, 250 and 450 L h-1) were tested in the system, and the device showed better responses at lower flow rates, indicating greater potential for application in lagoons. In the context of aquatic pollutant analysis, the proposed method offers significant advantages by minimizing solvent consumption and simplifying sample preparation, in accordance with the Principles of Green Analytical Chemistry. The device provides high robustness, reusability of extraction fibers, and compatibility with advanced chromatographic systems, ensuring reliable performance in complex matrices. Evaluated by the AGREE metric, the method demonstrates a favorable green profile, establishing IT-FEx as an innovative, sustainable, and competitive alternative to conventional extraction strategies.

Acknowledgements: Centro Federal de Educação Tecnológica de Minas Gerais, Fundação de Amparo à Pesquisa do Estado de Minas Gerais, Laboratório de Tecnologias Integradas.

MONITORING THE METABOLISM OF DAIRY COWS VIA ANALYSIS OF VOLATILE ORGANIC METABOLITES IN CERUMEN

Ícaro do Nascimento Camêlo*, Paulo Henrique Jorge da Cunha, Nelson Roberto Antoniosi Filho

Universidade Federal de Goiás

* Corresponding author: icarocamelo97@gmail.com

Brazil's dairy industry, one of the largest in the world, is seeking alternatives to improve animal health and welfare on farms. Analysis of volatile organic compounds in earwax is emerging as a promising tool for noninvasive monitoring. This study aimed to compare the VOC profiles in the cerumen of Jersey and Girolando dairy cows, subjected to different management systems, to identify specific biomarkers of NEB. To this end, cerumen samples were collected from 19 cows, 11 Jersey cows in compost barns, and 8 Girolando cows in semi-intensive systems during the dry phase and the first three months of lactation. The analysis was performed on an HS/GC-MS system using approximately 20 mg of cerumen and an internal standard, in vials at 180 °C for 60 min, with shaking at 500 rpm. The volatiles were introduced in splitless mode at 250 °C and separated on an NST-100-ms capillary column of polyethylene glycol. Helium was used as carrier gas with a constant linear velocity of. MS detection was performed by electron impact in scanning mode. The identification of the compounds was confirmed by the NIST11 library and by retention time relative to the internal standard. The analyses revealed different metabolic signatures between the breeds. In Jersey cows, significant differences were observed during the periods, that is, the animals exhibit changes between one period and another, with a prominent increase in fatty acids in the postpartum period, since there is intense mobilization of body fat associated with peak lactation in confinement. In contrast, the Girolando breed's profile was characterized by a greater abundance of ketones and alcohols, in addition to greater metabolic variation between periods and less standardization between each lactation phase. This trend is due to factors such as crossbreeding and different adaptations to the semi-intensive system. Aldehydes, ketones, and fatty acids were identified as potential biomarkers of oxidative stress and NEB. Therefore, the analysis of VOCs in cerumen is sensitive to differentiating metabolic responses influenced by breed and management system, with Jersey cows in confinement presenting a more drastic change in the lipid profile during lactation compared to Girolando cows.

Acknowledgements: UFG, LAMES-UFG, CAPES, INCT-ALIM.

MULTIRESIDUE AND MULTICLASS DETERMINATION OF VETERINARY DRUGS IN SOIL SAMPLES USING QuEChERS AND UHPLC-MS/MS

Muriel Schmidt, Gabriel Severo de Carvalho, Karine Reinke, Luana Floriano, Osmar Damian Prestes, Renato Zanella*

Laboratory of Pesticide Residues Analysis (LARP), Federal University of Santa Maria (UFSM), Brazil

* Corresponding author: renato.zanella@ufsm.br

The growth of the world population and increased consumer demand for food has led to a more intensive animal production system, mainly with confined animals. Veterinary drugs used on animals can reach the environment through the urine and feces of animals in pastures, aquaculture, or even indirectly, through the use of contaminated manure for fertilization. Given the ecotoxicity and potential adverse effects on human health of these compounds, especially antimicrobials, it is essential to monitor them in soil. Therefore, the aim of this study was to develop and validate a method for multiclass determination of veterinary drugs in soil by ultra-high performance liquid chromatography with tandem mass spectrometry (UHPLC-MS/MS) after a sample preparation step using a modified QuEChERS method. The sample preparation consisted of a two-step sequential extraction with a EDTA solution, followed by a mixture of acetonitrile containing formic acid and phosphate buffer (pH 3). The extract was partitioned using Na2SO4 and NaCl. The extract was cleaned by dispersive solid phase extraction (d-SPE) using C18, and the extract diluted with water before analysis by UHPLC-MS/MS on a Xevo TQ system (Waters, USA) using Acquity UPLC™ HSS T3 (100 × 2.1 mm, 1.8 µm) column. The mobile phase consisted of (A) ultrapure water and (B) acetonitrile:methanol (80:20, v/v), both containing 0.1% (v/v) formic acid at a flow rate of 0.400 mL min^{-1} in gradient elution. The proposed method was successfully validated for 33 compounds from the sulfonamide, quinolone, tetracycline, macrolide, and chloramphenicol classes showing good selectivity and sensitivity. The recoveries at three spike levels ranged from 70 to 110% with relative standard deviation ≤ 20%, and the method limit of quantification ranged from 8 to 16 µg kg-1. When applied to field-collected soil samples, trace levels of veterinary drugs were detected, demonstrating the importance of the proposed method.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

Occurrence and risk assessment of pesticide residues in spices and dried herbs using eco-friendly microextraction combined with GCxGC/MS

Jhonatan Bispo de Oliveira*[1], Helvécio Costa Menezes[1], Patterson Patrício de Souza[2], Zenilda de Lourdes Cardeal[1]

[1]Universidade Federal de Minas Gerais
[2]Centro Federal de Educação Tecnológica de Minas Gerais

* Corresponding author: jhonatanbo@hotmail.com

Spices and dried herbs are widely consumed and highly susceptible to pesticide contamination, but are often overlooked in food safety monitoring programs. This study presents the development and validation of an environmentally friendly analytical method based on direct immersion solid-phase microextraction using a hydrophilic microporous cartridge (HMCart-DI-SPME) in combination with comprehensive two-dimensional gas chromatography and mass spectrometry (GC×GC/MS) for the multiresidue determination of organochlorine and organophosphorus pesticides. Optimization of the method was performed using a two-stage, full factorial design to evaluate the effects and interactions of critical variables such as extraction time, temperature, equilibrium time, agitation speed and solvent composition. Optimal conditions — 70 °C, 60 min extraction, 15 min equilibration, 600 rpm stirring and 100 µL ethyl acetate as a modifier — significantly improved analyte recovery and method sensitivity. The method showed excellent analytical performance with limits of detection between 0.10 and 0.87 µg kg^{-1}, recoveries between 88.36 and 109.86% and high precision (RSD < 13%). A total of 44 commercial samples of spices and dried herbs collected in Belo Horizonte (Brazil) were analyzed, and 41 samples tested positive for at least one pesticide. Prohibited substances such as dieldrin (up to 7.23 µg kg^{-1}), parathion (8.79 µg kg^{-1}) and heptachlor epoxide (5.84 µg kg^{-1}) were frequently detected. However, the chronic non-carcinogenic risk assessment based on estimated daily intake (EDI) and hazard index (HI) values did not reveal a significant risk to consumers (HI < 1 for all compounds). This method stands out as a sensitive, selective and sustainable alternative for routine monitoring of pesticides in complex plant matrices. Its practical application has been demonstrated by analyzing real samples and comparing it with conventional methods. It offers higher sensitivity, lower solvent consumption and a better environmental footprint (AGREE score: 0.67). The results underline the importance of continuous monitoring to ensure food safety and regulatory compliance.

Acknowledgements: National Council for Scientific and Technological Development (Conselho Nacional de Desenvolvimento Científico e Tecnológico – CNPq), Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), Chemistry Department of Federal University of Minas Gerais (UFMG), and the Federal Center for Technological Education of Minas Gerais (CEFET-MG).

OCCURRENCE OF TETRACYCLINES, AMINOGLYCOSIDES, AND FLUOROQUINOLONES IN MILK BY LC-MS/MS

Maria de Fátima Gomides[1], Christian Fernandes[2], Mariem R. R. da Cunha[1], Maria Beatriz Abreu Gloria*[2]

[1]Funed, MG
[2]UFMG

* Corresponding author: mbeatriz.gloria@gmail.com

Milk is a nutritious and versatile food, widely consumed and used as an ingredient in several products. However, there is a concern regarding milk safety related to antibiotics, which are widely used in treating diseases (e.g., mastitis) and as growth promoters. The indiscriminate use of antibiotics may cause toxic or allergic reactions in susceptible individuals, an imbalance of the intestinal microbiota, teratogenic effects, and it may increase bacterial resistance. In this context, the objective of this study was to investigate the levels of aminoglycosides (gentamycin, neomycin), fluoroquinolones (ciprofloxacin, norfloxacin, enrofloxacin), and tetracyclines (tetracycline, oxytetracycline, chlortetracycline, doxycycline) in milk from the Brazilian market. For that, the antibiotic residues were extracted from the samples with 5% trichloroacetic acid, followed by centrifugation. LC-MS/MS was performed in a C18 (150 × 4.0 mm, 5 µm) column at 40 °C, with mobile phases composed of 0.1% pentafluoropropionic acid (A) and acetonitrile: methanol, 9:1 (B), in gradient elution. Standard curves were built in the matrix. 890 milk samples (257 powdered, 447 UHT, and 186 pasteurized) from PAMVet were evaluated. All antibiotics studied were detected in the samples. Overall, more than half (54.8%) of the samples contained some antibiotic. There was a higher prevalence of antibiotics in milk powder (91.8%), followed by pasteurized milk (48.9%) and UHT milk (36.1%). Doxycycline or norfloxacin residues, which are not allowed in Brazil, were detected in 18.4% of the samples, whereas in 9.4% both were detected. When comparing occurrence by geographic regions, there was a higher prevalence (66.4%) of antibiotics in milk samples from the southern region, whereas the northern region presented the highest non-compliance (27%) with Brazilian legislation.

Acknowledgements: We acknowledge the support from INCT-Alim, CAPES, FAPEMIG, and CNPq.

OFF-LINE MULTIDIMENSIONAL COUNTERCURRENT CHROMATOGRAPHY IN THE ISOLATION AND PURIFICATION OF CHEMICAL CONSTITUENTS FROM THE ETHANOL EXTRACT OF BRAZILIAN GREEN PROPOLIS

CRISTIANE CARDOSO DOS SANTOS*[1], Alicia Fontoura da Silva[2], Simone Nascimento[3], Rosane Nora Castro[1], Gilda Guimarães Leitão[4]

[1]Universidade Federal Rural do Rio de Janeiro
[2]Universidade Federal do Rio de Janeiro
[3]Agilent Brasil
[4]Universidade Federal do Rio de Janeiro

* Corresponding author: criscsrj@yahoo.com.br

Multidimensional countercurrent chromatography (MDCCC) is a versatile technique that is gaining popularity for the purification of compounds from complex natural product matrices. Offline MDCCC is particularly valuable for phytochemical investigations. Although it is more time-consuming, this approach eliminates the need for additional equipment and reduces peak broadening caused by sample dilution in the second dimension. Brazilian green propolis (BGP) is a natural resin collected by Apis mellifera L. bees and exhibits complex chemical composition. While phenylpropanoids, flavonoids, triterpenes and phenolic lipid derivatives have already been identified, a significant proportion of its constituents remains uncharacterized. Further research is needed to fully elucidate its complete chemical composition. The ethanol extract of green propolis (EEGP) was initially screened by liquid chromatography coupled to time-of-flight mass spectrometry (LC/Q-TOF-MS) for dereplication proposes, aiming to better understand its chemical composition and to assist in selecting suitable solvent system selection for its countercurrent chromatography (CCC) fractionation. EEGP was first fractionated (CCC1) using an aqueous biphasic solvent system composed of hexane-ethyl acetate-ethanol-water (1:0.8:1:1, v/v) in normal isocratic elution mode. This affording pure isolates of artepillin C and p-coumaric acid, along with isomeric mixtures of capillartemisin A/B and aromadendrin-4’-O-methyl ether/dihydrokaempferide. An offline second-dimension 2D-CCC (CCC2) fractionation of a non-polar fraction was performed using non-aqueous solvent system (hexane-chloroform-acetonitrile, 1:0.1:1, v/v), under reversed phase elution mode. This was followed by exclusion chromatography on Sephadex LH-20, yielding anacardic acid 19:1 as well as other phenolic lipid derivatives and cycloartenol triterpene. Further 2D-CCC x Sephadex LH-20 fractionation of a CCC1 subfraction resulted in the isolation of flavonoids such as betuletol, kaempferide, and isosakuranetin, along with the prenylated cinnamic acid derivative drupanin. This workflow enabled the annotation of 92 compounds in EEGP by LC/Q-TOF-MS out of which 20 were isolated by MDCCC.

Acknowledgements: FAPERJ, CNPq and CAPES (Financing Code 001).

OPTIMIZATION OF A GREENER HPLC METHOD FOR QUALITY CONTROL OF RADIOPHARMACEUTICALS USING THE SELECTIVITY TRIANGLE AND MULTIVARIATE DESIGN: A CASE STUDY OF ^{18}F-PSMA-1007

Gabriela Lemos Ribeiro de Souza*, Paulo Salles Neto, Ildefonso Binatti

Centro Federal de Educação Tecnológica de Minas Gerais, CEFET-MG Belo Horizonte, MG, Brazil, 30421-169

* Corresponding author: gabrielalemosrds@gmail.com

High-performance liquid chromatography (HPLC) plays a crucial role in the quality control of radiopharmaceuticals, where high selectivity, reproducibility, and resolution are required. However, conventional methods often rely on acetonitrile (ACN) and phosphate buffers, which pose significant environmental, health, and cost-related concerns. This study presents a systematic strategy for developing and optimizing a greener HPLC method for the purity analysis of ^{18}F-PSMA-1007 by replacing ACN with methanol and phosphate buffer with trifluoroacetic acid (TFA). Method development was guided by the solvent selectivity triangle and experimental design tools. The Snyder solvent triangle was used to select the appropriate organic modifier and a full factorial design was conducted to identify significant variables and its interactions. The optimized method was performed in isocratic mode using a mobile phase composed of methanol and 0.075% TFA (60:40, v/v), with a flow rate of 0.5 mL/min, and column temperature of 40 °C. This setup provided sharp, symmetrical peaks and baseline resolution between the active compound and its main impurities.
The method was fully validated according to national and international guidelines (INMETRO, ANVISA, Eurachem), demonstrating selectivity, linearity (R^2 = 0.9778), precision (RSD

Acknowledgements: The authors would like to thank CDTN, CEFET-MG, IntechLab, and FAPEMIG for their support and contributions to this work.

OPTIMIZATION OF A METHOD USING A HONEYCOMB-LIKE 3D PRINTED DEVICE FOR ROTATING-DISK SORPTIVE EXTRACTION OF MULTICLASS CONTAMINANTS FROM BREAST MILK

Anna Carolina Nickel Meireles*[1], Sofia Aquino Monteiro[2], Camila Scheid[2], Jean Lucas de Oliveira Arias[1], Sergiane Caldas Barbosa[1], Josias de Oliveira Merib[2]

[1]Universidade Federal do Rio Grande - FURG, Laboratório de Análise de Compostos Orgânicos e Metais - LACOM, Rio Grande, Rio Grande do Sul, Brazil, 96203-900
[2]Universidade Federal de Ciências da Saúde de Porto Alegre – UFCSPA, Grupo de Estudos em Preparo de Amostras e Cromatografia - GEPAC, Porto Alegre, Rio Grande do Sul, Brazil, 90050-170

* Corresponding author: annacnmeireles@gmail.com

Breast milk is the main source of nutrition for newborns and infants. The WHO recommends exclusive breastfeeding for up to 6 months and supplementary breastfeeding up to 2 years or more. In human milk banks, milk undergoes microbiological quality control to ensure food safety for newborns. However, in Brazil, there are no standardized measures to assess the presence of contaminants in breast milk. Therefore, breast milk can be a potential vehicle for the transfer of contaminants from mother to child, such as pesticides, pharmaceuticals, and personal care products, which have toxic effects on the baby's development, such as neurological, gastrointestinal, and reproductive problems. Therefore, this study aims to develop an analytical method for the determination of emerging contaminants using RDSE with a 3D printed rotating disk and GC-MS/MS. Two types of filaments, polyamide and polyamide + 15% of carbon fiber (PA + 15% C), were evaluated for the extraction of 13 analytes (9 parabens, caffeine, atrazine, bisphenol-A, and benzophenone-3), and the PA + 15% C filament was chosen due to its greater response for most analytes. Then, two Doehlert experimental designs were performed, one for the adsorption step, using agitation (500, 800, and 1100 rpm) and adsorption time (20, 45, 70, 95, and 120 min) as variables, and another for the desorption step, using agitation (500, 800, and 1100 rpm) and desorption time (5, 10, 15, 20, and 25 min) as variables. Therefore, the optimized RDSE technique was performed as follows: the 3D-printed disk composed of PA + 15% C was placed in a tube, and 5 mL of sample solution (1:4, sample:water) was added. The disk was then shaken using a shaking platform for 45 min at 500 rpm. After the adsorption step, the disk was removed from the solution, transferred to another tube, and the desorption step was performed with 800 µL of acetonitrile, shaking on a platform for 10 min at 1100 rpm. Finally, the organic phase was injected into the GC–MS/MS. The optimized method will be validated according to the SANTE guide and will be further applied to the determination of contaminants in real samples.

Acknowledgements: The authors acknowledge the scholarship provided by CAPES and the financial support provided by CNPq, FAPERGS and FINEP.

OPTIMIZATION OF A SOLID PHASE EXTRACTION WITH LOW TEMPERATURE PARTITIONING OF EMERGING CONTAMINANTS FROM WATER SAMPLES USING LAB-MADE MODERATE POLAR SORBENT

Mara Rubia Reis Pereira*, Anizio Marcio de Faria

Federal University of Uberlândia, Institute of Exact and Natural Sciences of Pontal, Ituiutaba, MG, Brazil.

* Corresponding author: mara.pereira@ufu.br

Solid-phase extraction (SPE) is a widely used and easily modifiable technique for the extraction and preconcentration of compounds. Typically, SPE comprises four steps: conditioning, loading, washing, and elution. The washing and elution steps usually employ solvents with opposite characteristics and are crucial for extraction efficiency. In this proposal, aiming to simplify the procedure and reduce the use of solvents, these two SPE steps were replaced by low-temperature partitioning (LTP) for the extraction of four emerging contaminants (naproxen, ibuprofen, diuron, and fipronil) from water samples. The SPE sorbent was prepared in the laboratory by thermal immobilizing poly(glycidoxypropylmethylsiloxane) on 40-70 µm silica particles – Si(PGDMS) – at 90 °C for 12 h. The extraction of compounds via SPE-LTP was optimized in a univariate way, evaluating the sorbent mass (50 to 200 mg), eluent type (methanol, acetonitrile, and ethanol), sample volume (50 to 1000 mL), eluent volume (0.5 to 2.0 mL), and freezing time (2 to 6 h). The optimized method consisted of three steps: (i) conditioning of the solid phase with 10 mL of ultrapure water, (ii) passage of 500 mL of water sample fortified with emerging contaminants, (iii) removal of the solid phase from the cartridge and addition of 1.0 mL of acetonitrile for low-temperature partitioning at -20 °C for 3 h, and subsequent analysis of the liquid organic phase (extract) by high-performance liquid chromatography with diode array detection. The recoveries of the four compounds were in the range of 80-105%, with a relative standard deviation of less than 20%, indicating that the SI(PGDMS) sorbent showed adequate selectivity for compounds with different polarities, and the SPE-LTP method showed good accuracy and precision. The SPE-LTP method showed quantification limits of less than 0.050 µg/L for the compounds and a matrix effect of less than 5%, indicating that LTP effectively purified the extract. Thus, the approach presented for SPE using LTP to replace the washing and elution steps resulted in a simpler method with lower solvent consumption than traditional SPE.

Acknowledgements: FAPEMIG (APQ-1901-22 and PCE-00390-25), CNPq, and FINEP (01.13.0371.00).

OPTIMIZATION OF CHROMATOGRAPHIC ANALYSIS FOR CONTINUOUS MONITORING OF NATURAL GAS BURNING OF PRE-SALT LAYER

Lucas Gustavo Costa*, Valdislaine Maria da Silva, Solidônio Rodrigues de Carvalho, Valério Luiz Borges, Marcelo Braga dos Santos, Alam Gustavo Trovó

Federal University of Uberlândia

* Corresponding author: lucasgustavodacosta@gmail.com

Brazilian pre-salt natural gas (PS-NG) remains underutilized due to its high CO2 content, which lowers its calorific value and complicates its use with existing infrastructure. However, research on high-power-density linear engines suggests using PS-NG for electricity generation, which would contribute to monetize this resource at the same time diversifying the national energy matrix. A gas chromatography method was developed to monitor the gases produced when burning PS-NG. This method uses He as the carrier gas, a Carboxen 1010 PLOT column (0.32 mm × 30 m with a 15 µm film thickness) and TCD and FID detectors. However, the long analysis time (50 min) limits its use for continuous monitoring of 14 analytes: H2, O2, N2, CO, CO2, CH4, C2H6, C2H4, C3H8, C3H6, C3H4, (propadiene and propyne), C4H10 (n-butane and isobutane). Thus, to increase the efficiency and usability of the method, a rotatable central composite design (RCCD) was applied to evaluate three factors: the split ratio, the purge gas pressurization rate and the column oven heating rate. The retention time, height, and width of the chromatographic peaks were then used as responses. The optimized method (total He flow = 51.2 mL/min; Tinj = 200 ºC; TTCD = TFID = 250 ºC; split = 1:14; temperature ramp: 35 ºC – 0 to 6 min, 35 ºC to 240 ºC – 6 to 10.1 min at a rate of 50 ºC/min, 240 ºC – 10.1 to 28 min; pressure ramp: 16 kPa – 0 to 5 min, 16 kPa to 180 kPa – 5 to 11.3 min at a rate 26 kPa/min, 180 kPa – 11.3 to 14.3 min, 180 kPa to 320 kPa – 14.3 to 15.7 min at a rate of 100 kPa/min, 320 kPa – 15.7 to 28 min) reduced the total run time by 40 % (from 50 to 30 min) and improved the shape of the chromatographic peaks (area/height) by 21 % for CO2; 25 % for isobutane; 28 % for CH4 and n-butane; 32 % for propadiene; 34 % for propyne; 54 % for O2, N2 and C3H8; 65 % for CO; and 95 % for C3H6. Thus, RCCD optimization improved the accuracy of the results and reduced analysis time. This helps minimize costs and enables online monitoring, which is essential for making real-time adjustments to the engine and ensuring energy efficiency and environmental compliance.

Acknowledgements: FINEP (2420/22), FAPEMIG (040/2022) and CNPq (307137/2021–0)

Optimization of enantioselective separation of the pesticide cyflumetofen using polysaccharide-based stationary phases

Isabella Sandrini Vieira*, Anderson R. M. de Oliveira

Department of Chemistry, FFCLRP, University of São Paulo

* Corresponding author: isasanvieira@usp.br

Cyflumetofen (CIF) is a chiral pesticide widely employed for the control of mites and insects and, due to its chirality, may exhibit enantioselectivity both in efficacy against target organisms and in toxicity toward non-target species. CIF residues have already been detected in fruit and vegetable samples, which highlights the need for analytical monitoring and the assessment of potential human health risks. In this context, the enantioselective separation of CIF becomes essential for a better understanding of its biological activity and toxicological impact. To this end, a chromatographic screening was performed with the objective of identifying suitable conditions for subsequent enantioselective analysis of CIF in biological studies. Two distinct chromatographic modes were investigated: reversed-phase, employing water/organic solvent mixtures (20:80), and polar organic mode, using pure organic solvents such as isopropanol (IPA), ethanol (EtOH), acetonitrile (ACN), and methanol (MeOH). All analyses were conducted at 30 °C with an injection volume of 20 µL. For MeOH and ACN, a flow rate of 0.5 mL/min was applied, while for IPA and EtOH, a reduced flow rate of 0.3 mL/min was required due to the higher backpressure generated by these solvents. Chiral separation was assessed by monitoring the resolution between enantiomer peaks and peak symmetry. The screening was carried out on ten chiral columns containing stationary phases based on amylose or cellulose derivatives. In reversed-phase assays, evidence of separation was observed with IPA and EtOH on the Chiralpak AD-H column (150 × 4.6 mm, 5 µm). In polar organic mode, IPA provided more efficient separation, while EtOH also showed resolution potential, albeit less pronounced, on the same Chiralpak AD-H column. Based on these findings, the chromatographic conditions that exhibited the best performance were further optimized using the Chiralpak AD-H column with IPA as the principal solvent. The mobile phase was defined as IPA: H2O (70:30), with a flow rate of 0.5 mL/min and a column oven temperature of 25 °C, resulting in a total run time of 12 min. Under these conditions, a resolution greater than 1.5 between the enantiomers was achieved, which is suitable for subsequent biological investigations.

Acknowledgements: FAPESP (grant number 2024/20783-4) and CNPq (grant number 304319/2024-4), CAPES (finance code 001).

OPTIMIZATION OF METHANOLIC EXTRACT PREPARATION FROM HUMULUS LUPULUS PELLETS USING DOEHLERT DESIGN AND QUANTIFICATION BY HPLC-DAD

Débora Nascimento Eiriz*[1], Rafael Ribeiro de Lacerda[1], Victor Eduardo Zúñiga Pávon[2], Lucas Silva Abreu[1], Francisco Paiva Machado[2], Leandro Machado Rocha[2], Caio Pinho Fernandes[2], Lucas Mattos Duarte[1]

[1]Institute of Chemistry, Fluminense Federal University
[2]Faculty of Pharmacy, Fluminense Federal University

* Corresponding author: deboraeiriz@id.uff.br

The optimization of extraction procedures is essential to improve the recovery of bioactive compounds from natural matrices, ensuring efficiency and reproducibility in analytical and industrial application1,2. In this study, a Doehlert experimental design and response-surface methodology were used in conjunction with the desirability function approach to optimize the preparation of methanolic extracts from 0.5 g of Humulus lupulus L. (hop) pellets, Columbus variety, using dynamic maceration. The effects of three independent variables were evaluated: extraction time (15–180 min), the proportion of water in a MeOH:H_2O mixture of the extraction solvent (0–50% H_2O), and solvent volume (5–15 mL). The experimental matrix allowed the systematic exploration of factor interactions while minimizing the number of required assays. Following extraction, the samples were analyzed by high-performance liquid chromatography with diode array detection (HPLC-DAD) to quantify the principal bioactive components, namely xanthohumol and hop bitter acids (α- and β-acids). The Doehlert model provided a reliable prediction of the optimal conditions, which were experimentally validated, thereby confirming the robustness of the model. In conclusion, it proved to be an efficient tool for the multivariate optimization of hop extraction parameters, enabling the maximization of bioactive compound yields with reduced experimental effort. This approach highlights the importance of experimental design methodologies in natural product research, particularly when targeting compounds of technological, industrial and pharmacological relevance.

Acknowledgements: Financial support: CAPES, FAPERJ, CNPq. Institutional support: LTPN and the Analytical Center, Faculty of Pharmacy (LCAN-CMF), Fluminense Federal University.

OPTIMIZATION OF SAMPLE PREPARATION FOR QUANTIFICATION OF β-ALANINE AND CARNOSINE IN MUSCLE TISSUE BY LC-MS/MS

Taís Betoni Rodrigues*[1], Maria Eduarda Diniz[1], Bryan Saunders[2], Fernando Mauro Lanças[1], Álvaro José Santos-Neto[1]

[1]Laboratory of Chromatography (CROMA), São Carlos Institute of Chemistry, University of São Paulo, São Carlos, SP, Brazil
[2]Faculty of Medical Sciences, University of São Paulo, São Paulo, SP, Brazil

* Corresponding author: tais.betoni.rodrigues@usp.br

β-Alanine and carnosine are bioactive compounds involved in muscle physiology, commonly studied in exercise biochemistry and metabolic research. However, variability in reported outcomes suggests that supplementation may not be effective for all individuals, justifying the need for studies that identify determinants of a positive response. The quantification of these substances in biological samples is fundamental step for the evaluation of the response of each individual. Reliable quantification of these analytes in muscle tissue requires sensitive and selective methods such as liquid chromatography coupled–tandem mass spectrometry (LC-MS/MS). However, sample preparation remains a critical step that can significantly impact analytical performance, especially in complex biological matrices like muscle. This study aimed to optimize a sample preparation protocol to quantify β-alanine and carnosine in muscle by LC-MS/MS. Different sample preparation variables were evaluated, including extraction solvents (acetonitrile, hydrochloric acid and perchloric acid), temperature control, and tissue-homogenization strategy (with or without liquid-nitrogen freezing). Optimization was guided by peak shape, analyte peak area, and signal-to-noise ratio. Chromatographic separation was performed using an Acquity UPLC BEH HILIC (100 × 2.1 mm, 1.7 µm) column, maintained at 30 °C under gradient elution. Detection was carried out by ESI positive and in multiple reaction monitoring (MRM) mode. Acidic extraction under temperature control, combined with liquid-nitrogen freezing, yielded higher peak areas. Moreover, the use of $HClO_4$ for extraction allowed the detection of β-alanine also from bovine samples. Freezing with liquid nitrogen proved to be a critical step during the experiments. The optimized sample preparation protocol enables the detection of β-alanine and carnosine in bovine and poultry muscle by LC-MS/MS. Next steps include validating the protocol in human muscle samples.

Acknowledgements: CNPq nº314731/2021-0 and 309282/2025-0; FAPESP nº 22/07258-2, 21/06836-0, 25/12047-9, 23/07159-7, 17/02147-0; INCT nº 406760/2022-5.

OPTIMIZED LLE-LTP SAMPLE PREPARATION FOR FOOD SAFETY: ASSESSING AGROCHEMICAL RESIDUES IN PLANT-BASED MILK

Yuri Arrates Rocha*[1], Almir Custodio Batista Junior[1], Lauanne Rocha Silva[2], Heloísa Siqueira Santos[1], João Victor Borges Assis[1], Simone Nascimento[3], Andréa Rodrigues Chaves[1]

[1]Instituto de Química, Universidade Federal de Goiás, Goiânia, Brasil.
[2]Instituto de Química, Universidade Federal de Goiás, Goiânia, Brasil;.
[3]Agilent Brasil, Barueri, São Paulo, Brasil.

* Corresponding author: yuriarrates@hotmail.com

The demand for alternative food sources has grown significantly, primarily driven by ethical concerns and health-related issues such as lactose intolerance, milk allergies, and elevated cholesterol levels. This trend is largely motivated by the perceived sustainability and environmental benefits of plant-based products compared to conventional animal-based foods. However, studies addressing pesticide residues in these products remain limited, despite their potential risks for human health. Studying pesticide residues in plant-based milk (PBM) is particularly relevant, given that these products are commonly derived from crops (e.g. almonds, soybeans, oats, and other plant sources), which are often associated with the use of pesticides to enhance crop yield and production efficiency. The determination of these multiresidues is commonly driven by liquid chromatographic coupled to mass spectrometry systems (LC-MS). Due to the nature of the analysis technique, a sample preparation step is needed, to clean-up the sample and extract these analytes from the matrix. Conventional extraction methods for pesticides, like solid phase extraction and QuEChERS, involve multiple steps, laborious work and high consumption of solvents. As a simpler alternative, low-temperature partitioning (LTP) has been integrated into liquid-liquid extraction (LLE), allowing the use of fully miscible extractant solvents in aqueous samples. Upon freezing, the aqueous phase solidifies while the extractive organic phase remains liquid, enabling analyte partitioning and matrix cleanup in a single step. In this sense, the study aimed to determine multiresidues of 32 pesticides presented on PBM through LC-MS/MS analysis with optimized sample preparation based on LLE/LTP. The LLE/LTP method was optimized through a two-step DOE approach: an initial fractional factorial design (2^{6-2}) identified significant variables, followed by a full factorial design to refine conditions. Optimal extraction was achieved using 250 µL of sample, 250 µL of water, and 500 µL of acetonitrile, vortexed for 10 s and centrifuged for 1 min. A minimum of 4h at –20 °C freezing time was adopted. The supernatant was conducted by LC-MS/MS analysis. An Analytical Performance of the method was conducted, demonstrating excellent linearity, selectivity and low limits of quantification. Besides precision and accuracy values in accordance with validation guidelines.

Acknowledgements: INCT- ALIM; CNPq; CAPES; FAPEG .

OPTIMIZED MICROEXTRACTION APPROACH FOR PESTICIDE ANALYSIS IN WATER USING PDMS/BIOCHAR COMPOSITES FROM BEE POLLEN

Valentina Rojas Candia*, Alejandra Molina Balmaceda, Juan José Triviño, Daniel Arismendi, Pablo Richter

Department of Inorganic and Analytical Chemistry, Faculty of Chemical and Pharmaceutical Sciences, University of Chile, P.O. Box 233, Santiago, Chile

* Corresponding author: valentina.rojas.c@ug.uchile.cl

Sample preparation is a crucial step in the determination of analytes in real samples, aiming to eliminate or minimize matrix interferences and to preconcentrate target compounds to trace or ultra-trace levels. Several microextraction technologies have emerged as efficient alternatives for the analysis of liquid samples, although their performance strongly depends on the characteristics of the sorbent phase used. In recent years, various sorbent materials have been developed to enhance the extraction of organic compounds from complex matrices. Among them, composite sorbents have shown great promise, as they can combine multiple interaction mechanisms between the analytes and the sorbent, thereby improving extraction efficiency.

In this work, novel composite sorbent phases based on polydimethylsiloxane (PDMS) and bee pollen-derived biochar (BC), supported on canvas fabric, were designed and evaluated for the extraction of eight pesticides (carbofuran, chlorothalonil, indoxacarb, prophenophos, transfluthrin, tetramethrin, chlorpyrifos, and λ-cyhalothrin) from water samples using rotating disk sorptive extraction (RDSE). Composites with different PDMS/BC ratios were prepared, with the 10:1 (PDMS:BC) ratio showing the best adhesion to support and mechanical stability.

Chemical and hydrodynamic variables of the extraction process were optimized, with optimal conditions found at pH 6, 1% w/v NaCl, 3% v/v methanol (as a matrix modifier), 20 mL sample volume, 60 min of extraction time, and acetonitrile as the elution solvent. Extraction efficiencies were evaluated by high-performance liquid chromatography with diode array detection (HPLC-DAD), with recoveries between 8% and 44% and relative standard deviations (%RSD) from 0.8% to 13%. These results demonstrate the reproducibility of the method and highlight the potential of PDMS/BC composites as alternative sorbent phases for RDSE in the determination of pesticides in aqueous matrices, paving the way for future improvements in analytical sensitivity and robustness.

Acknowledgements: This work was supported by FONDECYT, Chile (Regular Project 1220225, Initiation Project 11240183) and ANID, Chile (National PhD scholarship 21230953).

Optimizing HS-SPME and static headspace-GC-MS for (semi-)volatile organic compounds profiling in virgin and post-consumer recycled polyolefins

Luis Eduardo Silva Nascimento*[1], Marisa Padula[2]

[1]Packaging Technology Center, Institute of Food Technology, Campinas, São Paulo, Brazil; Science Center for the Development of Solutions for Post-Consumer Waste: Packaging and Products (CCD Circula), Institute of Food Technology, Campinas, São Paulo, Brazil; Federal University of Pelotas (UFPel), Eliseu Maciel School of Agronomy, Department of Agricultural Science and Technology, Pelotas, Rio Grande do Sul, Brazil.
[2]Packaging Technology Center, Institute of Food Technology, Campinas, São Paulo, Brazil; Science Center for the Development of Solutions for Post-Consumer Waste: Packaging and Products (CCD Circula), Institute of Food Technology, Campinas, São Paulo, Brazil

* Corresponding author: luiseduardo_sn@hotmail.com

The safety of polyolefins (PO), particularly post-consumer recycled resins (PCR), has raised increasing concern for food-contact applications. While HS-SPME provides higher efficiency in analyzing (semi-)volatile organic compound semi-VOCs, static headspace (SHS) remains widely used in service laboratories due to its lower cost. Thus, the present study aimed to characterize the profile of semi-VOCs in virgin and PCR polyolefin pellets, including high-density polyethylene (HDPE) and polypropylene (PP), using SHS and HS-SPME coupled to GC-MS. The study further employed multivariate optimization approaches, including Plackett–Burman and Central Composite Rotatable Designs. Three virgin samples and three PCR samples were analyzed, including one HDPE and two PP for each purity class. The sample preparation and injection system using SHS and HS-SPME was fully automated. Compound identification was based on deconvolution using the Unknowns Analysis software, in which the mass spectra were compared with the NIST 23 library, considering a score ≥ 80. In addition, the linear retention index, based on a series of alkanes with an acceptance window of ±30, was also taken into account. HS-SPME proved to be a powerful tool for revealing compounds not extracted by SHS. In PCR samples, HS-SPME extracted 81%, 51%, and 65% more compounds than SHS in R1, R2, and R3, respectively. For virgin samples, HS-SPME extracted 17%, 30%, and 4% more compounds than SHS in V1, V2, and V3, respectively. Among the compounds exclusively identified by HS-SPME, acetophenone, anthracene, and benzophenone were found in PCR samples, while naphthalene was observed in virgin samples. According to the International Agency for Research on Cancer (IARC), naphthalene, anthracene, and benzophenone are classified as possibly carcinogenic to humans. Other identified compounds were mainly hydrocarbons, originating from the natural degradation of polymers. Recycled samples showed a greater number of substances, likely due to the diversity of raw materials and contamination from the first use of PCR packaging. Therefore, HS-SPME may be more suitable for an exhaustive analysis of semi-VOCs, especially when the polymer is intended for food contact materials.

Acknowledgements: This study was financed by the São Paulo Research Foundation (FAPESP), Brazil. Process Number #2024/00347-5 and #2021/11967-6.

OTIMIZAÇÃO DA METODOLOGIA PARA DETERMINAÇÃO DE ÁCIDO FÓLICO EM FARINHA DE TRIGO POR CROMATOGRAFIA LÍQUIDA DE ALTA EFICIÊNCIA COM DETECTOR ULTRAVIOLETA (CLAE-UV)

Fabiano Narciso Paschoal*, Maria de Fatima Gomides, Mariem Rodriguea Ribeiro da Cunha, Lorena Thais Souza Dias1, Luciana Maria Bittecourt, Shirley Santana Silva Chaves, Fabiano de Oliveira Silva

Fundação Ezequiel Dias

* Corresponding author: fabiano.paschoal@funed.mg.gov.br

A carência de ácido fólico está associada principalmente a defeitos relacionados a má-formação do tubo neural em recém-nascidos, sendo considerada um problema de saúde pública. Uma das estratégias para reduzir e prevenir doenças é o enriquecimento de alimentos com micronutrientes. Diante disso, no Brasil, desde 2002, é obrigatório o enriquecimento das farinhas de trigo com ácido fólico. Atualmente, a RDC 150/2017 prevê a quantidade de fortificação de ácido fólico em farinhas de trigo de 140 a 220 µg/100g. Em Minas Gerais, a Secretaria Estadual de Saúde (SES), através da Vigilância Sanitária e em parceria com a Fundação Ezequiel Dias (FUNED), efetua um programa de monitoramento da qualidade dos alimentos, intitulado PROGVISA. Para realizar o monitoramento da fortificação de ácido fólico em farinha de trigo foi necessário otimizar e validar uma metodologia empregando a cromatografia líquida de alta eficiência com detector ultravioleta. Os parâmetros de validação avaliados foram linearidade, seletividade, recuperação, precisão e limites de detecção e quantificação, sendo aprovados segundo os critérios de desempenho preconizados no documento orientativo INMETRO DOQ-CGCRE-008. Foram analisadas 25 amostras de farinha de trigo sendo cinco coletadas pelo PROGVISA e 20 adquiridas em supermercado de Belo Horizonte. O estudo da linearidade foi realizado na matriz, assumindo sua presença, na faixa de 62,5 a 312,5 µg /100g e comprovada com base das premissas do modelo de regressão linear simples. A recuperação foi aceitável nos três níveis estudados, ficando entre 85,17% e 90,31%. Os desvios padrão relativos sob condições de repetibilidade e de precisão intermediária foram aceitáveis variando de 12,60% a 14,48% e 18,89% a 21,72%, respectivamente. Os limites de detecção e quantificação teóricos foram 4,549 e 15,162 µg /100, respectivamente. Os resultados mostraram que 11 amostras foram insatisfatórias, correspondendo a 44% do total avaliado, sendo que dessas 32% apresentaram um teor de ácido fólico abaixo do limite inferior estabelecido pela legislação. O método desenvolvido se mostrou adequado para realizar o monitoramento do teor ácido fólico em farinha de trigo comercializadas no estado de Minas Gerais.

OVERCOMING MATRIX COMPLEXITY: DEVELOPMENT OF SAMPLE PREPARATION METHODS FOR MULTIRESIDUE DETERMINATION OF PESTICIDES IN WILDLIFE USING UHPLC-MS/MS

Luana Floriano*, Jose Dilson Francisco da Silva, Daniela Wouters de Medeiros, Lais Pasinatto Santos, Renato Zanella

Laboratory of Pesticide Residues Analysis (LARP), Research Group for Chromatography and Mass Spectrometry, Federal University of Santa Maria, 97105-900 Santa Maria -RS, Brazil

* Corresponding author: luanaflorianoqmc@gmail.com

The intensive and expanding use of pesticides in Brazilian agriculture is a well-documented reality. While crucial for productivity, this widespread application raises significant concerns about its impact on ecosystems. The analytical determination of pesticide residues in biological matrices from wild animals presents challenges as complexity of matrices, limited sample amount, and the vast number of potential analytes. This work aimed to develop and validate comprehensive, sensitive, and robust multiresidue methods (>150 pesticides) for the determination of a wide scope of pesticides in a diverse wildlife animals, including mammals (tapirs, rodents, dolphins, and bats), insects (honeybees and wild bees), and fish. Methods included QuEChERS, salting-out liquid-liquid extraction (SALLE), and solvent-assisted salt liquid-liquid extraction (SASLE) for sample preparation. To achieve the necessary clean-up and mitigate matrix effects, extracts were purified using d-SPE with the sorbents C18, PSA and GCB. Final analysis was performed using UHPLC-MS/MS Xevo TQ-XS and APGC-MS/MS, both from Waters. The methods were validated assessing parameters such as linearity, precision, accuracy, recovery, matrix effects, LOD and LOQ. The developed methods proved to be efficient for the simultaneous extraction and quantification of over 150 pesticides from complex matrices such as muscle, fat, milk, liver, and urine at very low levels. Validation results confirmed that the methods are selective, accurate (recoveries 70-120%) and precise (RSD ≤20%). The application of these methods in a monitoring study revealed the presence of pesticide residues in several species. The data generated is indispensable for informing public policy, developing conservation strategies, and ultimately mitigating the environmental impact of agricultural practices on biodiversity.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

PECTIN MICROGELS AS AN EXTRACTING PHASE FOR ORGANIC COMPOUNDS IN AQUEOUS MATRICES

Andressa Marinho*[1], Daiani Canabarro Leite[2], Bruno José Gonçalves da Silva[1]

[1]Universidade Federal do Paraná
[2]Universidade Federal de Santa Maria

* Corresponding author: andressamar4@gmail.com

The global population increase is directly associated with industrial expansion, which consequently leads to the emission of harmful substances into the environment. Therefore, the monitoring of these substances is essential to better understand their effects on human health and to enable more effective control strategies. In this context, the demand for advanced sample preparation techniques in Analytical Chemistry has grown significantly, particularly to enhance the selectivity and pre-concentration of analytes. This need is especially critical in polar matrices, where highly polar compounds tend to interact more strongly with the matrix itself than with the extractive phase. This study proposes the development of a novel extractive phase based on pectin microgel, applied in dispersive micro-solid phase extraction (D-µSPE) of seven analytes selected for their distinct physicochemical properties (log Kow: –0.63 to 3.41; pKa: 1.62 to 10.47) and importance for public health monitoring, followed by determination via gas chromatography–mass spectrometry (GC/MS). The material, synthesized from pharmaceutical-grade pectin (PCusp), successfully extracted all analytes, demonstrating higher extraction efficiency for caffeine compared to butylparaben, which highlights its amphiphilic character and strong affinity for highly polar compounds. Scanning Electron Microscopy (SEM) micrographs revealed a highly porous structure, with the material forming predominantly spherical particles in the micrometer range when dispersed in aqueous media. The microgel exhibited a crosslinking degree of 36%, enabling it to swell up to 20 times its initial mass. After 24 hours, approximately 55% of the absorbed water was lost, indicating high water retention capacity and a low diffusion rate from the internal phase to the external medium. These characteristics confirm the material’s effectiveness as an extractive phase, promoting efficient analyte retention and entrapment within the polymeric network.

Acknowledgements: The authors are grateful to CAPES and CNPq for the financial support and scholarships.

PERFIL DE ÁCIDOS GRAXOS DE SNACKS CHIPS COMERCIALIZADOS EM FORTALEZA-CE

Cleidiane Gomes Lima[1], Felipe Sousa da Silva[1], Mairlane Silva de Alencar[1], Denilson Gonçalves Queiroz[1], Renata Oliveira da Silva[1], Luana Guabiraba Mendes[2], Crisiana de Andrade Nobre[3], Maria Aparecida Liberato Milhome[2]

[1]Núcleo de Tecnologia e Qualidade Industrial do Ceará - NUTEC
[2]Instituto Federal de Educação, Ciência e Tecnologia do Ceará (IFCE)
[3]Universidade Federal do Ceará (UFC)

Os snacks chips são feitos principalmente à base de farinha ou fubá de milho, geralmente frito ou assado e costumam ser temperados com sabores artificiais, como queijo, churrasco, cebola, bacon, entres outros. No entanto, as informações sobre sua composição química são insuficientes. Este estudo teve como objetivo caracterizar o perfil de ácidos graxos destes snacks chips. Foram analisados 4 tipos de snacks chips nos sabores pipoca doce (PD), pipoca sabor manteiga (PM), snack sabor costela (SC) e snack sabor cebola e salsa (SCS). Para a análise do perfil de ácidos graxos, as amostras foram esterificadas pelo método de prepraração de esteres metílicos do Adolfo Lutz. Os ácidos graxos foram determinados por Cromatografia em fase Gasosa por Detecção por Ionização de Chama (GC-FID), equipada com colunar capilar SP-2560 (100m x 0,25mm x 0,2µm), com o gás de arraste Nitrogênio (1mL/min), injeção no modo split (1:10), volume de injeção 1µL e temperatura do detector 260 °C. Os teores de gorduras totais variaram de 6,31% a 32,22%. Os valores dos ácidos graxos predominantes foram palmítico (1,27 - 8,64%), esteárico (0,15 - 1,12%), oléico (1,27 - 5,24%) e linoléico (3,34 – 16,35%). Os ácidos graxos trans, não foram detectados nas amostras, não excedendo o valor estabelecido pela legislação vigente, destinados ao consumidor final e nos alimentos ao serviços de alimentação. Desta forma, o estudo contribui fornecendo informações relevantes tanto para a indústria de alimentos quanto para os consumidores e órgãos reguladores.

Acknowledgements: Instituto Nacional de Ciência e Tecnologia – Alimentos (INCT-ALIM)
Núcleo de Tecnologia e Qualidade Industrial do Cceará (NUTEC)
Instituto Federal de Educação, Ciência e Tecnologia do Ceará (IFCE) – Campus Limoeiro do Norte.

PERFIL DE ÁCIDOS GRAXOS E IMPACTOS DA SECAGEM CONVECTIVA ASSISTIDA POR ULTRASSOM NA ESTABILIDADE OXIDATIVA DE SEMENTES DE ABÓBORA

Sâmela Leal Barros[1], Nahanna Pereira Barbosa[1], Ícaro Gusmão Pinto Vieira[1], Ana Júlia de Brito Araújo[2], Marcos dos Santos Lima[2], Lucicléia Barros Vasconcelos*[1]

[1]Universidade Federal do Ceará
[2]Instituto Federal do Sertão Pernambucano

* Corresponding author: lucicleia_barros@ufc.br

Este estudo analisou o impacto do ultrassom associado à secagem convectiva na composição de ácidos graxos e estabilidade oxidativa de farinhas de sementes de abóbora (Cucurbita maxima). Experimentos foram conduzidos nas condições controle (50°C, sem ultrassom), E1 (5 min de ultrassom, 30% de amplitude, 50°C) e E3 (5 min de ultrassom, 70% de amplitude, 50°C). A análise lipídica foi realizada por cromatografia gasosa acoplada à espectrometria de massas (CG-EM), e compostos fenólicos foram quantificados para avaliar seu papel antioxidante. Os resultados demonstraram que os ácidos graxos insaturados, como o ácido oleico (ω-9) e o ácido linoleico (ω-6), apresentaram maior concentração no controle (40,36% e 28,70%, respectivamente). Esses teores foram reduzidos em tratamentos com ultrassom, especialmente em E3 (37,50% e 26,00%, respectivamente), sugerindo que maiores amplitudes intensificam a degradação lipídica. Por outro lado, os ácidos graxos saturados, como o ácido palmítico e o ácido esteárico, apresentaram concentrações maiores nos tratamentos com ultrassom, alcançando até 16,20% e 16,71% em E3 e E1, respectivamente. Os compostos fenólicos detectados, como o ácido gálico e a procyanidina B2, demonstraram potencial antioxidante, mas seus efeitos foram limitados dependendo das condições de ultrassom. O tratamento E1 (30% de amplitude) preservou os maiores valores relativos de compostos fenólicos e exibiu a menor redução nos ácidos graxos insaturados, indicando que condições mais suaves de ultrassom favorecem o equilíbrio entre a preservação de antioxidantes e a estabilidade lipídica. Em contraste, em E3 (70% de amplitude), observou-se maior redução dos fenólicos e intensificação da degradação lipídica, destacando o impacto negativo de parâmetros mais agressivos. Embora os fenólicos detectados auxiliem parcialmente na manutenção da estabilidade lipídica, o potencial antioxidante apresentou limitações sob condições de maior amplitude de ultrassom. Medidas complementares, como a adição de antioxidantes externos (tocoferóis, ácido ascórbico) ou o controle atmosférico com gases inertes, são sugeridas como estratégias promissoras para potencializar a preservação dos ácidos graxos insaturados e ampliar a funcionalidade das farinhas de sementes. Conclui-se que a modulação dos parâmetros de ultrassom, em conjunto com estratégias adicionais de preservação, pode equilibrar a eficiência antioxidante dos fenólicos naturais com a conservação da qualidade lipídica, garantindo alto valor nutricional e maior potencial de aplicação industrial.

Acknowledgements: Ao CNPq por meio do Instituto Nacional de Ciência e Tecnologia em Química Analítica de Alimentos: Segurança de Alimentos e Caracterização de Alimentos Funcionais (INCT-ALIM). A FUNCAP por meio do projeto PDPG Edital 04/2021.

PERFIL DE COMPOSTOS FENÓLICOS DE EXTRATOS DE MORUS NIGRA POR RP-HPLC/DAD UTILIZANDO SOLVENTES EUTÉTICOS PROFUNDOS NATURAIS (NADES) E ETANOL

Tháila Pimentel Albuquerque Moura*[1], Lívia de Sousa da Cunha[1], Suzana Oliveira de Araujo[1], Larissa Íris da Silva Monteiro[2], Marcos dos Santos Lima[3], Ana Julia de Brito Araújo Carvalho[3], Lucicléia Barros de Vasconcelos Torres[1]

[1]Universidade Federal do Ceará
[2]Universidade Federal da Paraíba
[3]Instituto Federal do Sertão Pernambucano

* Corresponding author: thaila.pim@gmail.com

Esta pesquisa buscou identificar e quantificar os compostos fenólicos individuais dos extratos da folha da amora miura (Morus nigra) com diferentes solventes por RP-HPLC/DAD. Os extratos foram preparados na proporção de 1:10 (m/v) de pó da folha de amora para solvente. Os solventes eutéticos naturais profundos (NADES) foram preparados utilizando a mistura do cloreto de colina com dois ácidos orgânicos doadores de ligação de hidrogênio, ácido lático e o ácido cítrico, ambos utilizados individualmente com o cloreto de colina na proporção e razão molar de 1:1 (p/p) e dissolvidos com adição de 20% (m/m) de água. O solvente hidroalcoolico foi preparado na proporção de 50% (v/v). O perfil dos compostos fenólicos individuais por HPLC foi realizado utilizando o cromatógrafo líquido Agilent 1260 Infinity LC System equipado com bomba de solvente quaternário e sistema de desgaseificação (modelo G1311C), compartimento termostatizado para colunas modelo G1316A, amostrador automático modelo G1329B e detector de arranjo de diodos – DAD modelo G1315D. Foram quantificados 32 compostos fenólicos: 12 ácidos fenólicos, 2 aldeídos fenólicos, 1 estilbenos, 4 flavanonas, 8 flavonóis e 5 flavonóis. Os ácidos fenólicos foram os compostos que apresentaram os maiores teores com 2344,39 a 205,38 mg/kg, seguidos dos flavonóis com 1668,51 a 179,36 mg/kg. Dentro da família dos ácidos fenólicos, o composto que apresentou o maior teor foi o ácido clorogênico (70,24 a 1324 mg/kg). Entre os flavonóis, destacam-se a quercitina 3-glicosídeo (30,02 a 980,67 mg/kg). O extrato da folha da amora miura utilizando o solvente hidroalcoólico apresentou os maiores teores quantificados e identificados seguido do extrato que continha o cloreto de colina + ácido lático como solvente de extração. O solvente hidroalcoólico foi mais eficiente na extração, e os NADES, em especifico o doador de ligação de hidrogênio ácido lático, se mostraram promissores para compostos fenólicos individuais.

Acknowledgements: Ao CNPq por meio do Instituto Nacional de Ciência e Tecnologia em Química Analítica de Alimentos: Segurança de Alimentos e Caracterização de Alimentos Funcionais (INCT-ALIM)

PERFIL DE VOLÁTEIS EM KOMBUCHA ADICIONADAS DE PÓ DE SEMENTES DE AÇAÍ POR GS – MS

Mayrla Kauane Maia de Sousa*[1], Dhenica Pereira de Lima[1], Maria Edlane A. da Silva[1], Felipe Sousa da Silva[2], Mayra Gárcia Maia Costa[3], Maria Aparecida Liberato Milhome[1]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará (IFCE)
[2]Núcleo de Tecnologia e Qualidade Industrial do Ceará (NUTEC)
[3]Universidade da Integração Internacional da Lusofonia Afro-Brasileira (UNILAB)

* Corresponding author: mayrla.kauane.maia07@aluno.ifce.edu.br

As sementes de açaí, correspondem a 70 % do peso do total do fruto e possuem compostos biologicamente ativos e alto valor de fibra ainda pouco explorados cientificamente. A Kombucha consiste em uma bebida com propriedades probióticas proveniente da fermentação do chá da Camellia sinenses e uma Cultura Simbiótica de Bactérias e Leveduras (SCOBY) que tem ganhado espaço no mercado devido a seus benefícios à saúde. O suco de caju clarificado, conhecido por cajuína, é considerado patrimônio cultural do Nordeste,evido seu sabor e características únicas. Diante disso, o objetivo do trabalho foi avaliar os compostos voláteis - CVs formados após o processo de fermentação de kombucha elaborada com adição de pó torrado da semente do açaí (PSA) no processo de infusão de chá verde e saborizada com cajuína. As bebidas (elaborada -KPSA e controle- KC) foram fermentadas durante um período de 8 dias, com 5 g/L de chá verde, 50 g/L de sacarose e 10 mL/ L de cajuína, sendo adicionado de 5% de PSA no processo de infusão para a kombucha formulada-KPSA. Para determinar os possíveis CVs formados após a fermentação foram realizadas análises qualitativas, usando SPME/ GC-Q-MS (Thermo), com fibra polidimetilsiloxano-carboxen (PDMS-CAR, 80µm) nas condições de 65 ºC/ 10 min de exposição da fibra. A identificação dos compostos foi realizada através da similaridade dos picos, com auxílio da Biblioteca NIST, para identificação dos sabores e aromas de cada composto. As amostras apresentaram 12 e entre 12-17 CVs em KC e KPSA, respectivamente. Destes, foram identificados os compostos majoritários (>1%), sendo 9 CVs na amostra KC e 12 CVs na amostra com PSA, onde verificou-se a predominância de álcoois e ésteres. Os aromas e sabores predominantes foram de floral, frutado e doce. A adição do PSA acrescentou compostos que não estavam presentes na KC, como, os ácidos orgânicos, que naturalmente são formados durante a fermentação da kombucha, Dessa forma, as bebidas apresentaram características promissoras para a inovação de bebidas funcionais, o PSA contribui para utilização dos subprodutos do açaí.

Acknowledgements: INCT-CNPQ, PRAPG-CAPES, FUNCAP, NUTEC.

PERFIL QUÍMICO DOS COMPOSTOS ORGÂNICOS VOLÁTEIS DO FRUTO DE MELÃO (Cucumis melo L.) AFETADO PELA MANCHA BACTERIANA POR HS-SPME/GC-MS

Luana Kelly da Silva Ramos[1], Marilene Nunes Oliveira[1], Edenilson dos Santos Niculau*[2]

[1]Universidade Federal do Sul e Sudeste do Pará
[2]Universidade Federal do Norte do Tocantins

* Corresponding author: edenilson.niculau@ufnt.edu.br

A mancha aquosa, causada pela bactéria Acidovorax citrulli, é uma doença ainda sem controle, a qual provoca sérios problemas à cultura das cucurbitáceas, principalmente o melão, o que tem sido motivo de preocupação dada a importância econômica desta cultura. Há um reduzido número de estudos e informações quando se trata do patossistema meloeiro pós-colheita associado à bactéria A. citrulli. Nesse contexto, o presente trabalho tem como objetivo elucidar o perfil metabólico volátil da bactéria A. citrulli e do melão (Cucumis melo L.), bem como avaliar o extrato bruto da A. citrulli nos ensaios alelopáticos e fitotóxicos. Para extração dos Compostos Orgânicos Voláteis (COVs) foi utilizada a técnica de microextração em fase sólida via headspace (HS-SPME) e para caracterização, a técnica de cromatografia gasosa acoplada à espectrometria de massas (CG-EM). A cepa A. citrulli 180 (Aac180) foi cedida pelo Laboratório de Fitobacteriologia da Universidade Federal Rural de Pernambuco. As condições de produção e extração dos COVs foram otimizadas a partir de um planejamento experimental fatorial 23 no qual foram avaliadas as variáveis fibra de adsorção (PDMS/DVB e PDMS), temperatura de extração (30 °C e 50 °C) e tempo de extração (15 min e 30 min). A partir das condições ótimas (fibra de adsorção PDMS/DVB, tempo de extração 15 minutos e temperatura de extração 30ºC) foram explorados os COVs da A. citrulli e desta em associação com o melão. Foram identificados 10 COVs associados ao perfil químico da A. citrulli e 09 COVs na associação com o melão, sendo os componentes benzaldeído, álcool feniletílico e sorbato de etila exclusivos do processo de interação. Além disso, foram realizados os ensaios aleloquímicos e fitotóxicos do extrato da A. citrulli. O ensaio aleloquímico permitiu verificar o potencial uso de A. citrulli como recurso natural promissor a prospecção de substâncias com potencial bioherbicida, pela capacidade de inibir a germinação de sementes de alface. O teste de fitotoxicidade confirmou que o álcool feniletílico possivelmente pode ser o fitotóxico em plântulas de melão. Assim, sugere-se que este componente pode ser uma fitotoxina secretada pela bactéria no fruto.

Acknowledgements: INCT-ALIM; CAPES

Pesticides Multiresidue determination in processed foods by UHPLC-MS/MS and LPGC-MS/MS

Luiza Tiemi Morikawa Shiose, Yuri Limeira Freire, Graziela Cristina Rossi Moura Andrade, Claudia Maria Barbosa, Kleber Ribeiro Dutra, Sérgio Henrique Monteiro*

Pesticide Residue Laboratory, Reference Laboratory for Residues and Contaminants – Instituto Biológico, São Paulo, Brazil

* Corresponding author: sergio.monteiro@sp.gov.br

Pesticides are widely used in agriculture to increase crop productivity; however, their application may lead to residues in food during cultivation, storage, and even after processing, thereby posing risks to human health. Although Brazilian legislation establishes maximum residue limits (MRLs) for raw agricultural commodities, there are no defined MRLs for processed foods. Ensuring compliance with MRLs in raw foods is already a challenge, while for processed products it becomes virtually impossible due to the lack of legislation and monitoring. In this study, 66 processed food samples derived from five different crops (corn, wheat, soybean, orange, and grape), purchased from supermarkets in São Paulo city, Brazil, were analyzed. Sample preparation and extraction followed the QuEChERS method, with detection carried out using ultra-high-performance liquid chromatography coupled to triple quadrupole mass spectrometry (UHPLC-MS/MS, Vanquish/TSQ Quantis Plus system) and low-pressure gas chromatography coupled to triple quadrupole mass spectrometry (LPGC-MS/MS, Agilent 6890 A GC / 7000 system). Liquid chromatographic separation was performed on a Thermo Accucor aQ C18 column (2.1 × 100 mm, 6 µm) preceded by a guard column, using methanol and water-based mobile phases with ammonium formate and formic acid in a gradient up to 98% organic phase. The injection volume was 10 µL, with the column maintained at 25 °C. Gas chromatographic separation employed a low-pressure configuration (Rtx-5ms 15 m × 0.53 mm ID × 1.00 µm analytical column, 1 m × 0.53 mm ID integrated transfer line, and 5 m × 0.18 mm ID Hydroguard restrictor). The oven temperature program started at 75 °C for 0.5 min, ramped to 250 °C at 30 °C/min, followed by an increase of 10 °C/min up to 310 °C, held for 1.67 min, resulting in a total run time of only 14 min. Detection was performed on triple quadrupole mass spectrometers, using electrospray ionization in positive and negative modes for LC, and electron impact ionization at 70 eV in dMRM mode for GC. A total of 272 pesticides were investigated, including compounds not authorized for the analyzed crops, and prohibited residues were identified in all of them. The results demonstrate that industrial processing does not completely eliminate contaminants. Findings in processed foods highlight the urgent need to expand control measures and revise current legislation, addressing not only raw agricultural products but also foods in the form they are consumed, with the aim of ensuring food safety and environmental preservation.

Acknowledgements: FAPESP Processo: 2022/01101-4; CNPq INCT – ALIM / PIBIC

PHYTOCHEMICAL CHARACTERIZATION OF RIPE CARNAÚBA (Copernicia prunifera) FRUIT BY HPLC-DAD

Ruana Mara Rodrigues Lima[1], Laércio Galvão Maciel*[1], Vanessa Rodrigues Lima[1], Mariana de Oliveira Silva[2], Ruann Janser Soares de Castro[2], Virna Luiza de Farias[1]

[1]Federal Institute of Education, Science and Technology of Ceará (IFCE) – Limoeiro do Norte
[2]State University of Campinas (UNICAMP)

* Corresponding author: laercio.nirvana@gmail.com

The carnaúba fruit (Copernicia prunifera), native to Brazil's semi-arid region, is rich in nutrients, fibers, minerals, and bioactive compounds with antioxidant properties and potential health benefits. Despite its traditional use in the natural products industry, detailed studies on the phytochemical profile of the ripe fruit are limited. This study aimed to characterize the phenolic compounds in ripe carnaúba fruit using high-performance liquid chromatography with diode array detection (HPLC-DAD). Fruits were collected 150 days after the onset of growth in the rural area of Morada Nova, Ceará (latitude –5º10'34.9"S; longitude 38º15'28.3"W). After sanitation, the pulp was separated from the seeds, homogenized, and stored at –18 °C until analysis. Chemical constituents were analyzed using an HPLC system equipped with a Shimadzu ODS-A column (4.6 × 250 mm, 5 µm) in reversed-phase mode and a photodiode array detector (SPD-M10AVp, Shimadzu Co., Kyoto, Japan). Chromatograms were processed with Class-VP® software. Standards (Sigma–Aldrich, St. Louis, MO, USA) included phenolic acids (protocatechuic, vanillic, caffeic, p-coumaric, and sinapic) and flavonoids (rutin and quercetin). The ripe carnaúba fruit exhibited a phytochemical profile with notable concentrations of myricetin (2221.24 ± 19.85 $\mu g.g^{-1}$), gallic acid (376.00 ± 4.52 $\mu g.g^{-1}$), p-coumaric acid (137.76 ± 24.64 $\mu g.g^{-1}$), catechin (49.57 ± 0.40 $\mu g.g^{-1}$), and protocatechuic acid (39.76 ± 2.28 $\mu g.g^{-1}$). The high myricetin content highlights its antioxidant potential. This flavonoid also possesses antidiabetic and hypolipidemic properties and exerts beneficial effects against non-alcoholic steatohepatitis (NASH). This study demonstrates the utility of HPLC-DAD for analyzing phytochemicals in regional matrices, ensuring precision, reproducibility, and reliability, with direct implications for functional food development. These findings support further industrial and health-related research, highlighting carnaúba as a promising source of bioactive compounds and highlighting the importance of studying native species from the Brazilian semi-arid region.

Acknowledgements: Acknowledgements: The authors thank CAPES and CNPq for scholarship support, and IFCE, UNICAMP's Food Biochemistry Laboratory, and NUTEC for research assistance.

PLANEJAMENTO DE MISTURA COM RESTRIÇÃO E MATRIZ DE DOEHLERT NO PREPARO DE SOLVENTES EUTÉTICOS PROFUNDOS NATURAIS (NADES) E EXTRAÇÃO ASSISTIDA POR ULTRASSOM DE COMPOSTOS FENÓLICOS BIOATIVOS EM PRÓPOLIS E DETERMINAÇÃO POR HPLC-DAD

Luciano Almeida de Albuquerque*[1], Débora de Andrade Santana[1], Fábio de Souza Dias[2], Sérgio Telles Oliva[2]

[1]Universidade do Estado da Bahia - UNEB - Departamento de Ciências Exatas e da Terra - Salvador/Bahia
[2]Universidade Federal da Bahia-UFBA / Instituto de Química / Campus de Ondina

* Corresponding author: bioalbuquerque@gmail.com

A própolis, produto natural elaborado por abelhas Apis mellifera, é rica em compostos fenólicos bioativos com propriedades antioxidantes e terapêuticas, mas os métodos convencionais de extração apresentam desvantagens relacionadas ao uso de solventes tóxicos, elevado tempo e consumo energético. Neste estudo, solventes eutéticos profundos naturais (NADES) foram sintetizados a partir de ácido láctico, glicose e água, empregando planejamento de mistura com restrição e matriz de Doehlert para otimização das formulações. A extração dos compostos fenólicos foi realizada por extração assistida por ultrassom (UAE), técnica que intensifica a transferência de massa por cavitação, reduzindo tempo e solvente. Os extratos foram analisados por Cromatografia Líquida de Alta Eficiência com detector de arranjo de diodos (HPLC-DAD), utilizando coluna C18 e gradiente ternário otimizado, garantindo elevada seletividade e resolução. Foram identificados e quantificados 14 fenólicos. O método cromatográfico foi validado quanto à linearidade ($R^2 > 0,99$), precisão (RSD < 5%), exatidão (recuperações entre 93,5% e 107%) e limites de detecção/quantificação adequados, assegurando confiabilidade dos resultados. A avaliação por métricas verdes (AGREE) demonstrou alta conformidade com os princípios da Química Verde, destacando a substituição de solventes convencionais por NADES e a eficiência energética da UAE. Assim, a integração de planejamento experimental, uso de NADES e HPLC-DAD mostrou-se estratégia robusta, seletiva e sustentável, consolidando-se como contribuição relevante para a cromatografia aplicada a matrizes naturais.

Acknowledgements: CAPES, CNPq, FAPESB e GPQUAM

POLYSACCHARIDE-BASED STATIONARY PHASES FOR THE ENANTIOSELECTIVE SCREENING OF CHIRAL EMERGING POLLUTANTS USING LIQUID AND/OR SUPERCRITICAL FLUID CHROMATOGRAPHY

Leandro Oka-Duarte*[1], Giovanni Stoppa Baviera[1], Weston J Umstead[2], Quezia Bezerra Cass[3], Anderson Rodrigo Moraes de Oliveira[1]

[1]Department of Chemistry, FFCLRP, University of São Paulo
[2]Daicel Chiral Technologies Inc.
[3]Department of Chemistry, Federal University of São Carlos

* Corresponding author: leandro.oka@usp.br

Many emerging contaminants are chiral and may display enantioselective behavior in fate and effects. Nevertheless, they are often monitored as racemates, particularly organophosphate (OP) pesticides and organic ultraviolet (UV) filters that persist in soils and aquatic environments and may exhibit different toxicities and bioaccumulation in organisms. Enantioselective analyses are therefore essential for further investigation. Liquid chromatography (LC) and supercritical fluid chromatography (SFC) with amylose- and cellulose-based chiral stationary phases (CSP) are the most versatile options, given the diversity of available chiral selectors and their compatibility with different mobile phases. In this work, immobilized and coated chiral columns (150 × 4.6 mm, 5 µm; 250 × 4.6 mm, 5 µm; or 150 × 4.6 mm, 3 µm) were evaluated for stereoselective separation of the pesticides acephate and malathion with their main metabolites (methamidophos and malaoxon, respectively), as well as the UV filters (E)-enzacamene, trans-homosalate, (E)-octinoxate, octisalate, and octocrylene. A comprehensive screening was conducted under normal-phase (NP; hexane/alcohol or MTBE), reversed-phase (RP; water/organic), polar organic (PO; 100% organic) elution modes, and/or supercritical fluid (CO_2/alcohol or hexane–ethanol) modes, with flow rates of 0.3−1.0 mL/min in LC (within manufacturer-recommended pressure limits) and 3.0 mL/min in SFC (backpressure at 100 bar). Among the > 1000 conditions tested, CHIRALPAK® IG, IF, IK, AD, and AS showed the highest success rates, achieving baseline (Rs ≥ 1.5) or near-baseline (Rs ≥ 1.0) resolution for all analytes. Amylose-base chiral stationary phases under NP and PO (100% acetonitrile) provided the best enantioselectivity for hydrophilic OP pesticides, while RP and PO (100% MeOH/EtOH/2-PrOH) were more effective for hydrophobic OP pesticides and UV filters. Although not investigated for all analytes, amylose CSPs in SFC offered good separation alternatives in several cases, representing a potential substitute for NP and a complementary approach to RP and PO in LC. These findings highlight the importance of combining LC and SFC approaches to broaden the scope of enantioselective analysis.

Acknowledgements: CAPES (Finance Code 001), FAPESP (grant numbers 2024/20783-4) and CNPq (grant number 304319/2024-4).

PRECONCENTRATION OF BROMINATED PHENOLS USING NATURAL DEEP EUTECTIC SOLVENTS (NADES) AND DETERMINATION BY HPLC-DAD

Letícia Maria Effting*[1], Mariany Silva De Souza[1], Thifany Miyuki Terossi Makita[1], João Victor Pastorin De Carvalho[1], Cesar Ricardo Teixeira Tarley[2]

[1]Laboratório de Desenvolvimento de Métodos Analíticos (LADEMA), Departamento de Química, Universidade Estadual de Londrina (UEL), 86057-970 Londrina-PR, Brazil

[2]Laboratório de Desenvolvimento de Métodos Analíticos (LADEMA), Departamento de Química, Universidade Estadual de Londrina (UEL), 86057-970 Londrina-PR, Brazil e Instituto Nacional de Ciência e Tecnologia de Bioanalítica (INCTBio), Universidade Estadual de Campinas (UNICAMP), 13083-970 Campinas-SP, Brazil.

* Corresponding author: leticia.effting21@uel.br

Brominated phenols (BPs) are organic compounds that are generally used in various industrial sectors. For example, due to its antifungal effects, it is used as a wood preservative. Although the use of BPs is effective, some BPs are considered environmental pollutants and can be toxic to ecosystems. There are concerns about the accumulation of BPs in the environment and their impact on human health. BPs have high Kow, high lipophilicity, and even relatively high water solubility. Thus, determining BPs is of great interest. Accordingly, this study aims to develop a new, quick, easy, highly improved, and environmentally friendly liquid–liquid microextraction method using a natural deep eutectic solvent (NADES) for the preconcentration of BPs (2-bromophenol, 4-bromophenol, 2,6-dibromophenol, 2,4-dibromophenol, and 2,4,6-tribromophenol). The developed method will be used to analyze the presence of these analytes in wood. To evaluate the best hydrogen donor and acceptor (HBD and HBA) composition of NADES and the molar ratio of HBD and HBA, simultaneous extraction and preconcentration experiments were carried out, with the sample having a concentration of 50.0 µg L-1 of each BPs and 10% (m/v) of NaCl, 0.1 mol L-1 Britton-Robinson Buffer, the volume was adjusted to 40.0 mL with ultrapure water and maintained at pH 4.0 in a microextraction centrifuge tube. The extraction was performed using 200 µL of NADES, followed by vigorous agitation for 1 min and subsequent centrifugation at 3000 rpm for 1 min. Afterwards, approximately 20 µL of the rich phase was collected and diluted 2:1 (v/v) in methanol, and then injected into the HPLC-DAD. The best NADES for extraction and preconcentration are composed of menthol and acetic acid (2:1 molar ratio). To optimize the method, a 25-1 factorial design and Doehlert design were combined with the Derringer–Suich desirability function and response surface methodology. The microextraction of the BPs was optimized at pH 3.92 in the presence of 11.5% NaCl (w/v), vortex-assisted extraction time (108 s) with 100 µL of the NADES. Subsequently, the analytical parameters were determined, obtaining preconcentration factors (90.2–120.8), and low LOQs (0.49–1.47 µg L-1). The intra-day (n = 10) and inter-day (n = 10) precision, assessed as the percentage of relative standard deviation (%RSD) for concentrations of 5.0, 25.0, and 75.0 µg L-1 varied from 1.14 to 5.11%. The developed method will be applied for the analysis of BPs in wood samples. The NADES method for BPs extraction is expected to offer several advantages, including high sensitivity, simplicity, and alignment with green chemistry principles, because it uses environmentally friendly solvents (NADES).

Acknowledgements: CNPq, CAPEs, INCTBio, PPG-Química UEL, and LADEMA.

Preparation and characterization of a molecularly imprinted poly(TMPTA-co-EDMA-co-MAA) monolithic coating for stir bar sorptive extraction of acetamiprid in water

João Pedro Matos Silva*, William Oliveira Soté, Moacyr Comar Junior, Anizio Marcio de Faria

Universidade Federal de Uberlândia

* Corresponding author: pjoao3369@ufu.br

Sorbent microextraction techniques have driven advances in sample preparation. Among them, stir bar sorptive extraction (SBSE) stands out for its use of a polymer-coated magnet, allowing for analyte isolation and preconcentration in a single step. However, conventional extractive phases, such as polydimethylsiloxane and polyethylene glycol, have low selectivity, which limits the application of this technique. Polymeric monoliths based on methacrylates and functionalized through molecular imprinting (MIP) emerge as promising alternatives, offering high porosity, mechanical robustness, and selective sites. In this work, we synthesized a molecularly imprinted monolithic coating using acetamiprid as a template and applied it in SBSE for the selective extraction of this pesticide from aqueous samples. The coatings were synthesized via in situ copolymerization of trimethylolpropane triacrylate, methacrylic acid, and ethylene glycol dimethacrylate (5:5:20, w/w/w), using 2,2′-azobisisobutyronitrile as initiator and 70% porogen (toluene or 1,4-butanediol:isopropanol, 4:7, v/v). Non-imprinted polymer (NIP) coatings were prepared by thermopolymerization of 300 µL of the mixture in cylindrical molds containing a magnet (60 °C, 12 h, inert atmosphere). In contrast, MIP coatings were obtained by pre-complexation of methacrylic acid with acetamiprid (70 °C, 2 h), followed by polymerization. Template removal was achieved using three aliquots of a 9:1 (v/v) methanol:acetic acid solution, followed by washing with water. Spiked water samples (0.5 mg L^{-1}) were extracted by both NIP-SBSE and MIP-SBSE and analyzed by HPLC-DAD. The monolithic coatings exhibited mesoporous structures, with surface areas of 77 m^2 g^{-1} (NIP-SBSE in toluene) and 53 m^2 g^{-1} (NIP-SBSE in an alcohol mixture). Acetamiprid adsorption tests showed 46% retention for NIP-SBSE coatings. For MIP-SBSE, the coating synthesized with the alcohol mix porogen exhibited an imprinting factor (IF)

Acknowledgements: FAPEMIG (APQ-1901-22 and PCE-00390-25), CAPES, and FINEP (01.13.0371.00).

PREPARATION AND OPTIMIZATION OF DIETHYLAMINOETHYL CELLULOSE MONOLITHIC SORPTIVE STIR BARS FOR SBSE EXTRACTION OF 2,4-D FROM SURFACE WATER SAMPLES

Ana Clara Baldin Castro*[1], Maria Aparecida Barros[2], Anízio Marcio de Faria[1]

[1]Federal University of Uberlândia, Institute of Exact and Natural Sciences of Pontal, Ituiutaba, MG, Brazil.
[2]Federal University of Uberlândia, Institute of Chemistry, Uberlândia, MG, Brazil.

* Corresponding author: anaclaracastro@ufu.br

Simplified and miniaturized sample preparation techniques using natural and non-toxic materials are desirable for modern chemical analysis. Stir bar sorptive extraction (SBSE) is a technique that fits these characteristics and allows the evaluation of new sorbents as coatings for stir bars. In this work, we developed an SBSE coating of modified cellulose monoliths, optimized and characterized for the extraction of the herbicide 2,4-D from surface water samples. Initially, cellulose acetate powder was used as a precursor to produce the hierarchically porous monolithic sorptive bar inside a cylindrical mold with a centralized neodymium magnet (4x3 mm), using the temperature-assisted non-solvent induced phase separation method and octanol as porogen. The cellulose acetate monoliths were deacetylated with sol. NaOH 2 mol/L in ethanol at 25 °C for 24 h, resulting in cellulose monoliths with 8 mm x 4 mm dimensions. The modification of cellulose with diethyl aminoethyl chloride (DEAE) was optimized via rotational central composite design (RCCD), evaluating the temperature (45-65 °C), reaction time (2-4 h), and DEAE concentration (0.5-1.5 % w/w). The cellulose acetate, cellulose, and cellulose-DEAE monoliths were characterized morphologically and structurally. The new SBSE coating was tested in the extraction of the herbicide 2,4-D from water samples. The optimized reaction conditions for the cellulose modification by RCCD were 45 °C for 2.0 h and a DEAE concentration of 1.5 % w/w. Scanning electron micrographs indicated a highly porous honeycomb structure of DEAE-cellulose monoliths. Nitrogen adsorption isotherms indicated a surface area of 45 m2/g and a macroporous structure, corresponding to 55% of the total volume of the monolithic DEAE-cellulose, measured by the fluid saturation method. Infrared spectra recorded peaks in the 1000-1300 cm-1 region attributed to C-N stretching, confirming the modification of the cellulose. The coating was used in the SBSE of 2,4-D from surface water samples, achieving 90% recovery at pH 4.0 by electrostatic interaction mechanisms using methanol:acetic acid (99:1) as eluent. The monolithic DEAE-cellulose proved effective as a new SBSE coating for extracting and concentrating 2,4-D from surface water samples, simplifying the sample preparation process.

Acknowledgements: FAPEMIG (APQ-1901-22 and PCE-00390-25), CNPq, and FINEP (01.13.0371.00).

PRODUÇÃO DE QUEROSENE DE AVIAÇÃO A PARTIR DO CRAQUEAMENTO DE RESÍDUOS PLÁSTICOS

Lucas Ferrão Marinho*, Ana Luiza R. R. da Cunha, Lilian F. de Oliveira, Dayane C. da Costa, Nelson R. Antoniosi Filho

Universidade Federal de Goiás (UFG), campus II – Samambaia, Goiânia (GO)

* Corresponding author: lucasferrao@discente.ufg.br

O plástico, devido à sua facilidade de ser manejado, mediante temperatura e pressão, pode ser utilizado para a produção de uma infinidade de itens, sendo o substituto de produtos que são escassos na natureza. Entretanto com a grande produção, consequentemente a poluição plástica se tornou uma das piores no planeta terra. Tendo em vista essas situações diversos estudos buscam a valorização desses resíduos e uma das formas encontradas foi o craqueamento, podendo ser térmico ou utilizadando um catalisador. Essa técnica é amplamente utilizada na indústria petrolífera, para a obtenção de combustíveis e outros produtos de valor agregado. Assim, este trabalho tem como objetivo, otimizar a rota de craqueamento catalítico de plásticos para a produção de querosene de aviação, utilizando a técnica de cromatografia gasosa (GC) acoplada a espectometria de massas para análise dos produtos obtidos. Foram utilizados os resíduos plásticos de polietileno (PE), polipropileno (PP) e poliestireno (PS), a partir de um modelo simplex lattice, foi realizado um planejamento experimental de mistura, em que cada reação de craqueamento era utilizado somente um ou dois plásticos diferentes. Para a etapa de craqueamento foram realizadas em tempo de 90 minutos a uma temperatura constante de 360ºC e 600 RPM, com 20% m/m em relação a massa pesada de plástico. Os óleos obtidos das reações foram analisados em um cromatógrafo a gás GC 2010 Plus – MS QP2010 Shimadzu com autoinjetor AOC 5000. A coluna utilizada foi uma DB-5-MS nas dimensões 30 m x 0,25 mm x 0,25 µm. Os óleos obtidos a partir do craqueamento de PE, apresentaram olefinas e parafinas, com a cadeia variando entre 6 e 27 carbonos com rendimento líquido de 63%. Para o PP, o óleo foi composto majoritariamente por hidrocarbonetos iso-parafínicos, com a cadeia variando entre 7 e 24 carbonos, com um rendimento líquido de 74%, e a partir do craqueamento do PS foram encontrados hidrocarbonetos aromáticos, com rendimento de 85%. Apesar de precisar de etapas de melhoramento como destilação e hidrogenação, os produtos formados mostram grande potencial para formas alternativas de produção de querosene de aviação.

Acknowledgements: LAMES/UFG, IQ-UFG, CAPES, FUNAPE, INCT-ALIM

Prospection of phenolic compounds in extracts of Libidibia ferrea, Spondias mombin and Lippia origanoides by UPLC-QTOF-MS

Elisabeth Mariano Batista*[1], Paulo Riceli Vasconcelos Ribeiro[2], Kirley Marques Canuto[2], Elenilson de Godoy Alves Filho[1], Amélia Ruth Nascimento Lima[1], Antonia Carlota de Souza Lima[1], Ronaldo Ferreira do Nascimento[1], Luciana de Siqueira Oliveira[1]

[1]Federal University of Ceará
[2]Embrapa Tropical Agroindustry

* Corresponding author: elisabethmariano@hotmail.com

The chemical evaluation of native plants is essential to identify their potential as raw materials for obtaining bioactive compounds and natural products. This study aimed to prospect and characterize phenolic compounds present in aqueous extracts of the leaves of Libidibia ferrea (jucá), Spondias mombin (cajazeira), and Lippia origanoides (alecrim-pimenta), focusing on their potential applications in the pharmaceutical and food industries. Extracts of each species were obtained by decoction (100 °C) in distilled water and subsequently lyophilized. For analysis, each extract was resuspended in a methanol/water solution (50:50, v/v) and filtered through a PTFE membrane (0.22 µm). Analyses were performed using ultra-performance liquid chromatography coupled with quadrupole/time-of-flight mass spectrometry (UPLC-ESI-QTOF-MS), employing a C18 column and a mobile phase of water and acetonitrile acidified with 0.1% formic acid, applied in a linear gradient, with electrospray ionization in positive mode. The analyzed extracts revealed a wide diversity of phenolic compounds. In the L. ferrea sample, gallic acid, ellagic acid and its derivatives, corilagin, orientin, isoorientin, kaempferol O-hexoside, and hydrolyzable tannins were identified. These compounds are recognized for their antioxidant, anti-inflammatory, and wound-healing properties, and are widely used in herbal and cosmetic formulations. The S. mombin extract contained hydroxycinnamic acids, such as 3-, 4-, and 5-caffeoylquinic acids, as well as rutin, acacetin 8-C-glucoside, and ferulic acid derivatives—substances with established value as natural antioxidants, color stabilizers, and nutraceutical agents with protective effects against oxidative stress. L. origanoides, in turn, demonstrated the presence of iridoids such as shanziside and secologanoside, as well as flavonoids including quercetin, kaempferol, naringenin, and verbascoside. These compounds exhibit potential antimicrobial, antiviral, and hepatoprotective activities, making them valuable for both drug development and the preservation of food and natural cosmetics. The data obtained confirm the potential of these species as natural sources of bioactive compounds with potential applications as antioxidants, natural preservatives, and therapeutic agents. The analytical approach employed proved to be efficient in characterizing complex phytochemical profiles, contributing to the advancement of pharmacognostic studies and innovation in functional ingredient development.

Acknowledgements: CAPES, Federal University of Ceará, Embrapa Tropical Agroindustry.

PUTATIVE IDENTIFICATION OF DEGRADATION PRODUCTS BY LC-HRMS INTEGRATED WITH IN SILICO PREDICTION: A CASE STUDY OF A RIMINOPHENAZINE COMPOUND

Maryane Maria Barros de Farias-Ferreira*[1], Júlia Morais Fernandes[1], Anauara Lima e Silva[2], Josean Fechine Tavares[2], José Lamartine Soares-Sobrinho[1], Mônica Felts de La Roca Soares[1]

[1]Universidade Federal de Pernambuco
[2]Universidade Federal da Paraíba

* Corresponding author: maryane.farias@ufpe.br

Stability-indicating methods are fundamental in pharmaceutical quality control, especially when dealing with complex molecules prone to multiple degradation pathways. Riminophenazine derivatives, used in antimicrobial therapy, pose significant analytical challenges due to their redox activity, multiple ionizable groups, and halogenated aromatic rings. A combined theoretical and experimental approach was employed to elucidate degradation behavior under oxidative forced conditions and identify their products via high-resolution mass spectrometry. Forced degradation was performed in solution 3% hydrogen peroxide (H_2O_2) following ICH guidelines. Chromatographic separation was achieved using a Zorbax Eclipse Plus C8 column (250 × 4.6 mm, 5 µm) with gradient elution consisting of formate buffer and acetonitrile. Detection was performed by HPLC-DAD and further characterized by LC-HR-ESI-MS using a Bruker impact II™ Q-TOF system with ESI in positive mode. MS parameters included a capillary voltage of 4.5 kV, nebulizer pressure of 4.0 bar, and dry gas at 200 °C. Spectra were acquired from m/z 50 to 1500 every 2 s. Putative identification was guided by in silico predictions using Zeneth® software suggesting three main degradation products (DP1, DP2 and DP3). A peak at m/z 489.1329 ([M+H]+) matched two structural isomers (DP1 and DP2, 488.112 Da), not distinguishable by retention time. DP3 was identified at m/z 530.1592 corresponding to [M+2Na–H]+ of a compound with exact mass 504.112 Da. Isotopic patterns (M+2, M+4) confirmed the presence of one or two chlorine atoms in each species. The parent drug was identified at m/z 473 with fragmentation consistent with known pathways, including the loss of isopropyl and chlorobenzene moieties. While isolation was not achieved, spectral data proposed structures and mechanisms. This study highlights the relevance of integrating predictive software with LC-HRMS workflows for early-stage degradation profiling. The approach enables the identification even in the absence of standards offering a valuable tool for method development and regulatory submissions.

Acknowledgements: This work was supported by FINEP/MS/SCTIE/DGITIS/CGITS; No. 01.22.0372.00, and by iCEIS, CNPq; No. 406264/2022-8. M. M. B. Farias-Ferreira thanks CAPES for her master's scholarship.

QUALITY ASSESSMENT OF BRAZILIAN OLIVE OILS BY GC×GC-MS AND CHEMOMETRICS

Andre Cunha Paiva*[1], Glaucimar Alex Passos de Resende[1], Luidy Darllan Barbosa[2], Guilherme Post Sabin[3], Leandro Wang Hantao[1]

[1]Institute of Chemistry, UNICAMP, 13083-862, Campinas, SP, Brazil ; National Institute of Science and Technology in Bioanalytics, SP, Campinas, 13083-862, Brazil
[2]Institute of Chemistry, UNICAMP, 13083-862, Campinas, SP, Brazil
[3]OpenScience, SP, Campinas, 13092-103, Brazil

* Corresponding author: andrecp@unicamp.br

Olive oil is a typical food from the Mediterranean region, with Brazil ranking as the second-largest importer of its high-quality form extra-virgin olive oil [1]. Beyond its nutritional value, the oil is highly appreciated by consumers for its unique sensory characteristics, which are directly related to its volatile composition. While some C6 and C5 aldehydes and alcohols are known to provide positive attributes (e.g., green, fruity, and fresh) in olive oil, the presence of volatiles associated with undesirable mushroom and rancid perceptions will yield oils with low sensory quality [2]. These defects may originate from the use of overripe olives, cross-contamination during olive oil processing, and adulteration, for instance. Moreover, precise control of olive oil quality remains a challenge for the oil producers and the research community as the current techniques sometimes lack effectiveness, which is due to the constantly evolving methods of adulteration and the fact that the edible-oil sensory characteristics are strongly dependent on the olive cultivar, harvest region, ripeness, and extraction conditions. This challenge can be addressed by leveraging highly informative analytical setups, such as comprehensive two-dimensional gas chromatography coupled with mass spectrometry (GC×GC-MS). To explore this, here we profiled the volatiles from 236 olive oil samples using headspace solid-phase microextraction (HS-SPME) and GC×GC-MS. Chemometric modelling via Partial Least Squares Discriminant Analysis (PLS-DA) successfully differentiated and classified the samples based on their sensory quality grade: non-defective (extra-virgin olive oils) versus those with sensory defects (virgin and lampante olive oils). This approach not only validated the importance of known quality markers, such as (E)-2-hexenal (green - positive attribute), (E,E)-2,4-hexadienal (fresh – positive attribute), and 1-octanol (mushroom - defect), but also uncovered other, less-documented volatiles as promising new indicators to differentiate between quality grades.

References

[1] Stilo F, Alladio E, Squara S, Bicchi C, Vincenti M, Reichenbach SE, Cordero C, Bizzo HR, J. Food Compost. Anal., 2023, 115.
[2] Stilo F, Jiménez-Carvelo AM, Liberto E, Bicchi C, Reichenbach SE, Cuadros-Rodríguez L, Cordero C, J. Agric. Food Chem., 2021, 69.

Acknowledgements: The authors thank UNICAMP, CNPq, CAPES, Petrobras, and FAPESP for funding our research.

QUALITY EVALUATION OF HERBAL SUPPLEMENTS THROUGH THIN LAYER CHROMATOGRAPHY

Letícia Firmino de Oliveira, Vanessa Gonçalves Medeiros, Ivanildes Vasconcelos Rodrigues, Andréia Peraro do Nascimento*

Pharmacy Department, Federal University of Juiz de Fora, campus Governador Valadares, Governador Valadares, Minas Gerais, Brazil

* Corresponding author: andreia.peraro@ufjf.br

Distravi is a dietary supplement based on medicinal plants, widely sold in health food stores in eastern Minas Gerais and also online. Its label lists the presence of Erva baleeira (Cordia verbenacea), Chapéu de couro (Echinodorus grandiflorus), Ginger (Zingiber officinale), Canela de velho (Miconia albicans), and Chestnut of India (Aesculus hippocastanum). This product is described as a natural anti-inflammatory dietary supplement to help relieve body pain, especially joint and muscle pain, such as back pain, arthritis, osteoarthritis, osteoporosis, herniated disc, chikungunya, bursitis, and knee pain. The objective of this study was to preliminarily analyze the quality of this product, sold in capsule form, through average weight assays and Thin Layer Chromatography (TLC). Standard alcoholic extracts were prepared with each of the medicinal plants mentioned in the formulation and with the homogenized powder from the contents of the Distravi capsules. These extracts were subjected to TLC following the parameters for solution preparation, mobile phase preparation, and developer preparation in accordance with the Brazilian Pharmacopoeia and scientific articles. Silica gel F254 plates were used as the stationary phase, and the mobile phases tested were: butyl alcohol, water, and ethyl acetate (25:50:5); dichloromethane, methanol, and water (95:5:0.2); chloroform, acetone, and toluene (6:2:5); and ethyl ether, methanol, and water (75:15:1.2). Sulfuric anisaldehyde was used for development, followed by heating to 100 °C. The average weight of the capsules was 0.3635 g and RSD= 4.09%, a result in accordance with pharmacopoeial specifications. In the TLC analyses evaluating the presence of plant extracts in the capsule contents, a distinct chromatographic profile was observed between the supplement and the extract standards. Since there were no spots with the same retention factor (Rf) values for both, it was not possible to identify the presence of the medicinal plants mentioned on the label. Regarding the physical characteristics, the powder contained in the capsules was white, generally not compatible with the color of plant extracts. Considering the divergence of the chromatographic profile of the supplement with that of the reference extracts, new TLC analyses should be performed to compare the contents of the capsules with substances with recognized anti-inflammatory action, as well as using more advanced techniques to verify the presence of any constituent of the supplement.

QUANTIFICATION OF ACEPHATE IN TOMATOES BY PSI-MS/MS

Eduardo Lima Nascimento*, Camila Cíntia Sousa Melo Brito, Jean Carlos Pereira Sousa, Tauã Emanuel Silva, Yuri Arrates Rocha, Lívia Flório Sgobbi, Boniek Gontijo Vaz, Andréa Rodrigues Chaves

Universidade Federal de Goiás (UFG)

* Corresponding author: eduardolima@discente.ufg.br

The increasing use of organophosphorus pesticides such as acephate (ACE) in agriculture poses risks to human health and the environment, demanding fast and reliable analytical methods for monitoring. Conventional chromatographic techniques (GC-MS/LC-MS) offer high sensitivity but require laborious sample preparation and large solvent volumes. This study proposes a method for ACE determination in tomatoes using tandem mass spectrometry with paper spray ionization (PSI-MS/MS) on paper substrates coated with polyhydroxyalkanoate (PHA) polymer. The technique features operational simplicity, low sample volume, and rapid analysis, with the paper acting as both sample support and ionization source. PHA functionalization aims to enhance selectivity and sensitivity. Triangular chromatographic papers (1 cm) were functionalized by immersion in an aqueous PHA solution (10 mg/mL) for 1 hour, followed by drying at 50 °C. Commercial tomato pulp (Solanum lycopersicum 'Roma') was macerated to prepare a 1:1 (w/v) methanolic extract, centrifuged, the supernatant was vacuum-dried and resuspended in methanol acidified with 1% formic acid, applied to blanks and samples. PSI-MS/MS analyses used a Thermo Scientific LTQ-XL mass spectrometer (positive ion mode). The monitored precursor ion was m/z 206, fragmented to m/z 165, characteristic of acephate's sodium adduct. The method was optimized for rapid analysis (≤3 min). Comparative tests confirmed higher ACE signal intensity on PHA-coated paper versus unmodified substrates or polyacrylamide-coated ones, significantly improving ionization efficiency and sensitivity. Validation demonstrated excellent linearity (20–400 µg/kg; R^2 = 0.999), precision (CV < 16%), and recoveries (99.5–105%). The LOD was 0.24 µg/kg and LOQ 13.25 µg/kg. This study proves PHA-functionalized substrates in PSI-MS/MS enable sensitive, selective, and rapid screening of pesticide residues in tomatoes, offering a promising strategy for food safety monitoring.

Acknowledgements: FAPEG, CNPQ

QUANTIFICATION OF CARBON DIOXIDE TO ASSESS THE EFIFICIENCY OF SUSTAINABLE FLAME RETARDANTS USING HEADSPACE GAS CHROMATOGRAPHY WITH A BARRIER DISCHARGE IONIZATION DETECTOR

Amanda Alves Soares*[1], Aline Vaz da Silva[1], Jhonatan Bispo de Oliveira[2], Patrícia Santiago de Oliveira Patrício[1], Patterson Patrício de souza[1]

[1]Centro Federal de Educação Tecnológica de Minas Gerais
[2]Universidade Federal de Minas Gerais

* Corresponding author: aalvessoares89@gmail.com

Fire in urban and natural environments poses an increasing threat, causing significant damage. The global flame retardant market reflects this trend, with growing interest in sustainable alternatives that combine high efficiency, low environmental impact, and cost-effectiveness. In this context, a suppressant composed of lightweight expanded clay incorporated with carbonate salts was developed. A key mechanism of action of the developed suppressant involves the release of carbon dioxide (CO2). Thus, the aim of this study was to develop an analytical methodology capable of quantifying CO_2 release to assess the efficiency of the suppressant. Headspace (HS) coupled with Gas Chromatography (GC) was employed, and analyses were performed on a Shimadzu Nexus 2030 gas chromatograph with a Barrier Discharge Ionization Detector (BID). This detector provides high sensitivity and universal response, suitable for CO2, whose detection is challenging with conventional detectors. The procedure involved weighing 1.000 g of sample into 20 mL vials. Then, 8.00 mL of 2 mol/L sulfuric acid was added to trigger the reaction of carbonated salts. After 1 hour at 58 ºC, 3.00 mL of the gas phase was collected using a Shimadzu MSG-2030 manual sampler and injected into the GC. The method demonstrated precision of 3.4% (repeatability) and 20.9% (intermediate precision), recovery of 105.7% detection and quantification limits of 0.0050 and 0.023 mg CO2/g, respectively, and linearity confirmed by residual analysis and R2=0.9989. Samples released up to (4.19 ± 0.25) mg CO2/g of suppressant, demonstrating the method’s effectiveness for rapid and sensitive monitoring of flame retardant efficiency.

Acknowledgements: FAPEMIG, CNPq, LIGHT S/A, PPGMQ-MG, CEFET-MG, and INTECHLAB for providing the opportunity to carry out this work.

RAPID AND SENSITIVE TARGET SCREENING OF GUT MICROBIAL SHORT-CHAIN FATTY ACIDS IN FECES USING GC-APCI-QTOF-MS

Renato Cardoso Leal Netto, Keila Nascimento Cavalcante, Daniel Rodrigues Cardoso*

University of Sao Paulo

* Corresponding author: drcardoso@usp.br

The analysis of short-chain fatty acids (SCFAs) remains challenging due to their low molecular weight and high polarity, which often lead to poor chromatographic retention, weak detector response, and strong matrix effects. Conventional approaches typically require derivatization to improve volatility, stability, and detection, but this step increases experimental complexity, being laborious, and introduces potential analytical errors. Here, we present a fast and sensitive gas chromatography-mass spectrometry method using atmospheric pressure chemical ionization (GC-APCI-HRMS) that enables the direct detection of free SCFAs without derivatization. The efficiency of APCI arises from its soft ionization mechanism, which favors the formation of molecular ions ([M-H]-) in negative mode, thereby minimizing fragmentation while enhancing selectivity and sensitivity compared to electron ionization (EI). The method was developed, optimized, and validated using both full scan and pseudo-multiple reaction monitoring (pseudo-MRM) acquisition modes. In addition, GC-APCI-QTOF-MS was systematically compared with GC-EI-Q-MS and electrospray ionization (ESI) in liquid chromatography-mass spectrometry (LC-MS) for SFCAs analysis in biological samples. The limits of detection (LOD; 12,8 - 93,5 µM) and quantification (LOQ; 38,9 - 283,4 µM) achieved highlight the robustness and sensitivity of GC-APCI-HRMS establishing it as a powerful tool for high-throughput targeted screening of gut microbial SCFAs. This approach represents a significant advancement in simplicity, speed, and cost-effectiveness, with broad potential applications in clinical diagnostics and biological process monitoring.

Acknowledgements: INCT-Alim and FAPESP (23/17201-0)

RAPID NUTRITIONAL ASSESSMENT OF VEGETABLE OILS USING A SPREADSHEET AND GAS CHROMATOGRAPHY

Jossemyller Ferreira Damascena*, Patrícia Fontes Pinheiro, Maria Eliana Lopes Ribeiro de Queiroz, André Fernando de Oliveira, Fábio Junior Moreira Novaes

Federal University of Viçosa

* Corresponding author: jossemyller.damascena@ufv.br

Spreadsheets were developed in Microsoft Excel software to assist in the processes of identifying and quantifying fatty acids (FA) in plant matrices using gas chromatography, whose profiles inform nutritional indices (Atherogenicity (AI), Thrombogenicity (TI), polyunsaturated fatty acid/saturated fatty acid (PUFA/SFA), Hypo and hypercholesterolemic ratio (HH) and between linoleic acid and α-linolenic acid (LA/ALA)) and potential applications of the lipid matrix. The spreadsheets are fed by importing data generated by the chromatography software, minimizing transcription errors caused by manually copying data, and increasing the efficiency and reliability of results. They also reduce the analyst's time spent processing chromatographic data and organize the results more clearly for the composition of the analytical report. This contributes to streamlining the analysis of large volumes of data in laboratory routines and for the evaluation of foods with potential impact on cardiovascular health. This study presents the development steps for the spreadsheets, as well as the demonstration and validation of their use with different vegetable oils (Avocado, Junça, Olive, Tucuma, and Coffee). The FA profile of these oils revealed significant differences in their lipid compositions, with a predominance of monounsaturated FAs, especially oleic acid (47-59%), for all samples, except Coffee oil (12%), which, in turn, stood out for its high concentration of linoleic (37%) and palmitic (33%) acids. The calculated nutritional indices reinforce the functional potential of these oils, especially regarding the AI, 2.0 in all samples, except Coffee oil (= 1.54). In particular, Tucuma oil stood out with the lowest AI (0.11) and TI (0.22), in addition to the highest HH value (7.22), indicating its high nutritional quality. Despite being uncommon in the daily diet of Brazilians, Tucuma and Junça oils presented significant benefits, demonstrating their potential for functional and healthy diets. Avocado oil, in turn, had intermediate values for all indexes evaluated, standing out as a balanced and promising food for a healthy diet. Olive oil, widely known and consumed, remained an excellent dietary option due to its robust nutritional profile and well-documented benefits. Coffee oil presented less favorable IT and HH indexes for oral consumption; however, it is rich in linoleic acid, an essential omega-6, suitable as an ingredient for dermocosmetics, especially for oily and acne-prone skin.

Acknowledgements: This work was supported by Fundação de Amparo à Pesquisa de Minas Gerais
(FAPEMIG—Process Grants: APQ-01574-22).

Residues of Glyphosate and AMPA in beeswax by HPLC-fluorescence

Ana Paula Ferreira de Souza*[1], Isabella Eloá Araujo da Silva[2], Nadia Regina Rodrigues[1]

[1]Division of Analytical Chemistry, CPQBA, UNICAMP, Brazil
[2]Institute of Chemistry, UNICAMP, Brazil

* Corresponding author: anapfs@unicamp.br

The relationship between pollinating insects, such as bees, and plants is crucial for the maintenance of natural and agricultural ecosystems. However, the intensification of modern agricultural practices exposes these insects to a variety of agrochemicals, such as the herbicide Glyphosate (GLY) and its metabolite, AMPA. Exposure to these compounds can cause significant harm to bees, including damage to the nervous system, behavioral changes, and the loss of taste sensitivity and memory. In this context, the present study developed and apply an analytical method for the detection of GLI and AMPA in Brazilian beewaxes, using HPLC-FLD. For this purpose, 18 beewax samples from the state of São Paulo were analyzed. The sample preparation procedure was optimized using a 2^3 factorial design and the best conditions for the extraction of GLI and AMPA from the beeswax samples was established. The analytical method was validated according to SANTE (2020) guideline, demonstrating selectivity, linearity, sensitivity, precision, and accuracy. The limits of quantification (LOQ) for GLI and AMPA were established at 0.05 mg kg^{-1}. The application of the method to the samples shown that only one sample contained residues of both analytes, although at concentrations below the LOQ. Additional analyses in beekeeping matrices, such as honey and pollen, to obtain a complete cenario of the contamination and the real risk to which pollinators are exposed would be necessary.

Acknowledgements: Acknowledgements: The authors thank CNPq to provide PIBIC scholarship, and to EDUCORP/UNICAMP for their assistance in the dissemination.

Revealing the migration of (semi)-volatile organic compounds from virgin and post-consumer recycled polyolefins into food simulants by DI-SPME-GC-MS

Luis Eduardo Silva Nascimento*[1], Marisa Padula[2]

[1]Packaging Technology Center, Institute of Food Technology, Campinas, São Paulo, Brazil; Science Center for the Development of Solutions for Post-Consumer Waste: Packaging and Products (CCD Circula), Institute of Food Technology, Campinas, São Paulo, Brazil; Federal University of Pelotas (UFPel), Eliseu Maciel School of Agronomy, Department of Agricultural Science and Technology, Pelotas, Rio Grande do Sul, Brazil.

[2]Revealing the migration of (semi)-volatile organic compounds from virgin and post-consumer recycled polyolefins into food simulants by DI-SPME-GC-MS

* Corresponding author: luiseduardo_sn@hotmail.com

This study aimed to characterize the migration profile of (semi-)volatile organic compounds (semi-VOCs) from virgin and post-consumer recycled (PCR) polyolefin pellets, including high-density polyethylene (HDPE) and polypropylene (PP), into food simulants. The selected simulants were 10% ethanol, 3% acetic acid, and 95% ethanol, representing alcoholic, acidic, and lipophilic food matrices, respectively. Analyses were performed using direct immersion solid-phase microextraction (DI-SPME) coupled with gas chromatography–mass spectrometry (GC-MS). Prior to analysis, five different fibers—DVB/PDMS/CWR, acrylate, DVB/PDMS, PDMS, and Carbon WR—were tested to evaluate extraction efficiency. Among them, DVB/PDMS provided the best performance and was selected for subsequent analyses. Multivariate optimization was carried out using Plackett–Burman (PB) and Central Composite Rotatable Designs to establish optimal DI-SPME and GC-MS conditions. The PB design evaluated extraction parameters—extraction time (X1), incubation/extraction temperature (X2), agitation (X3), and incubation time (X4)—as well as instrumental parameters—GC injector temperature (X5), fiber desorption time (X6), initial hold time of the temperature ramp (X7), initial temperature of the temperature ramp (X8), final temperature of the temperature ramp (X9), heating ramp rate (X10), final hold time (X11), and column flow rate (X12). Three virgin and three PCR samples were analyzed, comprising one HDPE and two PP pellets for each purity class. The pellets were exposed to the food simulants for 10 days at 60 °C. The PB design identified X1, X2, X5, and X10 as the most significant factors influencing extraction. Under optimized conditions, 126, 55, 99, 32, 31, and 27 compounds were identified in samples R1, R2, R3, V1, V2, and V3, respectively, when using the acidic simulant. For the alcoholic simulant, 134, 66, 98, 30, 20, and 27 compounds were detected, while the lipophilic simulant yielded 129, 74, 94, 41, 43, and 38 compounds. Overall, PCR samples (R1–R3) exhibited substantially higher levels of semi-VOCs compared to the virgin samples (V1–V3). Special consideration should be given to PCR materials, as they may contribute to a significantly higher migration of compounds into food.

Acknowledgements: This study was financed by the São Paulo Research Foundation (FAPESP), Brazil. Process Number #2024/00347-5 and #2021/11967-6.

SCREENING OF SOLVENT SYSTEMS FOR THE FRACTIONATION OF THE ETHYL ACETATE EXTRACT FROM Siparuna cymosa Tolm. LEAVES BY COUNTERCURRENT CHROMATOGRAPHY

Adérito José Cavele*, Diégina Araújo Fernandes, Gilda Guimarães Leitão

Instituto de Pesquisa de Produtos Naturais - Universidade Federal do Rio de Janeiro

* Corresponding author: ajcavele2@gmail.com

Countercurrent chromatography (CCC) is a liquid–liquid partitioning technique widely recognized for its efficiency in the separation and isolation of natural products. Among the critical factors influencing CCC performance, the choice of an appropriate solvent system (SS) is paramount, as it determines the selectivity, resolution, and recovery of target compounds. Siparuna cymosa Tolm. (Siparunaceae) has been reported to contain a diversity of bioactive metabolites, including alkaloids and flavonoids. This study aimed to evaluate and compare the partitioning behavior of compounds across seven biphasic SS to identify the most suitable composition for the CCC fractionation of the ethyl acetate extract from the leaves of S. cymosa (SCAE). This extract was first analyzed by HPLC-DAD, revealing five major peaks. The UV-Vis spectra confirmed characteristic absorptions of flavonoids at 250–280 nm (Band II) and 330–370 nm (Band I), and alkaloids at 260–300 nm. Seven SS were tested by the test-tube partitioning test method: hexane–ethyl acetate–methanol–water (HEMWat; 6:6:6:6, 4:6:4:6, 3:6:3:6, and 1:6:1:6) and ethyl acetate–butanol–water (EBuWat; 9:1:10, 8:2:10, and 7:3:10). A 25 mg sample of the extract was shaken with each SS, and after equilibration, both upper and lower phases were analyzed separately by TLC and HPLC-DAD. Partition coefficients (K) of target compounds were visually estimated based on spot intensity and calculated according to compound concentrations in both phases. Preliminary TLC results indicated that EBuWat 8:2:10 and 7:3:10 provided the most balanced distribution of target compounds, which was confirmed by HPLC analysis for alkaloids (Rt: 7.57 and 33.03min.) and flavonoids (Rt: 18.30 and 38.18min.). These systems yielded K values within the optimal range (0.5

Acknowledgements: CAPES, CNPq and FAPERJ.

SELECTED REACTION MONITORING OF PETROLEUM MARKERS USING LOW-PRESSURE GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY (LPGC-MS/MS)

Lucas Pessôa de Araujo*[1], Allyson Leandro Rodrigues dos Santos[1], Alexandre Varão Moura[1], Yuri Cominatto Mignone[1], Leandro Wang Hantao[2]

[1]Institute of Chemistry, University of Campinas (IQ, UNICAMP)
[2]Institute of Chemistry, University of Campinas (IQ, UNICAMP); Center for Energy and Petroleum Studies (CEPETRO, UNICAMP), Center for Energy Planning (NIPE, UNICAMP)

* Corresponding author: l240117@dac.unicamp.br

Organic petroleum biomarkers can be used in geochemistry as age-diagnostic, thermal maturity, and source-rock origin correlation parameters.[1] Traditional methods used for the molecular characterization of such biomarkers rely on gas chromatography coupled with mass spectrometry (GC-MS). The analysis of saturated and aromatic biomarkers in oils requires increased peak capacity, but exhibits excessively long chromatographic runs (>120min). In this context, fast GC analysis is a promising method for increasing sample throughput in routine analysis. Low-pressure gas chromatography (LPGC) was first described in 1962 and consists of placing the outlet of a short, wide-bore analytical column under vacuum conditions[2]. A short restriction capillary is used to maintain the considerable pressure across the column, but it generates enough impedance to allow for constant flow control. However, while successful applications have been reported, applications of LPGC-MS in organic geochemistry are still incipient. In this work, we characterize important petroleum markers using LPGC-MS. The saturated (SAT) and aromatic (ARO) fractions were isolated using liquid chromatography. Both fractions were analyzed by LPGC-MS/MS using selected reaction monitoring (SRM) mode. Important primary measures were used to compare the performance obtained with 1D-GC and LPGC. Experimental parameters, such as temperature programming and column flow, were carefully adjusted to preserve chromatographic resolution, resulting in a significant decrease in analysis time (approximately 5×).

Acknowledgements: Acknowledgements: CAPES, CNPq, FAPESP, PETROBRAS.

SELECTION OF THE OPTIMAL HPLC COLUMN AND METHOD VALIDATION FOR QUANTIFYING XANTHOHUMOL AND HOP BITTER ACIDS IN HUMULUS LUPULUS L. EXTRACTS BY HPLC-DAD

Débora Nascimento Eiriz*[1], Rafael Ribeiro de Lacerda[1], Natália Martins Libório[1], Victor Eduardo Zúñiga Pávon[2], Lucas Silva Abreu[1], Francisco Paiva Machado[2], Leandro Machado Rocha[2], Caio Pinho Fernandes[2], Lucas Mattos Duarte[1]

[1]Institute of Chemistry, Fluminense Federal University
[2]Faculty of Pharmacy, Fluminense Federal University

* Corresponding author: deboraeiriz@id.uff.br

Accurate quantification of the bioactive compounds in hop extracts—xanthohumol and the bitter acids (α- and β-acids)—is essential for both quality control and research in brewing and natural product applications. This study compared three reversed-phase UPLC columns (A–C) against the Hops-14 method from American Society of Brewing Chemists (ASBC) reference conditions, and developed HPLC–DAD methods tailored to extracts prepared from Humulus lupulus L. (cv. Columbus). Ground hop pellets were extracted using four solvents (methanol, ethanol, acetonitrile, and acetone) combined with four techniques—static maceration (SM), dynamic maceration (DM), Soxhlet extraction (SX), and ultrasound-assisted extraction (UA). The resulting extracts were filtered and analyzed by HPLC–DAD on each column, and chromatographic performance was qualitatively benchmarked following the ASBC procedure, in accordance with the International Council for Harmonisation (ICH) guidelines and ANVISA RDC n0 166./2017. Column screening evaluated retention behavior, resolution of critical pairs, peak symmetry, efficiency, analysis time, and robustness to matrix effects. The best-performing column was then selected, and a quantitative method for xanthohumol and hop bitter acids at appropriate detection wavelengths was fully validated—assessing linearity, selectivity, sensitivity, precision, accuracy/recovery, robustness, and system suitability. Among the columns tested, Column C provided the most favorable overall chromatographic performance. The validated method proved suitable for routine quantification of xanthohumol and hop bitter acids in different hop matrices. Extraction outcomes depended strongly on both solvent and technique; notably, dynamic maceration with methanol consistently yielded the highest concentrations of the target analytes. The findings show that co-optimizing the chromatographic system (column choice) and the sample-preparation strategy is essential to maximize analyte recovery and achieve robust, reproducible quantification of hop bioactives.

Acknowledgements: Financial support: CAPES, FAPERJ, CNPq. Institutional support: LTPN and the Analytical Center, Faculty of Pharmacy (LCAN-CMF), Fluminense Federal University.

Selective Detection HPLC Assays Via In-Column Derivatisation

Arianne Solive*[1], Colin Pipe[2], Tony Edge[2], Matt James[2], Andrew Jones[3], R.Andrew Shalliker[4]

[1]Avantor, 1 The Markham Centre, Station Road, Theale, Reading RG7 4PE, UK; Avantor, Minas y Cebollati, Montevideo, 11200 Uruguay; 3. Western Sydney University, South Parramatta, NSW 2151, Australia
[2]Avantor, 1 The Markham Centre, Station Road, Theale, Reading RG7 4PE, UK
[3]Chemika, 119 Magowar Road, Giarraween, NSW 2145 Australia
[4]Western Sydney University, South Parramatta, NSW 2151, Australia; Chromaspeed Pty Ltd. Tonsley SA 5042 Australia

* Corresponding author: arianne.soliven@avantorsciences.com

Selective detection assays via HPLC post-column derivatization (PCD) have many applications, particularly in the food industry. The advantages over pre-column derivatization include reduced sample manipulation and the ability to work with less stable derivatization products. The main disadvantage is the introduction of dead volume, due to the need for a reactor to facilitate the derivatisation reaction. During In-column derivatisation (ICD) the reaction mainly occurs within the column's frit and can overcome the dead-volume and mixing issues associated with the 'T-piece' and additional tubing associated with conventional PCD. Hence, ICD reduces the post-column dispersion contribution that is inherent in PCD assays.

In this study, we highlight the chromatographic and detection advantages comparing the selective detection of amino acids derivatized with O-phthalaldehyde using a novel ICD column format compared to a conventional PCD reaction loop approach. An interlaboratory study highlighted a gain in peak area and efficiency was achieved when the post-column tubing volume was between 80-120 µL for the ICD assays, a significantly smaller volume compared to 500 µL for the conventional PCD assay.

We then demonstrate ICD's ability to perform other reactions that target antioxidants and phenolic compounds; robust assays which provide a unique and difficult to falsify profile for the authentication of consumer products. The increased pressures from consumer demand, global supply chain and climate change have highlighted the need for routine, alternative and sophisticated assays for identifying fraudulent counterfeit products.

Acknowledgements: Johnny Lima, Nova Analítica; Jose Cuadro, Zachary Stellbgerg, and Leandro Kasamatsu, Avantor for their additional support.

SELECTIVITY OF THE Hexane-EtOAc-MeOH-H2O SYSTEM IN THE ISOLATION OF COMPOUNDS FROM Siparuna decipiens BY COUNTERCURRENT CHROMATOGRAPHY

Diégina Araújo Fernandes*[1], Ana Beatriz Santana Garcias[1], Marianna Lessa Quintanilha[1], Simony Carvalho Mendonça[2], Gilda Guimarães Leitão[1]

[1]Instituto de Pesquisa de Produtos Naturais – UFRJ
[2]Faculdade Farmácia – UFRJ

* Corresponding author: dieginafernandes@gmail.com

Countercurrent chromatography (CCC) is an efficient liquid–liquid partitioning chromatography technique widely used for isolating and purifying natural products. Selecting an appropriate solvent system (SS) is critical, as it influences separation efficiency and compound purity. Siparuna decipiens (Siparunaceae), native to the Amazon, has been traditionally used in Brazilian folk medicine to treat fever, colds, and rheumatism. Its dichloromethane extract showed antiviral activity, with over 80% inhibition in Calu-3 cells at 50 µg·mL^{-1} and cell viability above 80% at 200 µg·mL^{-1}, indicating a favorable safety profile. Given this potential, the present study aimed to evaluate the partitioning behavior of compounds in five biphasic SS and identify the most suitable one for fractionating the dichloromethane extract of S. decipiens (SDD). The extract was first analyzed by HPLC-DAD, which revealed four major peaks. The UV–Vis spectra confirmed characteristic absorptions, with flavonoids at 250–280 nm (Band II) and 330–370 nm (Band I), and alkaloids in the 260–300 nm range. The SS (HEMWat: hexane–ethyl acetate–methanol–water) were tested in the following ratios: 5:5:5:5, 3:7:3:7, 3:7:4:6, 3:7:5:5, and 3:7:2:8. A 10 mg sample of the extract was shaken with each SS, and after equilibration, both the upper and lower phases were analyzed separately by TLC and HPLC-DAD. The partition coefficients (K) of the target compounds were visually estimated based on spot intensity and calculated from the compound concentrations in both phases. Preliminary TLC results indicated that HEMWat 5:5:5:5 provided the most balanced distribution of the target compounds, which was confirmed by HPLC analysis of the alkaloids (Rt: 26.7 and 31.5min) that exhibited blue fluorescence under UV light (365 nm), while the other two compounds (Rt: 21.8 and 28.6 min) appeared as yellow spots under the same wavelength. This SS yielded K values for the target compounds within the optimal range (0.5

Acknowledgements: Acknowledgements: CAPES, CNPq and FAPERJ.

SERUM METABOLOMIC PROFILE IN POST-WEANING PROTEIN-RESTRICTED C57BL/6 MALE MICE TREATED WITH TUDCA

Giovanna de Brito Rodrigues Rosa*[1], Mariana Feitosa Custódio[1], Kênia Moreno de Oliveira[2], Israelle Netto Freitas[2], Everardo Magalhães Carneiro[2], Ana Valéria Colnaghi Simionato[3]

[1]Laboratory of Biomolecules Analysis Tiselius, Institute of Chemistry, Universidade Estadual de Campinas, SP, Brazil
[2]Laboratory of Endocrine Pancreas and Metabolism, Institute of Biology, Universidade Estadual de Campinas, SP, Brazil
[3]Laboratory of Biomolecules Analysis Tiselius, Institute of Chemistry, Universidade Estadual de Campinas, SP, Brazil; National Institute of Science and Technology in Bioanalytics, Brazil

* Corresponding author: g222644@dac.unicamp.br

Malnutrition is a serious public health problem that commonly affects children in developing countries, and early protein restriction is associated with peripheral insulin resistance, type 2 diabetes, and fat accumulation, even in the presence of low body weight. Experimental evidence shows that bile acids exert neuroendocrine effects that regulate intermediary metabolism and energy expenditure, with tauroursodeoxycholic acid (TUDCA) standing out in this regard. Therefore, this study aimed to investigate the untargeted metabolomic profile of serum from male C57Bl/6 mice subjected to a restricted protein diet and subsequently treated intraperitoneally with 300 mg/kg of TUDCA during the last 15 days of life, in order to identify biomarkers related to these pathogenic processes and the therapeutic response to TUDCA. In accordance with ethical guidelines for animal use (Ethics Committee approval nº 6190/2023), post-weaning mice were randomly assigned to two groups (n = 5 each): one fed a normoproteic diet (14% protein) and the other a protein-restricted diet (6% protein) for 105 days. During the last 15 days, both groups received intraperitoneal TUDCA treatment (300 mg/kg), being designated as Control TUDCA (CT) and Restricted TUDCA (RT), respectively. At the end of the treatment, blood was collected and the obtained serum was prepared for metabolite extraction and derivatization, including methoximation and silylation. Untargeted metabolomic analysis was performed by gas chromatography–mass spectrometry (GC-MS) using an HP-5MS column (30 m × 0.25 mm × 0.25 µm), following the Fiehn library protocols. Chromatograms and spectra were processed in MS-DIAL 4.93 to generate a molecular features table, which was filtered in Excel and preprocessed in NOREVA 2.0. Multivariate analysis in MetaboAnalyst 6.0 showed proper QC clustering and repeatability by PCA. PLS-DA with four latent variables achieved $R^2 = 0.99$, $Q^2 = 0.83$, and Accuracy = 1.0 by leave-one-out cross-validation. The study is at the metabolite annotation stage, with biological interpretation pending. However, preliminary analyses indicate that TUDCA induced distinct metabolic changes, mainly involving carbohydrate and lipid pathways.

Acknowledgements: The authors acknowledge funding from FAPESP, CNPq and CAPES, as well as UNICAMP for providing the necessary infrastructure to support this research.

SILICAL GEL OR COUNTERCURRENT CHROMATOGRAPHY? WHAT'S THE BEST CHOICE FOR CURZERENE ISOLATION FROM EUGENIA UNIFLORA LEAF'S ESSENTIAL OIL

André M. Marques*, Flavia da C. Camillo, Ana Luiza Berenger, Lavinia C. Britto, Vagner P. da Silva, Maria Raquel Figueiredo

Laboratório de Tecnologia para Biodiversidade em Saúde/TecBio, Farmanguinhos, Fundação Oswaldo Cruz (FIOCRUZ) Rio de Janeiro, RJ

* Corresponding author: andre.marques@fiocruz.br

The species Eugenia uniflora L., popularly known as "pitangueira", belongs to the Myrtaceae family, and its essential oil have potential for industrial and pharmaceutical applications. However, isolating the major constituents from essential oils is challenging due to the large number and structural similarity of secondary metabolites present in the mixture. In this work, silica gel column and countercurrent chromatography (CCC) efficiency were compared to separating the main volatile metabolite present in E. uniflora's essential oil (SisGen No. AB5D582). The leaves were collected in Fiocruz Foundation and subjected to hydrodistillation for two hours separately in a modified Clevenger apparatus, yielding 1.0% (V/W). The essential oil was analyzed by GC-FID and GC-MS. The chemical characterization suggested the presence of Eugenia uniflora chemotype rich in curzerene, since the main volatile constituent found was the sesquiterpene curzerene (41.0%). A total of 2.0g and 211.0 mg of crude essential oil were used in the silica gel column and CCC separation process, respectively. For column separation process, 198 samples were collected in 48h of separation using 3.0L of n-hexane (100%) as solvent. In total, 161.0 mg of curzerene enriched fractions (67.0%) and 188.0mg of isomers mixture (curzerene (33.0%) and atractylone 66.0%), obtained from fractions 130-142 and 143-161, respectively. The optimized system composed of n-hexane/acetonitrile/methanol (5:5:1) was chosen for CCC separation. A total of 160 fractions were collected, with the rotation maintained at 870 rpm. In this process, tail-to-head mode was used. Curzerene (25.5mg) was obtained from fractions 18-30, with purity above 95.0% with total solvent consuming of 600mL. Compared to classical adsorption separations, the HSCCC technique proved to be faster and efficient in a single step separating process of sesquiterpenes with very similar structures and polarities in less than 2h.

Acknowledgements: Acknowledgements: The authors thank CNPq and Farmanguinhos/FIOCRUZ.

SIMULTANEOUS MULTICLASS DETERMINATION OF PESTICIDES AND VETERINARY DRUGS IN MEAT USING A HIGH-THROUGHPUT QuEChERSER METHOD WITH SPE CLEAN-UP AND UHPLC-MS/MS

Theo Samborski*, Luana Floriano, Martha B. Adaime, Renato Zanella, Osmar D. Prestes

LARP- Universidade Federal de Santa Maria

* Corresponding author: theo.samborski@gmail.com

The use of pesticides and veterinary drugs in food-producing animals is essential for livestock production and food safety, but their residues can pose potential risks to human health. Simultaneous analysis of multiple compounds in complex matrices, such as meat, is challenging due to the high fat and protein content [1]. Previous QuEChERS methods were effective for pesticides but did not include veterinary drugs, highlighting the need for a single method capable of covering multiple classes [2]. In this study, a robust multiclass method was developed and validated for the simultaneous determination of 120 pesticides and 20 veterinary drugs in bovine muscle using the QuEChERSER. Two grams of muscle were homogenized and spiked with working standard solutions and internal quality control standards before extraction. Samples were extracted with acetonitrile:water (4:1, v/v) and shaken for 10 min, followed by clean-up using a 40 mg EMR-Lipid SPE cartridge to remove lipids and other matrix interferences. A 250 µL aliquot of the eluate was diluted with 750 µL of ultrapure water, centrifuged at −5 °C and 15,000 rpm for 5 min, and filtered through a 0.22 µm nylon filter prior to injection in a UHPLC-MS/MS system. Chromatographic separation was performed on a BEH C18 column with a total run time of 10 min. The system was operated in ESI± modes using multiple reaction monitoring, with two transitions monitored for each analyte. Recovery tests at the spike levels 5, 10, and 20 µg kg^{-1} yielded satisfactory results with RSD ≤ 20% and accuracy, in terms of recovery, from 70 to 120%. Matrix effects were assessed by comparing solvent and matrix-matched calibration curves. Combined matrix-matched calibration curves showed excellent linearity ($r^2 > 0.99$), with a method limit of quantification of 10 µg kg^{-1} for all analytes, demonstrating that the method enables the simultaneous quantification of multiple classes of analytes with high precision and reliability. This approach provides a practical and efficient solution for routine high-throughput analysis of complex food matrices, reducing the need for multiple methods and improving laboratory efficiency.

References:
[1] Mookantsa, S. O. S.; Dube, S.; Nindi, M. M. Foods 14(5) (2025) 720.
[2] Monteiro, S. H.; Lehotay, S. J. et al. J. Agric. Food Chem. 69(4) (2021) 1234–1245.

Acknowledgements: INCT-ALIM/CNPq 406760/2022-5, CAPES, FAPERGS and UFSM.

SÍNTESE DE CARBONATO DE GLICEROL A PARTIR DE GLICEROL E DIMETIL CARBONATO: AVALIAÇÃO COMPARATIVA DE CATALISADORES

Leonardo R. P. dos Santos*, Rayssa J. B. Motta, Vinícius S. F. Viana, Jamerson W. Silva, Janaína H. Bortoluzzi, Simoni M. P. Meneghetti, Mario R. Meneghetti

Universidade Federal de Alagoas

* Corresponding author: leonardoraphael75@gmail.com

O dimetil carbonato (DMC) destaca-se como insumo química estratégico na química verde, reunindo baixa toxicidade, biodegradabilidade, possibilidade de produção a partir de CO_2 e ampla versatilidade sintética. Em contraste com reagentes perigosos como o fosgênio, o DMC viabiliza reações de carbonilação sob condições brandas, seletivas e ambientalmente seguras. Entre suas aplicações, sobressai-se na produção de carbonato de glicerol (CGli) através da transesterificação do glicerol, coproduto da indústria de biodiesel, com alta seletividade em condições suaves. Essa rota agrega valor a um resíduo de baixo custo, fortalece a economia circular e reduz impactos ambientais. O CGli apresenta amplo potencial industrial, atuando como solvente de baixo impacto, intermediário em síntese de polímeros e resinas, componente em eletrólitos para baterias de íons de lítio e aditivo em combustíveis, cosméticos e fármacos. A catálise exerce papel central no seu processo de produção, modulando tanto o rendimento quanto a seletividade. Neste estudo, foram avaliados os catalisadores MgO, SnO2, óxido misto SnMg e óxido de dibutilestanho (DBTO), além de uma condição não catalisada. A metodologia foi adaptada de Ochoa-Gómez (2009) e Jitjamnong et al. (2024), empregando proporção molar glicerol:DMC de 1:4, temperatura de 75 °C e tempo reacional de 5 h. O SnMg apresentou a maior conversão de glicerol (60%) com seletividade de 47% para CGli, sugerindo que a incorporação de Sn promoveu maior atividade catalítica, possivelmente por alteração da densidade eletrônica dos sítios básicos. Em seguida, observaram-se conversões de 33% para SnO2, 17% para MgO e 6% para DBTO. Quanto à seletividade, o MgO foi o mais seletivo (68%), ainda que sua conversão tenha sido inferior. De acordo com Ochoa-Gómez (2009), catalisadores heterogêneos, embora limitados por difusão, favorecem a formação do carbonato frente a subprodutos. As análises de GC-MS confirmaram a formação de CGli, validando os resultados. Assim, evidencia-se que a performance catalítica não depende apenas da força básica, mas também da acessibilidade dos sítios ativos e da interação entre glicerol e superfície catalítica, fatores-chave para rotas mais sustentáveis e eficientes.

Acknowledgements: Os autores agradecem o apoio do CNPq, CAPES, FAPEAL e FINEP pelo financiamento deste estudo.

Size Exclusion Chromatography and FTIR as Complementary Tools for Rapid Assessment of Biodiesel Oxidative Degradation

Cristiane Gimenes de Souza*[1], Beatriz Lima de Souza[2], Renan de Oliveira Muniz[3], Débora França de Andrade[4], Luiz Antonio d`Avila[3]

[1]Petroleum and Biofuels Chemical Program, PRH 20.1, Institute of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil
[2]School of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil
[3]Program in Chemical and Biochemical Processes Engineering, School of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil
[4]Institute of Chemistry, Federal University of Rio de Janeiro, Cidade Universitária, Rio de Janeiro, Brazil

* Corresponding author: cristianegimenes@yahoo.com.br

Biodiesel is a renewable biofuel produced by the transesterification of triacylglycerols from vegetable or animal feedstocks. In Brazil, its addition to fossil diesel became mandatory in 2008, with blending levels gradually increased over the years as part of the pro-biodiesel policy. The growing production and commercialization of biodiesel in the country reinforce the need to monitor its quality, with oxidative stability being a critical parameter. Due to its high susceptibility to oxidation, biodiesel may generate degradation products capable of causing filter plugging and engine corrosion.

Oxidative degradation occurs mainly through chain radical reactions triggered by exposure to high temperatures, light, or oxygen. These reactions proceed in three stages (initiation, propagation, and termination), leading to the formation of compounds that alter fuel properties. Currently, the Brazilian regulation establishes the Rancimat test (EN 14112) as the reference method for assessing biodiesel oxidative stability. Despite its wide use, this method is time-consuming, lasting up to 10 hours, which limits its applicability for routine quality control.

In this context, the present work proposes the application of size exclusion chromatography (SEC) as a complementary technique, combined with Fourier-transform infrared spectroscopy (FTIR), to provide faster insights into oxidative degradation. Commercial biodiesel samples were analyzed before and after oxidation in the Rancimat. FTIR analyses were conducted in the 4000–400 cm^{-1} range using KBr pellets. For SEC, 100 µL of biodiesel was injected into two Ultrastyragel columns of 100 Å and 50 Å (25 cm × 0.77 cm), using tetrahydrofuran as the mobile phase, refractive index detection, a flow rate of 1.0 mL/min, and a total time of 25 min.

It is expected that, in addition to functional group characterization by FTIR, SEC will allow the rapid detection of higher molar mass products, such as oligomers, thus providing an efficient and early indication of biodiesel degradation. This approach shows potential for routine laboratory applications, contributing to faster and more effective monitoring of biodiesel quality.

Acknowledgements: Acknowledgements: The authors thank FUJB and CNPq for the financial support.

SOLVENT SYSTEM SELECTION FOR COUNTERCURRENT CHROMATOGRAPHY ISOLATION OF COMPOUNDS FROM COMMERCIAL COPAIBA OLEORESIN

Aylla Lopes Haick[1], Brendo Araújo Gomes[2], Valdir Florêncio da Veiga Jr.[3], Suzana Guimarães Leitão[2], Mário Geraldo de Carvalho[4], Gilda Guimarães Letão*[1]

[1]Instituto de Pesquisas em Produtos Naturais Walter Mors - Universidade Federal do Rio de Janeiro
[2]Faculdade de Farmácia - Universidade Federal do Rio de Janeiro
[3]Departamento de Engenharia Química -Instituto Militar de Engenharia
[4]Instituto de Química - Universidade Federal Rural do Rio de Janeiro

* Corresponding author: ggleitao@ippn.ufrj.br

Copaiba oleoresin is a product of significant pharmacological interest, known for its antimicrobial, anti-inflammatory and wound-healing properties. It is extracted from the trunks of various Copaifera species and is a key resource for communities in the Amazon. The oleoresin consists of diterpenes and sesquiterpenes, which contribute to its bioactivity. Consequently, interest in isolating these compounds has grown, particularly using preparative reproducible and sustainable methodologies, with Countercurrent Chromatography (CCC) emerging as a promising technique. As a liquid-liquid chromatography technique, the selection of the solvent system (SS) is crucial and can be performed through a test-tube partitioning test. In this study, 50 mg of the oleoresin obtained from Adolfo Lisboa market (Manaus) was tested with fifteen SS in different proportions. Seven non-aqueous systems were tested: hexane-acetonitrile (1:1), hexane-methanol (1:1), hexane-acetonitrile-alcohol (MeOH or EtOH) (2:2:1 and 2:1:2), hexane-acetonitrile-ethyl acetate (2:2:1). Plus, eight aqueous systems: hexane-ethanol(or methanol)-water (2:2:1, 4:3:1 and 5:4:1), hexane-ethyl acetate-ethanol(or methanol)-water (1:1:1:1). After decantation, the upper and lower phases of each SS were analyzed by Thin-Layer Chromatography (TLC), using hexane:acetone (4:1) as the elution solvent and sulfuric vanillin reagent for visualization, allowing the estimation of the partition coefficient (K). Hexane-ethanol-water (5:4:1) exhibited a good distribution of compounds between the two phases, similar to some non-aqueous SS and was selected for fractionation of the oleoresin by High-Speed Countercurrent Chromatography (HSCCC), in reversed elution mode, considering the green nature of this SS in comparison with the non-aqueous ones. The results showed at least one pure diterpene derivative in the first eluted fractions and several semi-purified fractions. This study emphasizes that careful selection of the SS plays a vital role in enhancing the efficiency of CCC, highlighting its potential as a sustainable and reproducible technique for isolating pharmacologically relevant compounds from Copaiba oleoresin and supporting its sustainable use across various applications.

Acknowledgements: Thanks to CAPES, CNPq, FAPERJ, and FINEP for their financial support

SOLVING COMPLEX DIE INJECTION PROBLEMS IN GAS CHROMATOGRAPHY: A CRITICAL LOOK AT OPTIC 4 MULTIMODE INJECTOR APPLICATIONS

Ana Beatriz de Morais Salero*, Cristiane Oliveira Silva

Nova Analítica Importação e Exportação LTDA

* Corresponding author: ana.salero@novanalitica.com.br

The introduction of the sample is of paramount importance for gas chromatography (GC), so there are several ways to perform the injection. Conventional injectors generally have limitations in terms of their versatility, efficiency in transferring the sample to the column and discrimination of compounds with different polarities and volatilities. Thinking about the evaluation of complex matrices, the identification of analytes of interest can often be compromised, making their quantification unfeasible and generating the need for prior sample preparation. As a result, it is necessary to use injectors suitable for certain types of analyses. In view of this scenario, the Optic-4 multimode injector developed by GL Science-, can be an alternative, since it allows to perform injections of gaseous, liquid and even solid samples, as this injection device presents refined control of the flow of carrier gas, rapid temperature and cooling ramps, allowing different injection modes, such as cold, large volumes, thermal desorption, pyrolysis and derivatization in the liner. In this sense, this work aimed to present a review of the applications described for Optic-4, critically analyzing its modes of operation and potential contributions to overcome the limitations observed in conventional injectors.The manufacturer GL Sciences makes available on its website, several applications using the OPTIC-4 multimode injector, including current topics such as microplastic analysis, volatile species in plastic and environmental materials, paints in works of art, among others. Among the various applications, we highlight here the analysis of microplastics by CG, it is necessary to take previous steps in sample preparation, such as pyrolysis, but when using OPTIC - 4, this entire process occurs at the time of injection, promoting agility in the analysis, minimizing errors in sample preparation, for example. Another application evaluated was the verification of volatile species in paints in works of art. This type of analysis requires sample preparation, which can often damage or even destroy these works, when using this type of injection, these problems can be minimized. In light of the results that the application notes made available by GL Science, the OPTIC-4 injector consolidates itself as a versatile and promising tool for the development of innovative chromatographic methods, with potential impacts on analytical chemistry, quality control and environmental science research.

Acknowledgements: This work was supported by GL Sciences through the provision of application notes and technical materials, which enabled the review of the applications of the OPTIC-4 multi-mode inlet.

Sour Beer: A Preliminary Study on the Identification of Blueberry Anthocyanins by LC-ESI-QqQ-MS/MS

Milene Teixeira Barcia*, Carla Andressa Almeida Farias, Juliana Alves Camponogara, Andreara Rodrigues dos Reis, Cristiano Augusto Ballus, Sandra Kunde Schlesner, Juliano Smaniotto Barin

Federal University of Santa Maria

* Corresponding author: milene.barcia@ufsm.br

Sour beers are distinguished by their acidity, which favors the addition of fruits rich in anthocyanins. These pigments are stable in acidic media, which enhances color and adds sensory value. Blueberry, a relevant source of anthocyanins, can enrich sour beer by contributing both coloration and bioactive compounds. In this context, the aim of this study was to identify the anthocyanins in a sour beer with the addition of blueberry extract, using LC-ESI-QqQ-MS/MS. As for the methodology, the extract was obtained from 100 grams of a mixture of blueberry cultivars (Bluegem, Climax, and Florida) extracted by Microwave Hydrodiffusion and Gravity (MHG), using 600 watts for 6 minutes. Subsequently, the extract was incorporated into a sour beer produced in collaboration with a local brewery (Zagaia Brewery). The anthocyanins in the sour beer were analyzed using LC-ESI-QqQ-MS/MS, with a reversed-phase C18 column and a binary solvent gradient comprising water, acetonitrile, methanol, and formic acid in varying proportions. Ionization was carried out in positive mode, using optimized nebulization, drying, and heating conditions to ensure proper fragmentation and detection of the analytes. A total of 20 anthocyanins were tentatively identified, representing all classes of anthocyanidins, with a predominance of delphinidins (5 compounds) and cyanidins (4 compounds). Of these compounds, 14 are hexoside derivatives (galactosides and glucosides) and 6 are pentosides (arabinosides), of which 3 also contain acyl groups in their structure, such as acetyl and malonyl. Six anthocyanins (delphinidin-3-glucoside, cyanidin-3-glucoside, malvidin-3-glucoside, petunidin-3-glucoside, peonidin-3-glucoside, and pelargonidin-3-glucoside) were confirmed (standards) by multiple reaction monitoring (MRM), with optimized chromatographic parameters for precursor (Q1) and fragment (Q3) ions, as well as the ideal voltages applied to the quadrupoles. Finally, this study enabled the characterization of anthocyanins in sour beer with blueberry extract, providing relevant information on the compounds present and contributing to the valorization of this product as a potential innovation in the market.

Acknowledgements: INCT-ALIM: Grant No. 406760/2022-5; CAPES: Finance Code 001; FAPERGS: Grant No. 21/2551-0002284-1 PPG; CNPq: PQ Fellowship.

SPECTROSCOPIC AND CHROMATOGRAPHIC CHARACTERIZATION OF TWO GARLIC SPECIES: ALLIUM SP. AND ALLIUM SATIVUM

Pedro Rian Barros da Conceição*[1], Thauane Maria Pereira da Silva[1], Eduardo Karvat Mikulski[2], Flamys Lena do Nascimento Silva[1]

[1]Universidade Federal do Norte do Tocantins
[2]Centro Universitário Tocantinense presidente Antônio Carlos

* Corresponding author: pedro.conceicao@ufnt.edu.br

The Allium genus comprises more than 500 species distributed globally, constituting the main botanical group of the Amaryllidaceae family. Leek (Allium porrum L.; Allium ampeloprasum var. porrum L.) is a plant whose origin is associated with the Mediterranean Sea region, having been widely introduced into the European continent. Garlic (Allium sativum), in turn, is a bulbous plant native to Central Asia, with cultivation records since Antiquity. In addition to being one of the most widely used seasonings in the world, garlic has a long history of use in traditional medicine, presenting numerous health and wellness benefits due to the presence of bioactive compounds with proven antioxidant potential, such as organosulfur compounds (Xie et al., 2023; Biancollilo et al., 2022). Among these compounds, S-alk(en)yl-L-cysteine sulfoxides and their derivatives stand out. Alliin (S-allyl-L-cysteine sulfoxide), predominantly present in raw garlic, is degraded by the action of the enzyme alliinase, which is released when plant tissues are ruptured. This reaction results in the formation of allicin (diallyl thiosulfinate), the main compound responsible for the bioactive properties of freshly crushed garlic. Due to its high instability and reactivity, the allicin molecule rapidly degrades, giving rise to a series of more stable organosulfur compounds, such as diallyl disulfide (DADS), diallyl trisulfide (DATS), diallyl sulfide (DAS), in addition to other compounds such as ajoenes and vinyldithiins (González; Santamaría, 2017; Locatelli et al., 2017). This study aimed to carry out the volatile chemical characterization of the oil, leaves, and bulbs of two garlic species, Allium sp. and Allium sativum, using the HS-SPME/GC-MS technique. The Allium porrum variety was cultivated in the city of Araguaína – TO. The characterization, carried out through the HS-SPME/GC-MS technique, allowed the identification of 32 volatile organic compounds (VOCs) in the oil and leaves of Allium sp. Among the major compounds, the following stand out: methyl 2-propenyl disulfide (methyl allyl disulfide), diallyl disulfide, diallyl sulfide, (E)-1-allyl-2-(prop-1-en-1-yl) disulfane, and (E)-1-methyl-2-(prop-1-en-1-yl) disulfane. Allium sativum, in turn, was acquired from markets in the city of Araguaína – TO, and its characterization allowed the identification of 12 VOCs in the fresh bulb. The main compounds found were diallyl disulfide, diallyl trisulfide, methyl 2-propenyl trisulfide, and (E)-1-allyl-2-(prop-1-en-1-yl) disulfane. Based on the results obtained, it was observed that both species present common sulfur volatile compounds, such as diallyl disulfide and (E)-1-allyl-2-(prop-1-en-1-yl) disulfane, which shows a similar chemical profile between the species.

Acknowledgements: I thank Federal University of Northern Tocantins (UFNT), Foundation for Research Support of Tocantins (FAPT), National Institute of Science and Technology of Food (INCT-ALIM), and Tocantinense University Center Presidente Antônio Carlos (UNITPAC) for support and contributions to this work.

Stability-Indicating HPLC Method for Simultaneous Analysis of Tenofovir Disoproxil Fumarate and Emtricitabine

Valdinéa Santos Dias1*, Stéfanno Souza Santos, Edith Cristina Laignier Cazedey

Universidade Federal da Bahia

* Corresponding author: vvm2901dias@gmail.com

Pre-exposure prophylaxis (PrEP) against the Human Immunodeficiency Virus (HIV) involves the administration of a fixed-dose oral combination containing tenofovir disoproxil fumarate (TDF, 300 mg) and emtricitabine (FTC, 200 mg), marketed as Truvada®. Ensuring the quality and stability of these drugs is essential for safe and effective therapy. This study aimed to develop and validate a stability-indicating analytical method (SIAM) by high-performance liquid chromatography (HPLC) for the simultaneous quantification of TDF and FTC in active pharmaceutical ingredients (APIs) and coated tablets. Forced degradation studies were performed under acidic, basic, neutral, and oxidative conditions to assess the method's selectivity. Chromatographic separation was achieved using a Zorbax® C8 column (250 × 4.6 mm, 5 µm) with a gradient mobile phase of methanol and water, at a flow rate of 1.0 mL/min and detection at 258 nm (TDF) and 280 nm (FTC). The method showed excellent linearity over the range of 5–50 µg/mL for both analytes ($r^2 > 0.999$), limits of detection of 0.5 µg/mL, and limits of quantification of 1.5 µg/mL. Precision (RSD < 2.0%), accuracy (recoveries between 98.0–102.0%), and robustness results met international guidelines (ICH Q2(R2)) and Brazilian regulations (RDCs 166/2017 and 964/2025). Degradation studies demonstrated significant TDF degradation under basic conditions and FTC degradation under oxidative stress, confirming the method's stability-indicating capability. These findings highlight the method as selective, reliable, and suitable for routine quality control of fixed-dose PrEP formulations containing TDF and FTC.

Acknowledgements: The authors acknowledge FAPESB-PPSUS under contracts n° SUS0012/202 - Research Program for SUS: shared management in health.

STRATEGIES FOR THE DEVELOPMENT AND OPTIMIZATION OF A HPLC METHOD FOR CREATINE ANALYSIS IN DIETARY SUPPLEMENTS

Gislaine Aparecida de Cássia Souza*[1], Jhonatan Bispo de Oliveira[2], Ingrid Amélia dos Santos Matusinho[1], Patterson Patrício de Souza[1], Ildefonso Binatti[1], Patrícia Santiago de Oliveira Patrício[1]

[1]Centro Federal de Educação Tecnológica de Minas Gerais
[2]Universidade Federal de Minas Gerais

* Corresponding author: Gislaineacsouza@gmail.com

Creatine (N-(aminoiminomethyl)-N-methylglycine) is a fundamental organic molecule in muscle metabolism and one of the most widely consumed dietary supplements in the world, making its quality control essential. In this context, high-performance liquid chromatography (HPLC) is proving to be one of the most widely used analytical techniques for quality control. The aim of this study was to develop and optimize an HPLC method for creatine using Design-Expert 13 software for experimental design software. Based on the United States Pharmacopeia method, preliminary tests were performed to adapt the mobile phase, replacing acetonitrile and phosphate buffer with a more sustainable solvent. A 2^3 factorial design was then used to evaluate the effects of mobile phase concentration, column temperature, and flow rate. The analytical method was validated by reversed-phase HPLC, where the elution and separation of creatine was performed under isocratic conditions with an ammonium sulfate solution, allowing UV detection. Multivariate optimization resulted in the best analytical conditions at a higher temperature (50 °C), a lower mobile phase flow rate (0.5 mL/min), and a lower ammonium sulfate concentration (0.03 mol). The combination of these parameters was decisive for the separation efficiency. The higher temperature reduced the viscosity of the mobile phase and improved the interaction between creatine and column. A lower flow rate ensured an optimal retention time, which enabled a more efficient separation and well-defined peaks. Finally, the lower mobile phase concentration optimized the elution strength, reducing potential interferences in UV detection and extending column lifetime. Validation of the method confirmed its reliability. The calibration curve, with concentrations from 30 to 130 mg/L, showed a coefficient of determination (R^2) of 0.9959. The method showed good precision, with a repeatability of 0.43%, intermediate precision of 5.96%, and a recovery of 99%. In addition, no matrix effect was observed, and the elution time of 1.9 min demonstrated the speed and solvent-saving capacity of the method, making the procedure more efficient and sustainable.

Acknowledgements: Laboratório de Tecnologias Integradas (Intechlab); Centro Federal de Educação Tecnológica de Minas Gerais (CEFET-MG); Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

Strategies for trace contaminant analysis in complex sample matrices

Arianne Soliven*[1], Andrés Pérez-Parada[2]

[1]Avantor, 1 The Markham Centre, Station Road, Theale, Reading RG7 4PE, UK & Avantor, Minas y Cebollati, Montevideo, 11200 Uruguay
[2]Departamento de Desarrollo Tecnológico – DDT, Centro Universitario Regional del Este (CURE), Universidad de la República, Ruta 9 y Ruta 15, CP 27000, Rocha, Uruguay.

* Corresponding author: arianne.soliven@avantorsciences.com

Various types of organic pollutants can be present in both food and environmental samples. This poster aims to showcase the practical applications of LC-FLD in the routine analysis of glyphosate in freshwater and agricultural soils. Additionally, an alternative rapid determination of Ochratoxin A in wines compared to the international official method (OIV-MA-AS-315-10) will be demonstrated, employing a simplified workflow with superficially porous column technologies. Furthermore, the presentation will delve into the environmental dissipation of rice pesticides, presenting large-scale multi-residue methods using LC-MS/MS. This overview will give insights into the analytical versatility and efficacy of LC and alternative column selections in addressing diverse challenges related to organic pollutant analysis for robust analysis with low backpressure

Acknowledgements: Johnny Lima, Nova Analítica; Jose Cuadro, Zachary Stellbgerg, and Leandro Kasamatsu, Avantor for their additional support.

Study of Potential Extractables and Leachables in Roasted Coffee Packaging by Using Dynamic Headspace GC/MS

Ana Caroline Martimiano*

Shimadzu do Brasil, Barueri, Brazil

* Corresponding author: ana.martimiano@shimadzu.com.br

Introduction: Extractables are compounds that migrate from materials to a product when exposed to conditions such as temperature, time, and specific solvents. Leachables are compounds that migrate from a material into the environment over time. The analysis of extractable and leachable compounds (E&L) plays a crucial role in several industries, ensuring product compliance and preserving the health and safety of the end consumer. In the context of the food industry, where daily consumables like coffee play a significant role, it is essential to ensure quality control from production to the end of its shelf life. In response to this demand, an investigation was conducted to assess the presence of potential compounds in roasted coffee packaging, including capsules by using the HS-GC/MS. Methods: To prepare the samples, several brands of roasted and ground coffee were chosen, packaged in different packaging. The samples were divided in 20 mL vials, considering different components, such as adhesive and non-adhesive parts, aluminum parts and box. Each element, such as the capsule's internal filter, metal body and top seal, along with the corresponding roasted coffee powders, was analyzed individually. Regarding analytical conditions, a highly sensitive method was developed using the HS-20 NX in trap mode, coupled to the Shimadzu GCMS-QP2020 NX. A crucial point of the analysis stands out for the remarkable sensitivity achieved, allowing up to 5 times concentration of analytes in trap mode, even during a qualitative analysis using the single quadrupole in Scan mode.
Results: The use of HS-20 NX in Trap mode with GC/MS enabled the identification of over 100 compounds, comparing the spectra with the National Institute of Standard and Technology (NIST) library. Among these compounds are potential E&L substances such as Acetone, Ethanol, Ethyl Acetate, Toluene and Cumene, as well as coffee aroma components. This technique demonstrates high versatility and efficiency by providing high analytical sensitivity capable of identifying compounds even at low concentrations, something unachievable by conventional methods. This evolution represents a notable advancement in coffee and food quality control, enabling precise detection of essential characteristics and components to ensure the excellence of the final product and consumer health.

Acknowledgements: The speaker would like to acknowledge this present work to Shimadzu Corporation and Shimadzu do Brasil.

Study of the chemical diversity in spondias tuberosa leaves during the phenological evolution stages: metabolomic and chemometric approaches associated with antioxidant and antiglycant activities

Francisco Wendell do Nascimento[1], Tamyris de Aquino Gondim[1], Lucas Alexandre Nobre da Silva[1], Jhonyson Arruda Carvalho Guedes[1], Guilherme Julião Zocolo*[2]

[1]Universidade Federal do Ceará
[2]Embrapa Agroindústria Tropical

* Corresponding author: guilherme.zocolo@embrapa.br

Spondias tuberosa (umbu) has been studied from the perspective of natural product and pharmacology, revealing relevant biological activities. Therefore, from the point of view of chemical and biological studies, deepening knowledge about this species is of great importance. Additionally, the evaluation related to the metabolic variations of the same species during different phenological evolution stages is also an interesting aspect of the research. Thereby, ultra-performance liquid chromatography coupled to mass spectrometry (UPLC-QToF-MSE) was used to trace the chemical profile from umbu leaves at different phenological stages, allowing the detection of 40 metabolites, which 16 were annotated, such as phenolics and anacardic acids. Furthermore, the use of chemoinformatics tools allowed obtaining information on phenological development in the three leaves phases: post-flowering (young leaves), full production and senescence. The antiglycation activity assay revealed a potential inhibition of the formation of advanced glycation end-products (AGEs) in the leaves at different phenological stages. The antioxidant activity was satisfactory and in agreement with previously reported results, evidencing the potential for using umbu leaves, currently completely discarded, as an alternative source of antioxidants, which may provide increased added value to the cultivation of umbu, stimulating family farming and the recovery of tree density in degraded areas.

Acknowledgements: Federal University of Ceara (UFC), National Council for Scientific Technological Development (CNPQ, Brazil), and CNPQ (406760/2022-5: INCT - CHAMADA Nº 58/2022).

SYNTHESIS OF GRAPHENE-BASED MATERIALS FOR USE AS SORBENTS IN THE PREPARATION OF BIOLOGICAL SAMPLES

Jussara da Silva Alves*, Fernando Mauro Lanças

Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brazil

* Corresponding author: jussaraalves@usp.br

Sample preparation is a crucial step in chromatographic analysis, as it aims to prepare the sample for introduction into the analytical system, directly influencing subsequent stages and optimizing both qualitative and quantitative results. There is a growing demand for the development of new techniques and extraction phases that enhance the efficiency and selectivity of analytical methods while meeting environmental requirements. Microextraction techniques, such as Disposable Pipette Extraction (DPX), have been developed to address this need, offering significant advantages over conventional techniques, including lower solvent consumption, reduced analysis time, and the potential for automation. In parallel, new sorbent materials have been explored to improve extraction quality, with emphasis on graphene oxide (GO), which exhibits unique properties such as a large surface area, multiple extraction mechanisms, and the ability to be functionalized with other materials, such as β-cyclodextrin (β-CD), demonstrating superior selectivity and efficiency compared to traditional sorbents. In this context, this work proposes the synthesis and characterization of graphene-based materials, integrating them into microextraction techniques for application in biological samples. Initially, the synthesis of GO supported on silica and functionalized with β-CD was carried out, where challenges related to silica integrity were observed, attributed to the reaction conditions. Currently, new GO syntheses are in progress and will be characterized by infrared spectroscopy for subsequent functionalization with β-CD through two distinct routes. The performance of the obtained materials is expected to be compared in the extraction of biologically relevant analytes, such as neurotransmitters and mycotoxins, using the DPX technique. Subsequent stages will focus on optimizing the synthesized phases and applying them to real samples. The expected results may contribute to the development of more selective and sustainable sorbent phases for sample preparation in chromatography.

Acknowledgements: CAPES [Grants: 88887.999341/2024-00] and INCT-ALIM financed this study.

SYNTHESIS OF SILICA MONOLITH NESTED IN MAGIC SPONGE AS A NEW EXTRACTOR PHASE FOR SORPTIVE EXTRACTIONS

Roberta Marcelino, Anizio Marcio de Faria*

Universidade Federal de Uberlândia | Instituto de Ciências Exatas e Naturais do Pontal

* Corresponding author: anizio@ufu.br

Silica-based monolithic sorbents have high mechanical strength and are easy to modify, allowing selectivity to be fine-tuned. However, silica monoliths become brittle and shrink significantly when they are larger than those produced inside capillary tubes. The polycondensation of organosilane inside sponges is a simple and efficient strategy for preparing larger, rigid, and shaped silica monoliths. In this work, a central composite design was carried out to optimize the synthesis of 1 cm3 silica monoliths nested melamine-formaldehyde sponges (magic sponge) for use as an extractor phase in sorptive extractions. The melamine-formaldehyde sponges were treated with a 1% HNO3 solution to prepare the silica monoliths. Then, the precursor mixture with tetraethoxysilane (TEOS) and urea were added into 1 cm3 cubes of the pretreated sponges. The sponges soaked with the monolithic solution were subjected to heat treatment under different conditions according to the experimental design. The best preparation conditions, which resulted in the highest mass, ~70 mg/cm3, of silica monolith in the sponges, were at a condensation temperature of 60 °C, 40 mg of urea, and 500 µL of TEOS. The silica monoliths nested in the sponge under optimized conditions were evaluated by optical stereomicroscopy, infrared spectroscopy, thermogravimetric analysis, macroporosity, specific surface area, and scanning electron microscopy. It was possible to observe the formation of the silica monolithic structure in the sponge pores (87.5% occupation of the sponge volume), with characteristic signs of silanol groups and siloxane bonds. The silica monoliths presented a characteristic structure, with a surface area of 160 m2/g and a structure containing interconnected micro- and macropores. In general, the silica monoliths nested in the melamine sponge presented a rigid, hierarchically porous structure, making their application in extraction processes viable, which would not be possible in the form of autonomous monoliths (without nesting).

Acknowledgements: FAPEMIG (APQ-1901-22 and PCE-00390-25), CNPq, and FINEP (01.13.0371.00).

Tailoring GC×GC workflows: Modulation, detection, and application strategies

Matthew Edwards*[1], Khaled Murtada[1], Jonathan Grandy[1], James Ogden[2], Steve Smith[2], Laura McGregor[2]

[1]Markes International and SepSolve Analytical, 826 King St N, Unit 15, Waterloo, N2J 4G8, Canada
[2]SepSolve Analytical, 4 Swan Court, Forder Way, Peterborough, PE7 8GX, UK

* Corresponding author: medwards@schauenburganalytics.com

The analysis of complex samples is often limited by the separation capacity of conventional gas chromatography, where co-elutions can obscure both qualitative and quantitative information. Comprehensive two-dimensional gas chromatography (GC×GC) addresses these challenges by coupling two columns with orthogonal selectivities, thereby delivering enhanced peak capacity, improved selectivity, and structured chromatographic patterns that facilitate interpretation.

This presentation will discuss the advantages of GC×GC across a broad spectrum of analytical applications, with emphasis on how modulation type, detector choice and overall system configuration influence performance. Thermal and flow-based modulation strategies will be compared in terms of sensitivity, robustness, and suitability for specific analytical tasks. Detector options will also be examined, including but not limited to, flame ionisation detection (FID) for reliable quantitation, sulfur chemiluminescence detection (SCD) for selective measurement of sulfur species, time-of-flight mass spectrometry (TOF MS) for rapid, comprehensive spectral data acquisition, and high-resolution MS for accurate mass determination and molecular formula confirmation.

Through selected case studies, the versatility of GC×GC will be illustrated across diverse sectors such as environmental monitoring, petrochemical characterisation, food and flavour profiling, and forensic science. The examples will highlight how the ability to couple different modulators and detectors enables analysts to tailor GC×GC workflows to their specific research or regulatory questions. Collectively, these insights will demonstrate how GC×GC serves as both a discovery platform for untargeted analysis and a quantitative tool for routine measurement, underlining its value in advancing separation science.

TERPENE PROFILES IN DRY-HOPPED CRAFT BEER: DYNAMICS DURING FERMENTATION AND MATURATION

Rafaella Silva Aredes[1], Fernando Cunha Peixoto[2], Leandro Alcoforado Sphaier[1], Vinicius Nunes Henrique Silva[1], Lucas Mattos Duarte[1], Flávia Ferreira de Carvalho Marques*[1]

[1]Universidade Federal Fluminense
[2]Instituto Militar de Engenharia

* Corresponding author: flaviamarques@id.uff.br

Dry hopping is a fundamental technique in craft beer production, enhancing and preserving hop-derived volatile aromatics that contribute to the beer's freshness and complexity. This study investigated the effect of dry hopping on terpene profiles, specifically focusing on the quantification of myrcene and β-caryophyllene using GC-MS during primary fermentation and maturation. The wort was prepared using a blend of barley and wheat malts. Primary fermentation was carried out at a controlled temperature using a dry Saccharomyces cerevisiae yeast suitable for ale production. Dry hopping began toward the end of fermentation, when residual sugar levels were already low. GC-MS analysis of hydrodistilled volatiles from the beer revealed initial concentrations of 15.53 μg L^{-1} of myrcene and 3.33 μg L^{-1} of β-caryophyllene. On the first day of dry hopping, these values nearly doubled, reaching 27.80 μg L^{-1} and 10.77 μg L^{-1}, respectively, while β-farnesene remained undetected. In the following days, concentrations declined: between days four and five, myrcene ranged from 16.33 to 17.36 μg L^{-1}, and β-caryophyllene from 3.64 to 5.84 μg L^{-1}. This reduction likely reflects the temperature drop in the fermenter from 18 °C to 5 °C, which limited volatile losses despite the presence of headspace. Maturation began on day four with the temperature reduction, decreasing yeast activity, minimizing the formation of unwanted metabolites, and favoring flavor stabilization and natural clarification. During this stage, average concentrations stabilized at 16.63 ± 0.88 μg L^{-1} for myrcene and 5.84 ± 0.40 μg L^{-1} for β-caryophyllene. The extraction of hop volatiles depends on factors such as compound solubility, essential oil composition, yeast strain, contact time, and processing conditions. Literature reports terpene concentrations ranging from 3 to 2382 μg L^{-1} for myrcene and 0.4 to 443 μg L^{-1} for β-caryophyllene; the values observed here fall within these ranges. Peak transfer of hop compounds occurred on the first day of dry hopping, consistent with previous studies. Additional hop-related volatiles were also detected, revealing a complex aromatic profile. The detection of α-cedrene during maturation suggests yeast-driven biotransformation. Fermentation monitoring with a refractometer and optimized dry hopping enhanced aroma extraction and sensory quality. These findings improve understanding of terpene behavior in dry-hopped beers and support process improvements in craft brewing.

Acknowledgements: FAPERJ, CNPq, PROGEM-UFF

TERPENE PROFILING IN HOPS: MULTIVARIATE OPTIMIZATION OF HYDRODISTILLATION AND GC-MS FOR BREWING USE

Rafaella Silva Aredes[1], Fernando Cunha Peixoto[2], Leandro Alcoforado Sphaier[1], Vinicius Nunes Henrique Silva[1], Lucas Mattos Duarte[1], Flávia Ferreira de Carvalho Marques*[1]

[1]Universidade Federal Fluminense
[2]Instituto Militar de Engenharia

* Corresponding author: flaviamarques@id.uff.br

Hops contribute not only to beer's bitterness but also significantly enhance its aroma through volatile terpenes. Characterizing hop essential oil is important for quality control and recipe development, especially in craft breweries. This study aimed to optimize a simplified hydrodistillation method for extracting hop essential oil, utilizing a multivariate experimental design and GC-MS. The method focused on quantifying three commercially relevant terpenes—myrcene, β-caryophyllene, and β-farnesene—and was optimized by varying hop mass, water volume, and hydrodistillation time. GC-MS analysis employed an HP-5ms column, with 1 µL injection in split mode (1:10), helium as carrier gas (1.0 mL min^{-1}), and full scan acquisition (m/z 40–400) under electron ionization (70 eV). The oven was programmed from 50 °C to 300 °C with multiple ramps, including a 20-minute isothermal period at 118 °C. Results showed that oil yield increased with lower hop mass and longer hydrodistillation time, likely due to improved solvent penetration and mass transfer. Myrcene was better extracted at shorter times, while prolonged extraction favored β-caryophyllene and β-farnesene. Optimal conditions were established at 0.900 g of hops, 75 mL of water, and 60 minutes of hydrodistillation. The optimized parameters also enabled the qualitative analysis of four hop varieties: Polaris, Perle, Ariana, and Hallertauer Magnum. The essential oil profiles of Perle and Hallertauer Magnum were consistent with literature, with myrcene ranging from 20–35% and 30–45%, and β-caryophyllene from 10–20% and 8–12%, respectively. Both varieties exhibited higher-than-expected levels of β-farnesene (1.5% and 1.8% vs.

Acknowledgements: FAPERJ, CNPq

TILE-BASED GC×GC-TOFMS PROFILING OF ACIDIC BIOGENIC INPUTS IN DELAYED-COKING LIQUID PRODUCTS

Nathália dos Santos Pontes*[1], Yasmin Guimarães Pedro[1], Vinícius Barreto Pereira[1], Vanessa Farelo dos Santos[1], Adriana Moret Borges[2], Andrea Resende Pinho[2], Gabriela Vanini Costa[1], Raquel Vieira Santana da Silva[1], Débora de Almeida Azevedo[1]

[1]Universidade Federal do Rio de Janeiro (UFRJ)
[2]CENPES-Petrobras

* Corresponding author: nathaliapontes@iq.ufrj.br

Bio-oil co-processing with heavy streams in refining processes has been evaluated to include renewable sources in the energy generation process. The characterization of its products is important because acidic substances can be detrimental to the refinery infrastructure and to the quality of the obtained products. In this context, the application of comprehensive two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC×GC-TOFMS) combined with a Tile-based fold change approach allows the filtering of results to focus on the largest fold change differences between sample sets with moderate to marked differences in composition. This work shows the use of the Tile-based approach compared to a traditional peak table approach to identify differential features related to biogenic acid contributions in liquid products from delayed coking of vacuum residue co-processed with 5% (BO5) and 10% (BO10) bio-oil by mass compared to a 100% petrogenic process. The liquid products were fractionated via KOH-impregnated silica column chromatography to isolate acidic compounds, which were derivatized with N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) and analyzed by GC×GC-TOFMS using DB-5MS (1D) and HP-17HT (2D) column sets. Data processing was performed using ChromaTOF and ChromaTOF Tile softwares, applying a signal-to-noise ratio of 10:1 and a minimum mass spectral similarity of 70% for compound identification as TMS derivatives. The relative fold-change threshold applied to ChromaTOF Tile was generalized logarithm-base-two fold-change (LG2FC). The conventional processing data showed that the linear acid contribution increased after the inclusion of bio-oil, with relative area ranging from 55% in the 100% petrogenic product to 64% in BO5 and 72% in BO10. However, ChromaTOF Tile processing allowed the rapid observation that phenolic derivatives had a greater influence on the compositional differentiation of the samples after the inclusion of bio-oil, where syringol, catechol and m-cresol were identified only in BO5 and BO10, demonstrating the biogenic contribution in these products with a reduction in processing time of more than 80%. Thus, the tile-based fold change approach proved to be faster and more representative for the initial discrimination of complex data generated by GC×GC-TOFMS, acting as a complement to the conventional detailed evaluation at the molecular level by the peak table approach.

Acknowledgements: Petrobras, Capes, FAPERJ, and CNPq for the financial support.

TIME-RESOLVED IN VITRO HUMAN COLONIC FERMENTATION OF DIETARY (POLY)PHENOLS: KINETIC PROFILING AND PATHWAY MAPPING BY LIQUID CHROMATOGRAPHY MASS SPECTROMETRY

Gonzalo Tereucán[1], Nicole Tosi[2], Sara Dobani[2], Carmen Carrieri[2], Bianca Romanelli[2], Letizia Bresciani[2], Karem Henriquez-Aedo[3], Pedro Mena[2], Mario Aranda*[1]

[1]Pontificia Universidad Católica de Chile
[2]University of Parma
[3]Universidad del Bío-Bío

* Corresponding author: mario.aranda@uc.cl

Dietary (poly)phenols move through gastrointestinal tract (largely unabsorbed) and reach the colon, where the gut microbiota extensively metabolize them into lower-molecular-weight phenolics that may underpin biological effects. However, how fermentation time shapes compound-specific kinetics and pathway topology across chemical scaffolds remains poorly defined. The objective of this work was to map, in a time-resolved manner, the bioconversion kinetics and pathway topology of selected dietary (poly)phenols during colonic fermentation applying liquid chromatography coupled to high resolution mass spectrometry (LC-HRMS). Ferulic acid (FA), trans-resveratrol (RSV), and myricetin (MYR) were incubated with a pooled human fecal inoculum and sampled at 2, 6, 24, and 48 h. Metabolites were recovered by liquid-liquid extraction and analyzed by LC-MS. FA showed a rapid 0-2 h reductive burst: parent FA is biotransformed to dihydroferulic acid, then at 6h, shifted to 3-/4-hydroxyphenylpropionic acids (3-/4-HPPA); and after 24 h hydroxybenzoates compounds were observed. A relevant decrease in total recovered phenolics was detected at 48 h. RSV proceeded via dual routes at 0-2 h, hydrogenation to dihydroresveratrol and C-C bond cleavage to 4-hydroxyphenylacetic/propionic acids followed by a 6-24 h phase dominated by 4-HPPA and accumulation of reduced stilbenes; by 48 h, 4-HPPA change to benzoates. MYR was scarcely detectable at baseline; early traces of quercetin/gallic acid preceded a delayed 4-HPPA surge (peak at 24 h), then conversion to benzoates and detection of 4-vinylphenol, with a pronounced loss of recoverable phenolics. These results proved the usefulness of LC-HRMS technique to mapping (poly)phenols fate during human colonic fermentation.

Acknowledgements: Thanks to FONDECYT N° 1251474 and 1251584; ANID Nº 21221474; Academy Installation Grant Nº 85220091 and FONDEQUIP EQY220018 and EQM210203.

TRIHALOMETANOS COMO INDICADORES DE RISCO À SEGURANÇA ALIMENTAR: DETERMINAÇÃO POR HS-GC-MS EM ÁGUA DESTINADA AO CONSUMO EM AMBIENTE ACADÊMICO

Patricia de Sousa Queiroz*, Joaquim Rodrigues de Vasconcelos Neto, Lucas Alexandre Nobre da Silva, Ronaldo Ferreira do Nascimento

Universidade Federal do Ceará

* Corresponding author: patriciasqtargino@gmail.com

Trihalometanos (THMs) são contaminantes cancerígenos que se formam durante o tratamento da água com cloro e outros desinfetantes. O grupo dos trihalometanos totais (TTHMs) inclui quatro substâncias químicas: clorofórmio, bromodiclorometano, dibromoclorometano e bromofórmio. No Brasil, o valor máximo permitido (VMP) para TTHMs para água potável é de 100 µg L⁻1, conforme estabelecido pela Portaria GM/MS nº 888, de 4 de maio de 2021, que define os padrões de potabilidade da água destinada ao consumo humano. A via mais significativa de exposição aos TTHMs é a ingestão direta de água potável, ou como resultado de sua inclusão em bebidas, ou da interação de alimentos com desinfetantes durante a produção. Muitos processos alimentícios requerem água para lavar, resfriar ou transportar o produto e, para esses casos, deve-se utilizar água potável. Assim, os THMs podem ser sorvidos pelos alimentos e entrar na via de exposição alimentar. Como há exposição significativa de humanos a THMs por meio de alimentos e bebidas, organizações internacionais (FAO/OMS) recomendaram o desenvolvimento de métodos para determinação desses compostos nessas matrizes. Nesse trabalho, foi desenvolvido um método rápido e direto para a determinação simultânea dos quatro THMs em amostras de água destinada ao consumo usando headspace acoplado com cromatografia gasosa-espectrometria de massas (HS-GC-MS). Os parâmetros da curva de calibração indicaram bom desempenho do método, com respostas lineares ($R > 0,99$ para todos os THMs), baixos limites de detecção (LD) e quantificação (LQ), com LD variando entre 0,10 e 0,15 µg L^{-1} e LQ entre 0,30 e 0,47 µg L^{-1}, demonstrando sensibilidade satisfatória, além de elevada seletividade confirmada por espectros de massas. O método foi aplicado em amostras de água de 18 bebedouros distribuídos no Centro de Ciências da Universidade Federal do Ceará. Os resultados revelaram que 50% das amostras analisadas apresentaram concentrações de TTHMs superior ao VMP. As concentrações mais elevadas de TTHMs ultrapassam o VMP em mais de 100%, evidenciando a importância do monitoramento desses contaminantes para garantir a qualidade e a segurança alimentar da comunidade acadêmica.

Acknowledgements: Laboratório de Análise de Traços - UFC, INCT – alimentos, CAPES

UHPLC-DAD METHOD DEVELOPMENT FOR THE DETERMINATION OF ALLERGENIC COMPOUNDS USING THE AQBD APPROACH

Bianca Furukawa de Godoi Passerine*, Marcia Cristina Breitkreitz

Institute of Chemistry, University of Campinas (UNICAMP)

* Corresponding author: b265998@dac.unicamp.br

A robust UHPLC-DAD method was developed for the determination of 17 fragrance allergens regulated by EU 1223/2009, following the Analytical Quality by Design (AQbD) framework. During the screening phase, different stationary phases, organic solvents, gradient times, and column oven temperatures were systematically evaluated using an A- and G-optimal design of experiments. In this phase, trend responses such as the total number of peaks and the number of peaks with resolution greater than 2 were used to avoid peak tracking, which is challenging due to the extensive crossover of peaks. These trend responses were used to identify the most promising chromatographic conditions. Based on these results, the BEH C8 column with acetonitrile was selected for method optimization. A rotatable central composite design (CCD) was then employed to assess the influence of gradient time, temperature, and flow rate on critical responses, including resolution of critical pairs, peak symmetry, and retention factors. The Method Operable Design Region (MODR) was established using Monte Carlo robustness simulations in Fusion QbD, accounting for both parameter variability (±3σ) and measurement uncertainty. Robustness was evaluated through process capability indices, with the CpK index functioning as the principal measure of robustness, as it not only quantifies variability but also ensures that all responses remain within specification limits. By setting CpK ≥ 1.33 as the acceptance criterion, the MODR was defined as the multidimensional space where all CMAs simultaneously achieved at least a 99.99% probability of meeting quality requirements, even under routine variability. The use of Monte Carlo simulations and process capability to build the MODR ensures that the method delivers reliable and reproducible results in real-world applications, accurately reflecting the predictions of the statistical models. Verification experiments confirmed both the predictive accuracy of the models and the robustness of the MODR. Therefore, this study highlights the applicability of the AQbD approach for the systematic development of a robust UHPLC method for the determination of allergenic compounds in commercial products.

Acknowledgements: The authors gratefully acknowledge the financial support provided by CAPES.

UHPLC-Q-TOF-MS/MS-Based Metabolomics for the Study of Plant-Insect Interactions in Soybean

Josicleia Oliveira Costa*[1], Fernando Mauro Lanças[1], Victoria Patricia Peña Arroyo[2], Felipe Christoff Wouters[2]

[1]Instituto de Química, Universidade de São Paulo, São Carlos, São Paulo, Brazil
[2]Universidade Federal de São Carlos, São Carlos, São Paulo, Brazil

* Corresponding author: cleia.95oliveira@gmail.com

Metabolomics, combined with liquid chromatography coupled to mass spectrometry (LC-MS), has proven to be an effective approach for analyzing complex metabolic changes in plants under biotic stress. This technique allows the identification and quantification of metabolites, providing insights into the metabolic dynamics related to plant defense. Advances in high-resolution mass spectrometry, such as UHPLC-Q-TOF-MS/MS, have expanded the capacity for detecting and annotating a wide range of compounds, increasing the sensitivity and selectivity of the analyses. Soybean (Glycine max L. Merrill), a crop of great economic relevance, is susceptible to herbivory by Spodoptera frugiperda (Lepidoptera: Noctuidae), which impacts productivity. This caterpillar stands out due to its high adaptability and resistance to traditional control methods, such as the use of insecticides, motivating the investigation of plants' natural resistance. The present study evaluated the natural resistance of soybean by assessing the induction of metabolites in young and mature leaves at vegetative stages VC, V2, and V5. For this purpose, UHPLC-Q-TOF-MS/MS was employed in an untargeted metabolomic approach, allowing broad metabolic coverage and annotation of compounds from different chemical classes, including fatty acids, phenolics, and terpenoids. The results showed that stages VC and V2 were the most responsive to herbivory-induced stress, presenting greater metabolic alterations. In contrast, stage V5 exhibited lower metabolic induction, with compounds exclusively related to primary metabolism. Fatty acids, phenolic acids, and terpenoids were the main metabolites detected during the vegetative phase, but their accumulation differed between young and old leaves, with young tissues appearing more inducible than older ones. These findings reinforce that leaf age and plant developmental stage directly influence the magnitude of metabolic induction. Furthermore, they highlight UHPLC-Q-TOF-MS/MS as a robust tool to investigate plant defense mechanisms and characterize herbivory-induced metabolic changes, providing insights into natural resistance in soybean and the importance of this technique in studying plant-insect interactions.

Acknowledgements: CAPES and INCT-ALIM financed this study

ULTRASOUND-ASSISTED EXTRACTION METHOD FOR THE ASSESSMENT OF PHENOLIC COMPOUNDS IN COCOA BEAN SHELLS BY LC-MS/MS

Fabiana Luvizon Germer*, Amanda Tavares Germano, Luciano Vitali, Eduardo Sidinei Chaves

Federal University of Santa Catarina

* Corresponding author: f.luvizon@posgrad.ufsc.br

The cacao (Theobroma cacao L.) is a major commodity and the primary raw material used in chocolate production. During the processing of cacao beans to obtain chocolate precursors (cacao nibs), by-products such as cacao bean shells (CBS) are generated. It is estimated that CBS account for approximately 10 to 17% of the total seed weight, resulting in a considerable volume of by-products with significant potential for valorization, given their high content in bioactive compounds. In this context, the present study aimed to develop an ultrasound-assisted extraction (UAE) method for further quantification of phenolic compounds in CBS using LC-MS/MS. Based on previous optimizations employing Response Surface Methodology (RSM), the optimal extraction conditions were found using 80 °C, a solid-liquid ratio of 250 mg 5 mL-1 (ethanol 40% v/v), and a 20 minutes of extraction time. The responses were assessed through total phenolic content (TPC) determined via the Folin-Ciocalteu method (769 nm), and antioxidant activity (AA), evaluated by DPPH radical scavenging (517 nm) (IC50%). The combined responses were analyzed using the multiple response (MR) function. The effect of particle size was evaluated through TPC of CBS (20.48 ± 1.29 mg GAE g-1), ground CBS (24.86 ± 1.70 mg GAE g-1) and ground and sieved CBS samples (250 µm) (29.80 ± 1.87 mg GAE g-1). The assay was performed in triplicate, and analysis of variance (ANOVA) indicated a statistically significant difference among the different particle sizes. Consequently, 250 µm particle size was select for subsequent studies. Under the optimized conditions, the experimental TPC was 30.55 ± 0.98 mg GAE g-1 and IC50 91.6%. The ethanolic extracts were partitioned with ethyl ether (three times), centrifuged, and the supernatants were combined, evaporated, and reconstituted in 1 mL of methanol for LC-MS/MS analysis. The limits of detection (LOD) ranged from 0.05 to 0.61 mg L-1 and the limits of quantification (LOQ) from 0.15 to 1.86 mg L-1. All R2 values were greater than 0.99. The main compounds identified were isoquercetin (11.47 ± 3.76 mg L-1), epicatechin (11.41 ± 1.75 mg L-1), catechin (8.65 ± 1.45 mg L-1), vanillic acid (0.36 ± 0.41 mg L-1), and protocatechuic acid (3.00 ± 0.42 mg L-1). These results demonstrate the potential of the method for extracting bioactive compounds from CBS and for the valorization of by-products from the cocoa industry.

Acknowledgements: The authors would like to thank the Federal University of Santa Catarina, CNPq and CAPES for their financial support.

UNLOCKING A-TYPE PROCYANIDINS: ANALYTICAL TOOLS TO SUPPORT ENZYMATIC CONVERSION STRATEGIES

Mariana Monteiro Mattos França*[1], Gabriel R. Martins[2], Ayla Sant'Ana da Silva[1]

[1]Instituto Nacional de Tecnologia, Rio de Janeiro, Brasil
[2]Universidade de São Paulo, São Paulo, Brasil

* Corresponding author: mariana.monteiro@int.gov.br

Procyanidins (PCs) are polyphenolic compounds found in various fruits and vegetables. PCs are oligomers and polymers of (+)-catechin and (-)-epicatechin, classified as A-type and B-type PCs based on the nature of the interflavan bond. While B-type PCs feature a single C-C bond between subunits, A-type possess at least one additional ether bond between two subunits. Also, only A-type PCs promote inhibition of adhesion and biofilm formation against uropathogenic bacteria, making them valuable bioactive compounds. However, A-type PCs are scarce in native Brazilian species, making the search for alternative production routes relevant. A promising approach involves the enzymatic conversion of B-type into A-type PCs using oxidases. However, yields of this conversion are poorly reported due to analytical limitations in distinguishing individual PC dimers. As separating and quantifying A-type and B-type PCs is crucial to evaluate enzymatic efficiency and optimize reaction parameters, this study aimed to adapt and validate a chromatographic method to calculate the conversion yield from PCs B1 to A1. Initially, a method commonly used to analyze PC-rich samples showed poor separation between PC A1 (tR = 49 min) and the broad polymeric peak eluting at 51 min (Rs = 0.8). The method employed an HPLC-DAD system with a Symmetry C18 column (250 × 4.6 mm, 5 µm) and mobile phases of 0.5% formic acid in water (A) and acetonitrile:phase A (80:20, v/v). To mitigate this, the gradient was modified by increasing %B to 20% at 46 minutes, improving separation (tR = 44 min, Rs = 6). The adapted method was validated for selectivity and linearity. In the selectivity test, the slopes of the calibration curves prepared with and without matrix were very similar, with ratios of 1.02 for PC B1 and 0.99 for PC A1, indicating no matrix effect beyond the natural interference of the analyte. Therefore, the method was considered selective. Additionally, the calibration curves of both dimers showed $R^2 > 0.99$, indicating a good fit to the linear model. Although the yield calculation focused solely on dimer B1, it is sufficient to compare the effectiveness of different oxidases in samples where this structural feature predominates. This method provides a reliable analytical tool to support future studies on the enzymatic conversion of PCs and the valorization of PC-rich residues.

Acknowledgements: FAPERJ (SEI-260003/013232/2024), Instituto Serrapilheira (Serra-1708-15009), CNPq (440645/2022-0).

Untargeted Analysis of Human Skin Derived Fibroblast Cells Exposed to Phthalates by GC-MS/MS

Nayara Silva Fraga*, Josimar Marques Batista, Michele Angela Rodrigues, Dawidson Assis Gomes, Zenilda de Lourdes Cardeal, Helvécio Costa Menezes

Universidade Federal de Minas Gerais

* Corresponding author: naysfraga@gmail.com

The pollution from improper disposal of plastics is rising, as they accumulate in soil, rivers, lakes, and oceans. These materials are often exposed to slow degradation, releasing harmful chemicals into the environment. Among them, phthalates are of particular concern due to their potential to disrupt the human endocrine system. Dermal contact is a key exposure route for these compounds, especially for low-molecular-weight compounds such as dimethyl phthalate (DMP) and diethyl phthalate (DEP), which are widely used in personal care products. In this study, human skin derived fibroblast cells were cultivated and exposed to a 0.42 g L-1 mixture of DMP and DEP 1:1. After exposure, the cells were collected and quenched with a cold mixture of 80% methanol: water, and the metabolites were extracted with a cold mixture of 1:1 methanol: acetonitrile. The extracts obtained were lyophilized for 3 h and then stored in an ultrafreezer (- 80 ºC). For analysis, the dried extracts were subjected to a rapid derivatization protocol using isobutyl chloroformate, and the resulting derivatives were then injected into a gas chromatography system coupled with tandem mass spectrometry (GC-MS/MS). A Nexis GC-2030 with a triple quadrupole TQ 8040 NX, both from Shimadzu, equipped with a HP-5MS column (30 m x 0.25 mm x 0.25 µm), was used for the chromatographic analysis. The volume of sample injected was 1.0 µL, and the injector operated at 280 °C in splitless mode for 0.5 min. The carrier gas was helium, at a flow rate of 1.5 mL min-1. The oven temperature program started at 50 °C, held for 7 min, and then raised to 300 °C at 10 °C min-1, holding for 2 min. The interface was maintained at 300 °C, and ionization occurred at an energy of 70 eV. The third quadrupole (Q3) was operated in SCAN mode for the m/z range of 50-500 for a fingerprint of the biological extracts. The GC-MS raw data files were processed in GCMS solution and AMDIS software. The control samples and the samples exposed to contaminants reveal distinct profiles, both in terms of the number of compounds detected and their intensity. These metabolic changes, resulting from the exposure, are crucial for elucidating the biochemical pathways disrupted by plastic contaminants and establishing high-resolution metabolomic signatures for toxicity assessment.

Acknowledgements: The funding for this study was provided by CNPq, CAPES, FAPEMIG, Finep and CEI-DQ/UFMG.

UNTARGETED LIPIDOMICS OF Staphylococcus aureus STRAIN WITH ALTERED STAPHYLOXANTHIN REVEALS MEMBRANE REMODELING AND SUGGESTS ASSOCIATION WITH ANTIMICROBIAL PEPTIDE RESISTANCE

Chiara Carazzone*, Juan E. González, Elizabeth Suesca, Chad Leidy

University of los Andes

* Corresponding author: c.carazzone@uniandes.edu.co

Staphylococcus aureus is a clinically relevant pathogen capable of causing infections ranging from mild to severe. Its resilience is partly due to membrane adaptations, including the production of staphyloxanthin (STX), a carotenoid that increases rigidity and protects against oxidative stress and host defenses. Disrupting STX biosynthesis not only compromises membrane integrity but may trigger compensatory remodeling of other lipid species—alterations that could redefine the bacterium's vulnerability and reshape its survival strategy under hostile conditions.

To explore how STX biosynthesis influences lipid remodeling, we analyzed a clinical strain (SA144), a crtM deletion mutant lacking STX (SA145), and a complemented strain (SA147) expressing a crtMN variant that restores STX with an additional double bond, yielding a structurally more rigid carotenoid. These strains were subjected to untargeted lipidomic analysis by HPLC-qTOF in both positive and negative ESI modes, allowing comprehensive characterization of membrane lipid profiles associated with the presence or absence of STX.

Notably, the STX-deficient mutant SA145 exhibited a marked increase in lysyl-phosphatidylglycerols (Lysyl-PG) and cardiolipins (CL), both associated with enhanced resistance to cationic antimicrobial peptides and modulation of membrane rigidity. Additionally, elevated levels of digalactosyldiacylglycerols (DGDG) and free fatty acids were observed, suggesting broader lipid remodeling in response to STX absence. In contrast, strain SA147, which produces a structurally reinforced STX variant, showed increased levels of phosphatidylglycerols (PG) and monogalactosyldiacylglycerols (MGDG), indicating a distinct lipidomic profile linked to the presence of the modified carotenoid. Lipid extracts from these strains also exhibited differential responses to antimicrobial peptides such as ATRA-1 and LL-37, shedding light on how membrane composition may influence peptide interaction and bacterial susceptibility.

Together, these findings underscore the pivotal role of STX in shaping the lipid landscape of S. aureus and reveal how its absence or structural modification triggers compensatory remodeling that impacts membrane behavior and peptide sensitivity.

UNVEILING THE BIOACTIVE LIPID POTENTIAL OF ZOPHOBAS ATRATUS LARVAE

Nayah B. Prado[1], Paulo Vitor F. Lemos[2], Aurora B. Andrade[1], Manuela Nascimento[3], Paulo R. Mesquita[3], Jania B. A. Silva[4], Denílson J. Assis[5], Lucas G. Cardoso[5], Ederlan S. Ferreira[1], Henrique R. Marcelino[1], Carolina Oliveira de Souza*[1]

[1]Federal University of Bahia
[2]Martin Luther University Halle-Wittenberg
[3]Agricultural Technological Center of the State of Bahia
[4]Federal University of Recôncavo da Bahia
[5]University of Salvador

* Corresponding author: carolods@ufba.br

The search for sustainable and functional lipid sources has drawn increasing attention to edible insects. While oils from Tenebrio molitor and Hermetia illucens have been extensively studied, the lipid fraction (LF) of Zophobas atratus larvae remains poorly characterized, despite its high lipid content and potential for innovative applications. This work provides the first comprehensive assessment of Z. atratus lipids, focusing on fatty acids, β-carotene, tocotrienols, and volatile compounds, which define nutritional quality, oxidative stability, and sensory attributes. Lipids were extracted by mechanical pressing at 40 °C. Fatty acids were identified as methyl esters by GC-MS, β-carotene quantified by UV-Vis spectrophotometry, tocotrienols determined by HPLC-FL, and volatile compounds profiled by HS-SPME-GC-MS. Thirteen fatty acids were detected, dominated by palmitic (36.23 %), oleic (29.64 %), and linoleic (22.96 %), representing nearly 90 % of the profile. The LF contained 45.41 % saturated and 54.60 % unsaturated fatty acids, with favorable nutritional indices such as atherogenicity (0.78) and hypocholesterolemic / hypercholesterolemic ratio (1.40). The relatively high saturated fraction supports oxidative stability compared with conventional vegetable oils. β-carotene was quantified at 16.75 mg/100 g, conferring antioxidant and pigmentation potential. Only α-tocotrienol was detected (0.05 mg/100 g), confirming a negligible contribution of this vitamin E derivative. Fifty volatile compounds across thirteen chemical classes were identified, with alcohols predominating (24.81 %), especially 1-decanol (73.68 %) and 2,3-butanediol (10.57 %), responsible for fatty, cocoa butter, and floral notes. In conclusion, Z. atratus lipids exhibit a distinctive profile enriched in functional bioactive compounds and volatiles that combine nutritional value, oxidative stability, and unique sensory attributes. These findings highlight the innovative potential of this underexplored insect species as a sustainable lipid source for food, feed, and cosmetic applications, reinforcing its role in advancing circular and bioeconomy-driven food systems.

Acknowledgements: CNPq, FAPESB, CAPES, INCT Midas, INCT Carne, INCITE Rede Pró-Alimento.

USO DE ETANOL EM CROMATOGRAFIA LÍQUIDA DE ALTA EFICIÊNCIA DE FASE REVERSA – ENSAIOS PRELIMINARES

Moacir Francisco de Brito*, Luciana B. Lopes

Instituto de Ciências Biomédicas - Universidade de São Paulo

* Corresponding author: mfbrito@icb.usp.br

Dada a justificada preocupação com a preservação ambiental, se torna necessário a busca por métodos analíticos menos agressivos ao meio ambiente. A técnica de CLAE em fase reversa freqüentemente utiliza grandes quantidades de solventes orgânicos tóxicos como metanol(metOH) e acetonitrila(ACN). Com a intenção de reduzir o consumo desses solventes, foi estudada a sua substituição por etanol(etOH) na fase móvel, para a análise quantitativa de quatro fármacos: cafeína(CAF), fenretinida(FRT), terbinafina(TBF) e itraconazol(ITZ). As separações cromatográficas de padrões destas substâncias foram realizadas em colunas de fase reversa de núcleo sólido (C18 de 2,6um, 100x3mm e 50x4,6mm) em dois equipamentos diferentes, Agilent 1100 e Shimadzu LC10Avp. Para CAF e FRT, foram realizadas comparações com três solventes: ACN+água, metOH+água e etOH+água. O equipamento utilizado foi o Agilent 1100 e a coluna de 100x3mm, onde se ajustou a “força” do solvente para tempos de retenção próximos (6,88, 7,77 e 7,99 min para CAF e 6,03, 11 e 6,77 min para FRT). Observou-se um aumento de pressão considerável diretamente proporcional a concentração do etOH (132, 134 e 156bar para CAF e 80, 160 e 260bar para FRT). Para a CAF, a concentração do etOH foi igual à da ACN (10%), enquanto que para a FRT, foi reduzida de 80% para 70%. Devido à viscosidade do etOH, gera-se uma pressão muito alta no sistema, o que é um fator limitante para o Shimadzu LC10Avp, usado na separação da TBF (metOH a 90%) e ITZ (ACN a 65%). Neste caso, utilizou-se coluna com menor comprimento e diâmetro maior (C18, 50x4,6mm 2,6um). A concentração de etOH foi ajustada para se aproximar dos tempos de retenção de cada método (valores médios de 6,480 para 6,538min e 5,657 para 5,050min para TBF e ITZ respectivamente). As áreas dos picos se mantiveram próximas para as quatro substâncias, mostrando sensibilidade similar. Os valores r2 obtidos após análise de curvas de calibração das substâncias (0,5-10ug/mL) foram praticamente idênticos (superiores a 0,99), demonstrando a viabilidade da troca dos solventes normalmente utilizados por etOH.

Acknowledgements: FAPESP (2018/13877-1, 2019/21910-1)

VALIDAÇÃO DE ENSAIOS DE DISSOLUÇÃO EM COMPRIMIDOS DE ARTEMÉTER/LUMEFANTRINA: CONTRIBUIÇÃO AO TRATAMENTO SEGURO E EFICAZ DA MALÁRIA

Andre Colonese*, Patrícia Condé de Lima, Daniela Silva Santana, Sthefany Maria Libonati Cury, Caroline Volpe da Cruz, Ricardo Luiz do Nascimento Maranho, Soraya M. Ochs, Mychelle Alves Monteiro

Instituto Nacional de Controle de Qualidade em Saúde / Fiocruz

* Corresponding author: andre.colonese@fiocruz.br

A malária permanece como um dos principais problemas de saúde pública mundial. De acordo com a Organização Mundial da Saúde (OMS), foram registrados 263 milhões de casos em 2023, distribuídos em 83 países endêmicos, contra 252 milhões em 2022. No mesmo período, os óbitos passaram de 600 mil para 597 mil. A doença, causada por parasitas do gênero Plasmodium spp., manifesta-se desde sintomas leves, como febre e calafrios, até complicações graves, incluindo insuficiência renal, distúrbios de coagulação e morte. Assim, o diagnóstico precoce e o tratamento eficaz são fundamentais para a redução da mortalidade. A combinação Arteméter + Lumefantrina é amplamente utilizada no tratamento da malária, e a garantia de qualidade desses medicamentos é essencial para assegurar sua eficácia terapêutica. Entre os ensaios de controle de qualidade, o teste de dissolução é classificado como ensaio de performance. Embora não esteja descrito em compêndios oficiais, foi identificado um método não oficial na Farmacopeia dos Estados Unidos (USP), o qual foi adotado como base para este estudo. O objetivo deste trabalho foi validar o referido método para o ensaio de dissolução de medicamentos de dose fixa combinada de Arteméter e Lumefantrina. Para tanto, o ensaio foi conduzido individualmente para cada princípio ativo. O arteméter foi analisado em meio aquoso (1 L), utilizando aparato 2 (pá) a 100 rpm por até 3 horas, com quantificação por cromatografia líquida de alta eficiência (detecção em 210 nm). Já a lumefantrina foi avaliada em meio de HCl 0,1 N contendo 1% de cloreto de benzalcônio (1 L), também em aparato 2 (pá) a 100 rpm por 45 minutos, com análise espectrofotométrica em 342 nm. Como critérios de aceitação, estabeleceu-se que para o arteméter não mais que 40% deveria estar dissolvido em 1 hora e não mais que 60% em 3 horas, enquanto para a lumefantrina não mais que 60% deveria estar dissolvido em 45 minutos. A validação incluiu seletividade, linearidade, repetibilidade, exatidão e efeito matriz. Os parâmetros avaliados atenderam aos critérios de aceitabilidade, confirmando que o método é adequado e confiável para o ensaio de dissolução da combinação Arteméter + Lumefantrina. Esse resultado contribui para fortalecer o controle de qualidade desses medicamentos, assegurando maior segurança e eficácia no tratamento da malária.

VALIDAÇÃO DE MÉTODO MULTIRRESÍDUO PARA ANÁLISE DE PRODUTOS PLANT BASED: ANÁLOGOS DO LEITE

Rafael Onilton de Oliveira Sales*[1], Felipe Sousa da Silva[2], Crisiana de Andrade Nobre[2], Jéssica Roberta Pereira Martins[1], Maria Aparecida Liberato Milhome[1]

[1]Instituto Federal de Educação, Ciência e Tecnologia do Ceará-IFCE
[2]Núcleo de Tecnologia e Qualidade Industrial-NUTEC

* Corresponding author: rafael.onilton61@aluno.ifce.edu.br

As bebidas à base de vegetais análogos aos produtos de origem animal foram desenvolvidas para substituí-los no mercado visando dietas mais saudáveis, um consumo mais consciente em respeito ao meio ambiente e de proteção aos animais, contemplar a população que possui restrições alimentares quanto a proteína do leite bovino e a lactose. O mercado plant-based cresce a cada ano com inovação frequente de novos produtos. Porém, os agrotóxicos que são utilizados nas práticas agrícolas para promover aumento na produção e qualidade do produto são usados indiscriminadamente, o que pode afetar a saúde dos consumidores de bebidas vegetais. Devido à complexidade dos agrotóxicos e a possibilidade de permanecerem presentes em produtos processados, se faz necessário à validação do método analítico para controle desses contaminantes em alimentos plant-based, análogos do leite. Diante desta problemática, este trabalho propõe-se em validar um método para detecção de seis agrotóxicos (Azoxistrobina, Bifentrina, Difenoconazol, Piriproxifen, Metalaxil-M e Tebuconazol), através do método de extração QuEChERS e detecção por cromatografia gasosa acoplado à espectrometria de massas (CG/Q-MS). Amostras de bebidas vegetais à base de castanha de caju comercializadas na região do Vale do Jaguaribe-CE foram analisadas no método multiresíduo. No estudo foram determinadas as seguintes figuras de mérito: seletividade, linearidade (homocesdasticidade), Limite de Detecção (LD), Limite de Quantificação (LQ), Exatidão e Precisão. O método foi validado seguindo as recomendações da Eurachem 2025. O estudo mostrou que todos os ingredientes ativos estudados apresentaram seletividade adequada, através da comparação da matriz com a amostra fortificada. O método apresentou linearidade na faixa de trabalho de 0,03 a 1,5 mg kg-1, com coeficiente de determinação R2 ≥ 0,9938, sendo classificados como heterocedásticos (necessitando de ajuste da curva), com exceção do Metalaxil-M (homocedástico). Os LQs obtidos para Azoxistrobina, Bifentrina, Difenoconazol, Metalaxil-M e Tebuconazol foram de 0,033 mg kg-1 e para Piriproxifen 0,0165 mg kg-1. Todos os valores foram inferiores aos limites máximos de resíduos (LMRs) estabelecidos pela Agência Nacional de Vigilância Sanitária (ANVISA) para as respectivas culturas. A exatidão foi obtida em três níveis de concentração, variando entre 70,02-109,43%. A precisão, expressa através do desvio padrão relativo DPR, manteve-se entre 6,40-9,73%. O método validado foi aplicado satisfatoriamente para análise das amostras de leite vegetal (castanha de caju), as quais não apresentaram resíduos dos agrotóxicos estudados. Assim, o estudo sugere a aplicação do método validado no monitoramento de resíduos de agrotóxicos em bebidas de base vegetal (plant-based) para garantir a segurança alimentar.

Agradecimentos: INCT-ALIM (CNPQ), PRAPG (CAPES), FUNCAP

Acknowledgements: INCT-ALIM (CNPQ), PRAPG (CAPES), FUNCAP

VALIDATION OF AN HPLC-PDA METHOD FOR COMPREHENSIVE DETECTION OF GROUP B TRICHOTHECENES IN BREAD

Andressa Cunha Lemos, Eliana Badiale-Furlong, Priscila Tessmer Scaglioni*

Universidade Federal do Rio Grande - FURG

* Corresponding author: priscilascaglioni@gmail.com

The aim of this study was to validate an analytical method for determination of group B trichothecenes – deoxynivalenol (DON), 3-acetyl-deoxynivalenol (3ADON), 15-acetyl-deoxynivalenol (15ADON), deoxynivalenol-3-glucoside (DON-3G), and nivalenol (NIV) – in commercial bread samples. For this purpose, high-performance liquid chromatography with a diode array detector (HPLC-PDA) was used, operating at 220 nm with a C18 column. The HPLC system operated at a flow rate of 0.5 mL/min and a temperature of 40 °C, using isocratic elution (water:acetonitrile, 50:50 v/v) for 10 min, and an injection volume of 20 µL. The analytes were extracted using the QuEChERS method with 3.5 g of sample and acetonitrile as the extraction solvent. The performance parameters evaluated included recovery, linearity, detection and quantification limits, accuracy, precision, sensitivity, and selectivity, in addition to chromatographic parameters (retention time, retention factor, selectivity, and resolution). Matrix calibration curves were established for each trichothecene. The validation results showed retention times ranging from 4.841 min (DON-3G) to 7.586 min (3ADON), selectivity between 1.12 and 1.37, and resolution of 4.20, indicating good separation between DON and 15ADON. The recoveries obtained ranged from 83.0% (NIV) to 100.7% (DON-3G), with a relative standard deviation of less than 20%, which is in accordance with the regulatory authorities for the development of analytical methods. The coefficient of determination was greater than 0.98 for all analytes; the detection and quantification limits of the method were 16.29 µg/kg and 53.57 µg/kg, respectively. The uncertainty ranged from 2.40% (DON-3G) to 33.40% (NIV). The method was applied to 30 samples of different types of commercial bread, with DON contamination above 1000 µg/kg observed in 36.7% of the samples, the maximum limit established by ANVISA for wheat-based foods. At least two trichothecenes were found in the same sample, and even in the absence of DON, NIV and/or DON-3G were detected. Whole wheat bread had contamination levels 1.3 times higher than white bread. In conclusion, the validated method shows analytical performance in accordance with official recommendations and proved to be adequate for the determination of group B trichothecenes in white and whole bread, highlighting the need for a multi-analytical approach to monitoring contaminants in food.

Acknowledgements: We thank CAPES for the grant awarded.

VOLATILOMIC ANALYSIS OF CERUMEN FROM HEALTHY HUMANS AND THOSE WITH BENIGN AND MALIGNANT TUMORS VIA HS/GC-MS

Rhyan César Santos Dias*[1], Anselmo Elcana de Oliveira[2], Nelson Roberto Antoniosi Filho[3]

[1]Laboratório de Métodos de Extração e Separação (LAMES/UFG), Instituto de Química Universidade Federal de Goiás (IQ-UFG)
[2]Laboratório de Química Teórica e Computacional, Instituto de Química Universidade Federal de Goiás
[3]Laboratório de Métodos de Extração e Separação (LAMES/UFG), Instituto de Química Universidade Federal de Goiás (IQ-UFG);

* Corresponding author: rhyancesarqmc@gmail.com

Benign tumors usually grow slowly and in a capsular form minimizing the likelihood of developing metastasis. When the tumor growths in an uncontrolled manner it can lead to several problems, such as an increased pressure on adjacent organs, metabolic changes, and even causing the death of the individual. Although imaging is widely used in clinical diagnosis, visual similarity is a factor that hinders accuracy and may lead to unnecessary surgeries or delays in appropriate patient treatment. Volatilomics has emerged as a tool for analyzing volatile organic compounds (VOCs) in samples such urine, feces, and earwax. Studies conducted by the research group at the LAMES UFG, Brazil, led by Professor Dr. Antoniosi Filho, have demonstrated the potential of volatilomics applied to cerumen samples in the diagnosis of malignant tumors both in early and advanced stages. The present study aims, for the first time, to apply the current methodology to cerumen samples from patients having benign or malignant tumors, and healthy individuals. In the overall, 81 earwax samples from patients with benign tumors (29), malignant tumors (27), and healthy individuals (25) were analyzed by HS/GC-MS using an NST 100-MS column (polyethylene glycol, 25 m x 0.25 nm x 0.30 µm). A Partial Least-Squares Discriminant Analysis (PLSDA) model applied to the processed data presented an accuracy of 0.782. The top 5 compounds with the highest vipscore for each class were: Formamide, N-methyl- for all groups, Acetamide; Octan-2-one, 3,6-dimethyl; Phenol and 1,4-diazabicyclo[4.3.0]nonan-2,5-dione, 3-methyl for the benign tumor group; Pentadecanoic acid; Oleic acid; Tetradecanoic acid and Hexadecanoic acid, methyl ester for malignant individuals; Pentadecanoic acid; Oleic Acid; Hexadecanoic acid, methyl ester and Dodecanoic acid for healthy individuals. The discrimination of groups based on VOCs found in earwax demonstrates the potential of the methodology in characterizing individuals with benign and malignant tumors. Two other PLSDA models were also constructed using the Benign versus Malignant and Benign versus Healthy groups, resulting in respective accuracies of 0.947 and 0.682. Further studies may indicate its effectiveness in clinical analyses, including as a minimally invasive sampling technique.

Acknowledgements: LAMES/UFG, IQ-UFG, CAPES, INCT-ALIM, HAC.

WORKFLOW PERSONALIZADO PARA MONITORAMENTO DE ÁCIDOS NAFTÊNICOS EM ÁGUA PRODUZIDA E ÓLEO UTILIZANDO GC-HRMS

Fabricio Gomes do Prado*, Lucas Paines Bressan, Leandro Wang Hantao

Unicamp

* Corresponding author: f204470@dac.unicamp.br

A água injetada nos poços para extração de petróleo, juntamente com a água de formação nativa, forma o que denominamos água produzida (PW). O contato direto entre água e óleo leva à partição e migração de compostos, incluindo os ácidos naftênicos (NAs), que são o foco deste estudo. Esses compostos são conhecidos pela indústria petrolífera por causarem diversos problemas operacionais como corrosão de estruturas e estabilização de emulsões. Atualmente, a caracterização dos NAs no óleo e na água produzida se dá por cromatografia gasosa acoplada à espectrometria de massas de alta resolução (GC-HRMS) e apresenta desafios analíticos significativos. A complexidade das matrizes, com sua ampla faixa de número de compostos, massas e polaridade, sobrecarrega os softwares comerciais disponíveis e demanda um tratamento de dados específico. As ferramentas convencionais demonstram limitações no processamento de dados altamente complexos e em grande volume, resultando em processos lentos e pouco eficientes. Diante desses desafios, este estudo teve como objetivo desenvolver um workflow personalizado e eficiente para quantificação de NAs em petróleo e PW utilizando GC-HRMS. As análises foram realizadas em um sistema GC Trace 1310 acoplado a um espectrômetro de massas de alta resolução FT-Orbitrap. O desenvolvimento de uma metodologia computacional personalizada em Python permitiu a obtenção e processamento automatizado de cromatogramas de íons extraídos (EIC) para compostos específicos individualmente por amostra. Parâmetros avaliados, como sensibilidade e coeficiente de correlação (R2), demonstraram que a abordagem personalizada alcançou resultados equivalentes aos obtidos com softwares comerciais, porém com um tempo de processamento 90% menor. Com isso, a metodologia desenvolvida ofereceu vantagens adicionais em termos de automação, flexibilidade e agilidade na análise de ácidos naftênicos em matrizes de petróleo e água produzida.

Acknowledgements: Petrobras, FAPESP, CNPq, CAPES.