

Plan Overview

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Title: Solventes eutéticos naturais: Síntese, caracterização e aplicações na determinação de As, Cd, Cr, Hg, Se e V em amostras ambientais por ICP-MS

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Project abstract:

O desenvolvimento de métodos de preparo de amostras que priorizam a redução e substituição de reagentes e solventes, manipulação mínima das amostras, emprego de fontes energéticas mais eficientes e menor risco ao operador e meio ambiente são temas relacionados à Química Analítica Verde. O emprego de solventes pode causar impacto ambiental e por isso há uma grande preocupação e busca em desenvolver novos materiais com menor toxicidade, baixo custo e mais seguros aos analistas. Os solventes eutéticos naturais (NADES) são uma nova possibilidade que apresentam vantagens como biodegradabilidade, baixa toxicidade e preparação simples. A síntese desses novos NADES à base de aminoácidos combinados com açúcares e ácidos orgânicos pelos métodos de aquecimento e agitação, por evaporação, síntese assistida por ultrassom (SAU) e por radiação micro-ondas (SAM) será desenvolvida. A caracterização destes novos solventes será realizada por meio de técnicas de espectroscopia de infravermelho (IV), termogravimetria (TG), calorimetria exploratória diferencial (DSC), medidas de densidade e viscosidade com intuito de avaliar a formação destes NADES. Após a síntese e caracterização dos solventes, estes serão aplicados em diversos métodos verdes de preparo de amostras (extração a pressão e temperatura ambientes, extrações assistidas por radiação micro-ondas (MAE) e por

ultrassom (UAE)), além de síntese concomitante com extração dos analitos pela técnica de dispersão da matriz em fase sólida (DMFS), em matrizes ambientais e tecidos biológicos. A determinação dos elementos potencialmente tóxicos As, Cd, Cr, Hg, Se e V será realizado por espectrometria de massas com plasma acoplado indutivamente (ICP-MS) com estudo das interferências inerentes à técnica. Alguns destes NADES serão avaliados para extração de contaminantes emergentes como os retardantes de chama (BRF's) e detecção por cromatografia gasosa acoplada com espectrometria de massas (GC-MS) em amostras de lodo doméstico e industrial.

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Solventes eutéticos naturais: Síntese, caracterização e aplicações na determinação de As, Cd, Cr, Hg, Se e V em amostras ambientais por ICP-MS

Os dados serão/foram desenvolvidos (criados) e coletados através do desenvolvimento de novas sínteses de solventes eutéticos, e todos os dados experimentais serão/foram realizados no laboratório de Inovação em Química Analítica Verde (LIQAV) com sede no Departamento de Química e Ciências Ambientais da UNESP em São José do Rio Preto-SP.

Serão/foram gerados dados qualitativos e quantitativos sobre a presença de contaminantes emergentes e inorgânicos em matrizes ambientais, além de gráficos, cromatogramas, espectros, imagens em formato .jpg e outros documentos associados ao estudo de desenvolvimento e aplicação de métodos analíticos sustentáveis e solventes eutéticos.

Registros em cadernos atas e logbooks e dados salvos nos próprios softwares dos equipamentos. O dados brutos coletados, o tratamento de dados em geral (planilhas Excel), imagens e figuras obtidas e geradas e armazenados com o proponente.

Todas as questões éticas serão cumpridas e respeitadas. Não haverá experimentos com seres humanos ou animais que necessitem de autorização pelos comitês de ética da UNESP-São José do Rio Preto-SP.

Os direitos autorais respeitaram as normas da UNESP e da FAPESP.

Os dados de pesquisa gerados serão preservados na nuvem em contas Google Drive e Dropbox, sob supervisão do proponente, onde serão armazenados dados brutos coletados, tratamento de dados em geral (planilhas Excel), imagens e figuras obtidas e geradas. Os dados serão/foram também armazenados em pasta protegida por senha no computador pessoal do pesquisador, e o backup será feito a cada atualização da análise dos dados. Em todos os casos, a FAPESP será mencionada como órgão financiador, além de constar como coproprietária da patente, de acordo com normas vigentes. Os dados obtidos serão mantidos sob sigilo do proponente responsável pelo projeto de pesquisa, até garantia de publicação dos metadados.

Serão gerenciados e o acesso será realizado pelo pesquisador responsável.

Os dados serão disponibilizados após a publicação dos resultados da pesquisa. A licença Creative Commons ou open Data Commons será aplicada sobre os dados, conforme recomendado pela biblioteca da UNESP. Os resultados da pesquisa estarão permanentemente disponíveis no Repositório Institucional da Unesp (<https://repositorio.unesp.br/>) e em base de dados internacionais.

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Por publicações em artigos nacionais e internacionais, além da produção de patente, referenciando a agência de fomento. Os dados estão disponíveis no Repositório Institucional da Unesp (<https://repositorio.unesp.br/>).

Os dados estarão disponíveis para reutilização por terceiros após a publicação dos resultados da pesquisa. Não serão aplicadas restrições à reutilização dos dados desde que respeitem as finalidades científicas e a ética na pesquisa e citações corretas, tanto do proponente e seus colaboradores, como da agência de fomento.

O pesquisador principal.

Os recursos aprovados pelo projeto de pesquisa.

Planned Research Outputs

Data paper - "Mixture Design and Physicochemical Characterization Of Amino Acid-Based DEEP Eutectic Solvents (AADES) For Sample Preparation Prior To Elemental Analysis"

Amino acid-based deep eutectic solvents (AADES) represent a new subclass of deep eutectic solvents (DES) in which at least one of the components must be an amino acid, offering advantages such as low toxicity, biodegradability and low cost. In this work, b-alanine was used as hydrogen bond acceptor (HBA) in the preparation of a total of 30 AADES mixtures, with the hydrogen bond donor (HBD) being malic acid (AADES 1), citric acid (AADES 2), or xylitol (AADES 3), together with the addition of water. A restricted mixture design was employed to optimize the ideal proportions of the AADES components, which were determined as (% m m⁻¹) 12.50 for b-alanine, 43.75 for the HBD component, and 43.75 for water (represented by molar ratio 1:2:17 for the three AADES mixtures), with lower values of density and viscosity being the desired responses. Solvents that have low density and viscosity provide greater efficiency in sample preparation procedures, due to faster mass transfer. The highest density and viscosity values were found for AADES 2, due to the greater presence of carboxyl groups in the molecular structure of citric acid, allowing the formation of more hydrogen interactions. The Herschel-Bulkley model provided the best fit to the rheological behavior of the AADES, with AADES 2 showing the highest consistency index. Solvatochromic analyses showed that these solvents had high polarity. Fourier transform infrared (FTIR) spectroscopy analysis revealed hydrogen interactions between the precursor components, confirming formation of the AADES. Thermal analysis revealed the ideal working temperature ranges for applying these solvents in sample preparation, with thermogravimetry (TGA) indicating maximum temperatures of 130 C for AADES 1 and 150 C for AADES 2 and AADES 3. Differential scanning calorimetry (DSC) revealed the minimum temperatures at which the solvents remained liquids, which were -13 0C for AADES 1, -22 0C for AADES 2, and -21 0C for AADES 3. Therefore, these AADES were shown to be promising solvents for application in sample preparation, being suitable for the extraction of polar compounds, as well as metals and semimetals. An EcoScale study was carried out, which confirmed that the preparation of the solvents could be considered an excellent green synthesis.

Data paper - "Natural deep eutectic solvent-based microwave-assisted extraction in the medicinal herb sample preparation and elemental determination by ICP OES"

In this study, a microwave-assisted extraction (MAE) method based on the natural deep eutectic solvent (NADES) was developed for the Cd, Cu, Fe, Mn, and Zn determination in medicinal herb samples. The experimental conditions were optimized and the method parameters were evaluated using certified reference material. The NADES composed of choline chloride-oxalic acid prepared in a microwave system showed better extraction rates and low-energy consumption. Optimal conditions in the MAE were obtained using 35 s of extraction time, 90% of microwave power, and a 50 mg/mL sample-solvent ratio. Recoveries in the range of 87–109% and relative standard deviation < 8.45% were obtained. The limits of quantification (mg kg⁻¹) were: 0.0233 (Cd), 0.0229 (Cu), 1.10 (Fe), 0.06 (Mn), and 0.67 (Zn). The medicinal herbs were analyzed and daily intake values were estimated for Cu (<0.20%), Fe (<18.1%), Mn (<13.8%), and Zn (<0.64%); concentrations above threshold values for Cd were found. The optimization of experimental conditions combined and the use of an eco-friendly solvent provided excellent analytical parameters in the proposed method.

Data paper - "Evaluation of Trace Elements in Marine Biological Tissues by Graphite Furnace Atomic Absorption Spectrometry After Sample Treatment with Formic Acid"

In this work, formic acid was used as an extracting solvent in a fast and accurate procedure for Cd and Pb determination in biological tissue by graphite furnace atomic absorption spectrometry (GF AAS). The procedure consists of adding formic acid to the sample, followed by heating and simple dilution before the determination of

the analytes by GF AAS. The accuracy of the procedure was assessed by the analysis of lobster hepatopancreas (TORT-3) and bovine liver (NIST 1577b) certified reference materials, reaching recoveries of 95–100% (Cd) and 106–97% (Pb), respectively. The precision was assessed by the relative standard deviation (RSD%), with values equal to 4.9% and 4.4% for Cd and Pb, respectively. The limits of quantification were 0.010 (Cd) and 0.053 (Pb) $\mu\text{g g}^{-1}$, being lower than the maximum values allowed by the main regulatory agencies. The proposed procedure was applied to samples of mollusks and different fish tissues from coastal areas in Brazil. For fish samples, concentrations ranged from 0.005 to 0.179 $\mu\text{g g}^{-1}$ for Cd and 0.055–16.71 $\mu\text{g g}^{-1}$ for Pb. In mollusk samples, the variation was 0.022–0.194 $\mu\text{g g}^{-1}$ for Cd and 0.232–3.478 $\mu\text{g g}^{-1}$ for Pb. The results obtained are below the maximum allowed limits, except for the sample of mollusk *Phacoides pectinatus*, which presented a Pb concentration twofold higher than ones recommended by regulatory agencies. The present study offers a promising, simple, high-frequency analytical procedure, low cost, and minimal environmental risk for the extraction of toxic elements in biological tissues. Also, providing low limits in compliance with the quantification limits of regulatory agencies.

Data paper - "(Re) thinking Towards a Sustainable Analytical Chemistry: Part I: Inorganic Elemental Sample Treatment, Part II: Alternative Solvents and Extraction Techniques"

Currently, there is a huge demand for the development of analytical methods for chemical analysis. Sustainable methods have aroused the interest of researchers in the last years. This paper reviews important technologies for digestion and solid-liquid extraction approaches, with emphasis in emerging greener methods for the elemental analysis of different samples. Analytical technologies such as Microwave-assisted wet digestion (MAWD), Microwave-assisted extraction (MAE), Ultrasound-assisted extraction (UAE), Microwave-induced combustion (MIC), Alkaline treatment, and liquid-liquid extraction and other alternative approaches for inorganic elements are highlighted. Application, advantages and limitations of these methods using diluted acids, ultraviolet radiation, alkaline reagents, less toxic solvents [i.e. deep eutectic solvents (DES) and its subclasses, as well as alternative solvents], and combination of different technologies are discussed. We also briefly present the role of direct analysis using different spectroscopy techniques such as Laser-induced breakdown spectroscopy (LIBS), Laser ablation coupled to plasma-based techniques (LA-ICP-MS/OES), Raman spectrometry, Near-infrared spectrometry (NIR), and X-ray fluorescence (XRF) which a minimum or no sample preparation. The chemometrics approaches applied for the development of the green analytical chemistry were also mentioned.

Data paper - "Synthesis of Natural Deep Eutectic Solvents using a Mixture Design for Extraction of Animal and Plant Samples Prior to ICP-MS Analysis"

Solvents with both low density and viscosity have the advantage of higher extraction efficiency due to lower diffusivity and consequently higher mass transfer. In this study, a mixture design was performed for the synthesis of three different natural deep eutectic solvents (NADES) using citric acid, malic acid, and xylitol. The optimized proportion for each of the three solvents synthesized was selected based on density and viscosity values. The NADES were characterized by infrared spectroscopy analysis, that showed characteristic bands of the initial reagents and the presence of hydrogen bonds confirming the formation of each deep eutectic solvent. Then, the NADES were used as solvents in ultrasound-assisted extraction (UAE) and microwave-assisted extraction (MAE) of biological tissue and plant material samples for the determination of As, Cd, Hg, Pb, Se, and V by inductively coupled plasma mass spectrometry (ICP-MS). The results for the proposed methods were compared to microwave-assisted acid digestion (MW-AD). The extraction recoveries ranged from 80 to 120% for most of the elements determined. The use of NADES as carbon sources improved the sensitivity of the As and Cd analyses, due to charge transfer reactions between the analyte and C+ and/or other carbon species. In addition, the Analytical Eco-Scale was used to assess the greenness of the proposed analytical procedures (UAE and MAE). It showed that the UAE and MAE methods provided excellent green analyses, while the MW-AD method was rated as an acceptable

green procedure.

Data paper - "Enhanced Extraction of Arsenic and Cadmium from Environmental Samples using a Natural Deep Eutectic Solvent and Determination by Inductively Coupled Plasma Mass Spectrometry."

A natural deep eutectic solvent (NADES) synthesised from malic acid, xylitol, and water was used as a solvent in ultrasound-assisted extraction (UAE) for the determination of As and Cd in fish and shellfish samples by inductively coupled plasma mass spectrometry. The formation of the solvent was confirmed by infrared spectroscopy analysis, which showed the presence of hydrogen bonds between the components. Evaluation was made of elemental determinations performed using standard and kinetic energy discrimination (KED) modes. Higher sensitivity was observed using KED mode, which could be attributed to charge transfer between carbon and the analytes when the NADES introduced into the plasma. The detection limits were 12.7 and 0.100 $\mu\text{g kg}^{-1}$ for As and Cd, respectively, and the accuracy of the extraction procedure was assessed by comparing methods. The Cd concentrations in the fish and shellfish samples were below the limits of quantification, while the As concentrations varied between 1.88 and 12.0 $\mu\text{g g}^{-1}$, exceeding the maximum values recommended by regulatory agencies.

Data paper - "A Novel Dispersive liquid-liquid Microextraction Using a Low Density Deep Eutectic Solvent-gas Chromatography Tandem Mass Spectrometry for the Determination of Polycyclic Aromatic Hydrocarbons in Soft Drinks"

Ready-to-drink teas can provide, if properly packaged, the taste and wellness character of traditional teas. Nevertheless, in tea processing, there may be several contaminations, among which polycyclic aromatic hydrocarbons (PAHs), anthropogenic contaminants that can present carcinogenic and mutagenic properties. In this work, a novel low-density deep eutectic solvent-based dispersive liquid-liquid microextraction (LDDES-DLLME) procedure followed by gas chromatography tandem mass spectrometry (GC-MS/MS) was optimized for analysis of 15 polycyclic aromatic hydrocarbons (PAHs) in ready-to-drink herbal-based beverages. The new deep eutectic solvent (DES) was synthesized with natural compounds (camphor and hexanoic acid). Several parameters of the extraction procedure such as type and volume of extraction solvent, type, volume of dispersive solvent, and time of extraction were evaluated to achieve the highest yield and to attain the lowest detection limits. The validated method showed very low limits of detection (0.01 $\mu\text{g L}^{-1}$) and quantification (0.2 $\mu\text{g L}^{-1}$), good inter- and intra-day precisions (RSD < 16.87%), and recoveries higher than 69%. The method was applied to 16 type of samples and it was found total PAHs levels ranging from 0.20 to 1.82 $\mu\text{g L}^{-1}$. The developed LDDES-DLLME showed a reliable and innovative alternative for the extraction of PAHs from beverages, cost-effective and environmentally friendly, and providing a satisfactory throughput.

Data paper - "Simple and Robust GFAAS Methods for Determination of As, Cd, and Pb in Hemp Products Using Different Sample Preparation Strategies"

Hemp is one of the most complete plants for industrial and consumer purposes. In the food industry, the main hemp product is the seed oil, which contains a wide spectrum of compounds such as amino acids and fatty acids that are essential for human health. Given its growing consumption, systematic studies were undertaken for the quantification of toxic elements (As, Cd, and Pb) in hemp products, such as seeds (shelled and peeled), oil, protein, and butter. Factorial designs were used to optimize the sample preparation and instrumental conditions, resulting in robust analytical methods. For the toxicity assessment, the samples could be previously treated in either acid or alkaline medium, achieving limits of quantification of 0.6 $\mu\text{g g}^{-1}$ (As), 0.04 $\mu\text{g g}^{-1}$ (Cd) and 0.4 $\mu\text{g g}^{-1}$ (Pb), and satisfactory values of accuracy (recoveries of 87–107%) and precision (relative standard deviation < 7%). The lead contents of hemp seeds were of concern (1.07–1.38 $\mu\text{g g}^{-1}$), since they were above the established limits (0.2 $\mu\text{g g}^{-1}$), while the cadmium levels could be considered safe. The As contents of the samples were all lower than the

limit of quantification of the proposed method.

Data paper - "ICP- quadrupole MS for Accurate Determination of Chromium in Environmental and Food Matrices"

Chromium determination in different matrices is very important, whether due to the harmful or beneficial effects of this element. The quantification of chromium present at very low concentrations in foods and environmental samples requires the use of highly sensitive analytical techniques, such as inductively coupled plasma mass spectrometry (ICP-MS). A major difficulty of ICP-MS concerns the overlap of spectral interferences with the analyte signal, which can be addressed using various strategies. In this work, a single method was proposed for Cr determination in different matrices, and the instrumental conditions were optimized with evaluation of the accuracy using CRMs of water (NIST 1640a), fish tissue (DORM-4), and soil (NIST 2709a). Statistical analysis showed that the best results for interference removal were obtained using a collision gas (helium) flow rate of 3 mL min⁻¹, which provided the lowest LOD, LOQ, and RSD values, with the highest accuracies in the CRM analyses. Analyses were performed in water samples collected from fountains in the municipality of Ibirá (São Paulo State), as well as still and sparkling bottled water samples. Tissue samples from different fish species (Abrotea, Pangasius, and Tilapia) were acquired in a local market and, samples of sludge and sediment were collected at Mariana city (Minas Gerais State, Brazil). The concentrations of total Cr determined in the samples of water (from 8 ± 0.1 to 34 ± 2 µg L⁻¹) and fish tissue (from 0.056 to 0.084 µg g⁻¹) were within the limits established by ANVISA, 50 µg L⁻¹ for water and 0.1 mg kg⁻¹ for fish. The range concentrations in the sludge and sediment (from 127 ± 1 to 221 ± 2 µg g⁻¹) exceeded the limit established by Brazilian Legislation (90 µg g⁻¹), CONAMA. The analytical technique presented LODs from 0.0009 to 0.3 µg L⁻¹, LOQs from 0.004 to 1.1 µg L⁻¹, RSDs from 5 to 14 %, and recoveries from 91 to 105 % for the CRMs. Satisfactory precision and accuracy of the method were achieved, plus a single analytical method for all samples.

Data paper - "Self-organizing map applied to the choice of internal standards for the determination of Cd, Pb, Sn, and platinum group elements by inductively coupled plasma mass spectrometry."

The behaviors of internal standards, according to different flow rates of the cell collision gas (He), were studied for the determination of Cd, Pb, Pd, Pt, Rh, and Sn in samples of fish and mollusks by inductively coupled plasma mass spectrometry (ICP-MS). The elements Bi, Ge, In, Sc, and Y were selected as internal standards, considering their masses and first ionization energies. Addition and recovery experiments were carried out at three concentration levels to evaluate the accuracy of the method applied for the analysis of two samples with different matrices. The results were evaluated using a self-organizing map (SOM). The best analyte/IS pairs were as follows: 114Cd⁺/74Ge⁺, 195Pt⁺/74Ge⁺, and 208Pb⁺/74Ge⁺. For 103Rh⁺, 106Pd⁺, and 120Sn⁺, greater accuracy was achieved without use of an internal standard. Helium gas (2.8 mL min⁻¹) was used in the collision cell for the analytes, except for Sn, and recoveries ranged from 98 to 101% under optimal conditions. The use of SOM as an exploratory analysis tool was an effective approach for selection of the most appropriate internal standards.

Data paper - "Solventes Eutéticos Naturais Profundos (NADES) no Preparo de Amostras de Rocha Fosfática e Suplemento Mineral para Determinação Elementar por Técnicas de Plasma."

Natural deep eutectic solvents (NADES) based on xylitol, citric acid, and malic acid were synthesized and used in ultrasound-assisted extraction (UAE) and heating-bath extraction of phosphate rock and mineral supplement samples. Arsenic, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, P and Zn were determined by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-optical emission spectrometry (ICP OES). The results showed the NADES as promising solvents for extraction of inorganic matrices compared to reference values and concentrations obtained using microwave-assisted acid digestion (MW-AD). Significant differences

were observed for some elements, suggesting different chemical interactions between the synthesized NADES and each monitored element. For analytes extraction of phosphate rock, UAE presented the best results for As, Cr and P. Zinc was extracted with UAE and heating bath. Concerning mineral supplement, no significant differences were observed for Ca (UAE), Cd (UAE and heating bath), K (UAE) and heating bath), Mn (UAE and heating bath), Na (UAE and heating bath), and P (UAE and heating bath). The NADES is a greener and a potentially alternative for the sample preparation compared to the official methods of analysis, can being used as selective extractor solvent in conventional sample preparation methods.

Patente - "Composições de Solventes Biodegradáveis ou Solventes Eutéticos Profundos Naturais Aplicados para Digestão e Extração de Elementos Inorgânicos em Amostras Vegetais"

[Gonzalez, M.H.](#); Santana, A.P.R.; Guimarães, T.G.S.; Patente: Privilégio de Inovação. Número do registro: BR10202001253, título: “*Composições de Solventes Biodegradáveis ou Solventes Eutéticos Profundos Naturais Aplicados para Digestão e Extração de Elementos Inorgânicos em Amostras Vegetais*”, Instituição de registro: INPI - Instituto Nacional da Propriedade Industrial. Depósito: 22/06/2020.

Capítulo de livro - "Química e sustentabilidade: Desenvolvimento de solventes verdes para o emprego em determinação elementar"

O desenvolvimento de tecnologias limpas e sustentáveis ainda é um grande desafio, mas vem ganhando espaço com a Química Verde. Com a conscientização da necessidade de diminuição e/ou eliminação de compostos tóxicos, a busca por métodos empregando reagentes menos prejudiciais ao meio ambiente tem aumentado gradativamente nos últimos anos. A síntese de novas classes de solventes verdes está de acordo com os princípios da Química Analítica Verde que possui como principais objetivos a substituição de solventes tóxicos, a redução do consumo de reagentes, menor consumo de energia, como também a minimização da geração e da toxicidade de resíduos provenientes de procedimentos analíticos. Os solventes eutéticos profundos naturais (NADES) são formados por metabólitos primários e/ ou compostos celulares, como aminoácidos, ácidos orgânicos, açúcares ou derivados de colina, oferecendo notáveis vantagens como biodegradabilidade, baixa toxicidade, estabilização de soluto, baixo custo e preparo simples. Neste capítulo serão reportados alguns trabalhos desenvolvidos no Grupo de Inovação em Química Analítica Verde (GIQAV) em colaboração com pesquisadores de Universidades Federais sobre síntese, caracterização e aplicação destes novos NADES. Serão abordadas a síntese e aplicação destes NADES em extração assistida por ultrassom (UAE) e extração assistida por radiação micro-ondas (MAE) em amostras de tecidos vegetal e biológico para determinação dos elementos potencialmente tóxicos como As, Cd, Hg, Pb, Se e V por espectrometria de massas com plasma acoplado indutivamente (ICP-MS), como também alguns outros macronutrientes e micronutrientes, entre eles: Ca, Cu, Fe, K, Mg, Mn, Na, P e Zn por espectrometria de emissão óptica com plasma acoplado indutivamente (ICP OES).

Planned research output details

Title	Type	Anticipated release date	Initial access level	Intended repository(ies)	Anticipated file size	License	Metadata standard(s)	May contain sensitive data?	May contain PII?
Mixture Design and Physicochemical Characterization ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Natural deep eutectic solvent-based microwave-assisted ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Evaluation of Trace Elements in Marine Biological ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
(Re) thinking Towards a Sustainable Analytical Chemistry ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Synthesis of Natural Deep Eutectic Solvents using ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Enhanced Extraction of Arsenic and Cadmium from Environmental ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
A Novel Dispersive liquid-liquid Microextraction Using ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Simple and Robust GFAAS Methods for Determination of ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
ICP- quadrupole MS for Accurate Determination of Carbon ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No

Title	Type	Anticipated release date	Initial access level	Intended repository(ies)	Anticipated file size	License	Metadata standard(s)	May contain sensitive data?	May contain PII?
Self-organizing map applied to the choice of inter ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Solventes Eutéticos Naturais Profundos (NADES) no ...	Data paper	Unspecified	Open	None specified		None specified	None specified	No	No
Composições de Solventes Biodegradáveis ou Solvent ...	Patente	Unspecified	Open	None specified		None specified	None specified	No	No
Química e sustentabilidade: Desenvolvimento de sol ...	Capítulo de livro	Unspecified	Open	None specified		None specified	None specified	No	No