

Trends in Analytical Chemistry

“(Re)-thinking Towards a Sustainable Analytical Chemistry: Part I: Inorganic Elemental Sample Treatment, and Part II: Green Alternative Solvents and Extraction Techniques” --Manuscript Draft--

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Abstract:	Currently, there is a huge demand for the development of analytical methods for chemical analysis. Sustainable methods have aroused the interest of researches in the last years. This paper reviews important technologies for digestion/extraction of samples, 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 new extraction approaches are highlighted. Application, advantages and limitations of these methods using diluted acids, ultraviolet radiation, alkaline reagents, less toxic solvents [deep eutectic solvents (DES) and its subclasses, and 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.
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Opposed Reviewers:	
Response to Reviewers:	



São José do Rio Preto, 19th, February, 2021.

Editor in Chief
Prof. Dr. Elena Ibañez Ezequiel

Dear Professor Ibañez,

We are submitting the review entitled “(Re)-thinking Towards a Sustainable Analytical Chemistry: Part I: Inorganic Elemental Sample Treatment, and Part II: Green Alternative Solvents and Extraction Techniques” for your evaluation and possible publication in **TrAC - Trends in Analytical Chemistry**. Green analytical chemistry (GAC) plays an important role towards sustainable analytical procedures development. In this review, the state-of-art of the analytical methods in agreement with the green analytical principles, for inorganic elemental analysis was thought, in order to improve the literature regarding to this topic. Part I: describes important currently digestion/extraction/solubilization sample treatment strategies, focusing greener analytical methods for the elemental analysis in several samples. The use of diluted acids, alkaline reagents, less toxic solvents, and the combination of different strategies of sample preparation are discussed. Part II: a bibliometric analysis was applied to analyze emerging research hotspots, providing to identify new trends and the state-of-art of the sample preparation towards sustainable technologies. The development of green analytical chemistry is focused on replacing conventional mineral acids by alternative green solvents.

Thank you in advance for your attention, time and editorial assistance.

We are looking forward to hearing from you at your earliest convenience.

Yours sincerely,

A handwritten signature in black ink, appearing to read "Mario Henrique Gonzalez".

Mario Henrique Gonzalez

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**TRENDS IN ANALYTICAL CHEMISTRY (TrAC)
REVIEW PROPOSAL**

PROPOSED TITLE: (Re) thinking Towards a Sustainable Analytical Chemistry for Inorganic Elemental Analysis – Part I: Greening Sample Treatment, and Part II: Green Alternative Solvents and Extraction Techniques

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PROPOSED SUBMISSION DATE: 10th, February, 2021.

PREFERRED HANDLING EDITOR(S): Please indicate which of the [listed](#) Contributing Editor(s) of TrAC you feel is best suited to judge your proposal (please list a maximum of 3 in order of preference).

1. Elena Ibáñez Ezequiel, Ph.D.

2. Gangfeng Ouyang

3. Damià Barceló

1) Please comment on the current importance of the field (Max. 100 words)

Green analytical chemistry (GAC) plays an important role towards sustainable analytical procedures development for inorganic analysis. The numbers of studies addressing green sample preparation procedures have increased considerably over the last twenty years, being remarkably important during the last decade (2011-2020), where about 90% of the articles were published. In this context, the development of sample preparation methods that providing reduced consumption of reagents and solvents, as well as easy/minimal sample handling, using the energy sources in a sustainable way, employing miniaturized and automated analytical methods in agreement with the Green Chemistry Principles.

2) What are the implications for the wider scientific community? (Max. 100 words)

The implications and benefits for the scientific community refer to the knowledge of the state-of-art of the analytical methods in agreement with the green analytical principles for inorganic elemental analysis in several samples. In addition, this review reports the alternative solvents as well as the miniaturized and automatized analysis techniques that are currently poorly discussed. The purpose of this review is dealing with a systematic approach to different sample preparation methods, contributing not only to the development of green analytical chemistry, but also to its greater popularization, promoting the sustainable analytical procedures studies.

3) To which communities will your article appeal? (Max. 60 words)

The proposal of this review is focused in the areas of analytical chemistry, biochemical research methods, food science technology, and spectroscopy, as well as multidisciplinary chemistry. Industries and quality control services, that develop analytical methods employing microextraction techniques, greener chromatographic methods, and extraction/digestion using environmentally friendly solvents, with subsequent inorganic analysis by spectroscopy techniques.

4) Please comment on any other reviews published on a similar topic, justifying why there is room for another review. Please list any relevant reviews.

In this review, the state-of-art of the analytical methods in agreement with the green analytical principles, for inorganic elemental analysis was thought, in order to improve the literature regarding to this subject. It is important to mention, that few studies were found in the literature, mostly covering the elemental analysis in accordance with the conventional sample treatment strategies. In the review conducted by Stanisiz et al. (2014), the authors reported the ionic liquids (IL's) application, employing the liquid-phase microextraction (LPME), as sample preparation strategy for inorganic elements determination. Maredo-Piñero et al. (2015) reviewed microextraction techniques, and their advantages and the disadvantages of the currently developments and future prospects. Espino et al. (2016), reviewed studies about the Natural Deep Eutectic Solvents (NADES) reporting different procedures for NADES synthesis and their applications in several areas of chemistry. In the review conducted by Plotka-Wasyłka et al. (2017) the use of IL's in agreement with the microextraction techniques was reported, for inorganic and organic determination. Cerutti (2019) also reviewed the extraction methods in environmental analysis and the application of the the deep eutectic solvents (DES) and IL's, in the speciation chemical analysis. Santana-Mayor (2020) reported that the DES as one of most promising alternative to the use of toxic organic solvent toxic. The use of the DES, highlighting the diferent NADES and their application in the chromatography and eletrochemistry techniques. Although in these studies, the alternative solvents has been reported showing the intrinsic properties and their efficiency in the extraction/solubilization of the target analyte, conventional analytical strategies for several purposes are currently employed in the most of studies reported. However, the purpose of this review is to report the state-of-art of the aplication of these alternative solvents in agreement with the miniaturized and automated analytical strategies, poorly discussed in the literature, highlighting the analytical innovations/details that the Green Analytical Methods have been contributing for the greater development of the analytical chemistry.

[1] A. Santana-Mayor, R. Rodríguez-Ramos, A.V. Herrera-Herrera, B. Socas-Rodríguez, M.A. Rodríguez-Delgado, Deep eutectic solvents. The new generation of green solvents in analytical chemistry. *TrAC, Trends Anal. Chem.* (2020) 116108, <https://doi.org/10.1016/j.trac.2020.116108>.

[2] J. Płotka-Wasyłka, M. Rutkowska, K. Owczarek, M. Tobiszewski, J. Namieśnik, Extraction with environmentally friendly solvents. *TrAC, Trends Anal. Chem.* 91 (2017) 12-25, <https://doi.org/10.1016/j.trac.2017.03.006>.

[3] M. Espino, M.A. Fernández, F.J.V. Gomez, M.F. Silva, Natural designer solvents for greening analytical chemistry. *TrAC, Trends Anal. Chem.* 76 (2016) 126-136, <https://doi.org/10.1016/j.trac.2015.11.006>.

[4] E. Stanisiz, J. Werner, A. Zgoła-Grześkowiak, Liquid-phase microextraction techniques based on ionic liquids for preconcentration and determination of metals. *TrAC, Trends Anal. Chem.* 61 (2014) 54-66, <https://doi.org/10.1016/j.trac.2014.06.008>.

[5] Cerutti, S., Pacheco, P.H., Gil, R., Martinez, L.D. Green sample preparation strategies for organic/inorganic compounds in environmental samples(Review), *Current Opinion in Green and Sustainable Chemistry*, Volume 19, October 2019, Pages 76-86, <https://doi.org/10.1016/j.cogsc.2019.08.007>

[6] Moreda-Piñero, J., Moreda-Piñero, A, Recent advances in combining microextraction techniques for sample pre-treatment(Review), *TrAC - Trends in Analytical Chemistry* Volume 71, September 01, 2015, Pages 265-274, <http://dx.doi.org/10.1016/j.trac.2015.02.025>

5) Please provide section headings along with a brief discussion of each section and associated key references.

(Re) thinking Towards a Sustainable Analytical Chemistry –
Part I: Inorganic Elemental Sample Treatment.

Introduction

In this review, an overview about the role of analytical methods development and sample preparation employing the sustainable methods were discussed. Moreover, the use of spectroscopy technologies for the direct solid sampling and chemical inspection of samples were also briefly discussed.

1. Sample treatment strategies proposed in Analytical Chemistry

1.1. Microwave-assisted wet digestion

The microwave energy discussed highlights the sample preparation that employs diluted acids and the efficiency of the single reaction chamber system, where the high pressures and temperatures achieved, allow the use of larger amount of sample, compared to the conventional system besides the digestion of different matrices in a single run. Another approach that makes the MAWD a greener preparation strategy is related to the ultraviolet radiation (MW-UV) association increasing the digestion efficiency in the presence of diluted acids for the digestion of the complex matrices.

1.2. Microwave-assisted extraction (MAE)

The use of less toxic and/or diluted reagents, in accordance with the MAE strategy was reported, and more currently, the MAE technique can also be employed in a miniaturized form, meeting the principle of green analytical chemistry (GAC).

1.3. Ultrasound-assisted extraction (UAE)

The analytical methods employing the UAE are reported, focusing in the use of different apparatus for the ultrasound radiation showing their advantages and limitations in order to promote more green methods and saving energy. Moreover, UAE can be combined with other extraction and/or preconcentration methods to make them greener.

1.4. Microwave-induced combustion (MIC)

An overview about MIC is described, pointed out a great advantage related to the possibility of varying the composition of the absorbing solution according to the analytical technique, as well as the physical-chemical characteristics of the analytes. In the MIC procedure, several chemical compositions can be employed for the absorbing solution, in addition to the water and diluted acids that are commonly used. High digestion efficiencies have been reported using alkaline absorbing solutions. The use of water or diluted solutions (*i.e.* diluted HNO_3 , HCl , NH_4OH , among others) is highly compatible with atomic spectrometry techniques promoting the waste reduction and in agreement with most principles of green chemistry.

1.5. Alkaline treatment

The use of the alkaline reagents involves digestions, extractions and formation of slurries for the quantification of the analytes afterwards. As demonstrated by the reported studies, the use of alkaline solutions, in general make the sample preparation step simpler and faster, besides the possibility of employing reduced amount of sample and reagent consumption, according to some green analytical chemical principles.

1.6. Direct solid sampling analysis with minimum or no sample treatment

In this context, the analytical techniques especially designed for direct analysis are associated with several advantages and, as discussed in the review, in concordance with most GAC principles. For instance, the technological advances made possible the development of simpler as well as portable instrumentations (such as for LIBS, Raman, XRF, and NIR), also called “handheld” instruments. Prominent in the green chemistry scenario, are those spectroscopic methods that have been adapted for in-line/real-time measurements. Indeed, besides the real-time analysis having a continuous sampling of all material in-progress in a flow configuration, it also prevents the formation of hazardous substances and the environmental pollution.

Conclusion

Nowadays, there are in the literature several analytical methods combining the miniaturization strategies, using diluted reagents and smaller mass of samples, increasingly promoting awareness for the minimum waste generation according to high analytical

throughput. The application of greener advanced technologies for the chemical analysis has been remarkably important, providing analyzes with adequate accuracy and high analytical throughput, free of laborious sample preparation steps, which has revolutionized the sustainable analytical chemistry area.

(Re) thinking Towards a Sustainable Analytical Chemistry –
Part II: Green Alternative Solvents and Extraction Techniques

1. Introduction

In this topic, the publications related to sample preparation were identified using the Expanded Science Citation Index (SCI-E) in the Clarivate Analytics Web of Science[®] (WoS) database. All the papers retrieved were evaluated using a bibliometric map for co-occurrence analysis of author keywords. The growth of analytical methods aiming at green chemistry during the last couple of decades has demonstrated how fundamental scientific approaches can be developed that combine environmental, health and safety, and economic targets.

2. Solvents for sample preparation in inorganic analysis

Due to the fundamental role of solvents in the sample preparation stage, together with the interest in studying and developing new green solvents, this part is focused on strategies based on new extraction media that can replace conventional solvents, employing environmentally friendly reagents in analytical methodologies targeting inorganic analysis.

2.1 Ionic liquids (ILs)

Ionic liquids (ILs) have been widely studied as alternatives to replace organic solvents [20,21]. The future application of ILs in sample preparation requires them to be less toxic and more biodegradable. Furthermore, it is important that future developments should incorporate the recycling and reutilization of IL wastes [42].

2.2. Deep eutectic solvents (DES) and natural deep eutectic solvents (NADES).

These solvents are formed using combinations of organic compounds that result in a eutectic mixture with a melting point below those of the individual precursors [43]. NADES are attractive as promising environmentally friendly materials, with excellent extraction properties, easy preparation, and low cost. Their high viscosity can be a significant disadvantage, although there are cases where this problem has been overcome.

2.3. Water

Water is the safest and most environmentally friendly solvent that can be considered for use in different procedures. Pressurized hot water extraction (PHWE), also called subcritical water extraction (SWE), is one of the methods of using water as an extractor solvent [75]. PHWE employs pressurized water under controlled conditions of elevated temperature and pressure [76].

3. Extraction approaches for inorganic elements

Will be presented the main advances for the analytical extraction techniques more reported in the literature, and the green analytical chemistry techniques employed in the preparation of samples for the extraction or preconcentration of inorganic analytes are liquid-phase microextraction (LPME), dispersive liquid-liquid microextraction (DLLME), solid-phase extraction (SPE), solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), stir bar microextraction (SBME), and cloud point extraction (CPE).

4. Conclusions

The future perspectives for green analytical chemistry should include continued efforts to develop new solvents for use in green extraction procedures, as well as improved microextraction techniques, including those suitable for elemental analysis, for which there are still relatively few published works in the literature.

LEAD AUTHOR CV

Please provide a very brief CV of the leading author and a list of papers/reviews published in the last **three years** which qualify them for writing this review.

Since 2016, our research team, known as Group of Green Analytical Chemistry (GIQAV), together with Brazilian researchers has been dedicated to the development of green analytical methods for qualitative and quantitative analysis by spectrometric techniques. During this period, we published about 10 papers regarding to the sustainable synthesis of natural deep eutectic solvents (NADES) in accordance with different sample treatment strategies for inorganic determination in several samples. The research team has also expertise in the development/optimization of analytical methods employing the absorption and emission atomic spectrometry, including Graphite Furnace Absorption Atomic Spectrometry (GFAAS); Inductively Coupled Plasma Emission Atomic Spectrometry (ICP OES) as well as Inductively

Coupled Plasma Mass Spectrometer (ICP-MS). The studies are also developed to establish the nutritional and/or toxic potential, in terms of the inorganic constituents present in complex matrices. In our studies, the chemical/spectral interferences from the matrix are overcome applying suitable reactional (sample treatment) and instrumental conditions leading to the reliable analytical results.

1. 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 *Journal of Chromatography A*, v. 1635, p.461736, **2020**. <https://doi.org/10.1016/j.chroma.2020.461736>.
2. Synthesis of natural deep eutectic solvents using a mixture design for extraction of animal and plant samples prior to ICP-MS analysis. *Talanta*, v. 216, p.120956, **2020**. <https://doi.org/10.1016/j.talanta.2020.120956>.
3. Enhanced extraction of arsenic and cadmium from environmental samples using a natural deep eutectic solvent and determination by inductively coupled plasma mass spectrometry. *International Journal of Environmental Analytical Chemistry*, v. 2, p. 1-12, **2020**. <https://doi.org/10.1080/03067319.2020.1826460>.
4. Simple GFAAS Method for Determination of Pb, As, and Cd in Cannabidiol Extracts Used for Therapeutic Purposes. *Journal of the Brazilian Chemical Society*, v. 000, p. 1-4, **2020**. <http://dx.doi.org/10.21577/0103-5053.20190252>.
5. Natural deep eutectic solvents for sample preparation prior to elemental analysis by plasma-based techniques. *Talanta*, v. 199, p. 361-369, **2019**. <https://doi.org/10.1016/j.talanta.2019.02.083>.
6. Sustainable synthesis of natural deep eutectic solvents (NADES) by different methods. *Journal of Molecular Liquids*, v. 293, p. 111452, **2019**. <https://doi.org/10.1016/j.molliq.2019.111452>.
7. Use of multiple lines for improving accuracy, minimizing systematic errors from spectral interferences, and reducing matrix effects in MIP OES measurements. *Microchemical Journal*, v. 143, p. 326-330, **2018**. <https://doi.org/10.1016/j.microc.2018.08.032>.
8. Bioaccumulation and Acute Toxicity of As(III) and As(V) in Nile Tilapia (*Oreochromis niloticus*). *Chemosphere*, v. 217, p. 349-354, **2018**. <https://doi.org/10.1016/j.chemosphere.2018.11.013>.
9. Determination of vanadium in water samples from Brazilian mineral spring (Ibirá Spa) using ICP-MS. *Environmental Nanotechnology, Monitoring & Management*, v. 8, p. 48-52, **2017**. <http://dx.doi.org/10.1016/j.enmm.2017.04.005>.
10. Evaluation of Distribution and Bioaccumulation of Arsenic by ICP-MS in Tilapia (*Oreochromis niloticus*) Cultivated in Different Environments. *Journal of the Brazilian Chemical Society*, v. 28, p. 2455-2464, **2017**. <http://dx.doi.org/10.21577/0103-5053.20170101>.

March 03, 2022

Dear Elena Ibáñez Ezequiel, PhD

Contributing Editor - Trends in Analytical Chemistry

We are pleased to present the second reviewed version of the manuscript entitled ***“(Re)-thinking Towards a Sustainable Analytical Chemistry: Part I: Inorganic Elemental Sample Treatment, and Part II: Green Alternative Solvents and Extraction Techniques”*** - Manuscript Number: TRAC-D-21-00060R1. The manuscript was reviewed and all corrections and suggestions were taken into account and are highlighted in yellow in the corrected version. Please, find below the answers for the referee queries/comments.

We thank you very much for the opportunity and suggestions to improve the manuscript and its impact.

We are also thankful for your kind editorial assistance and time, and we hope that the revised manuscript is in the desired quality required by Trac.

Yours sincerely,



Professor Mario Henrique Gonzalez
São Paulo State University (UNESP)
mario.gonzalez@unesp.br

Answers to reviewer's comments

Reviewer 1: The authors have included some more contributions to the sample treatment for trace element analysis, in two sections, e.g. sample treatments using MW or UAE, among others, in the first part, and alternative extraction techniques (miniaturized most of them) in the second part. This separation is a bit misleading, as in the first part extraction techniques are also reviewed (e.g. UAE, MAE). Perhaps, it should be made clear that the first section mainly copes with digestion and solid-liquid extraction approaches, whereas the second with liquid-liquid extraction and other alternative approaches. It should be taken into account, that at present, there are many sources in the literature addressing these techniques under the standpoint of green chemistry, and new insights should be provided so that there is a real contribution to the field of trace element analysis.

Answer: *The authors agree with the reviewer, and the information about digestion process, solid-liquid extraction, and liquid-liquid extraction approaches were added in the abstract. The discussions about the green analytical chemistry with emphasis in elementary analysis was inserted in the review. The changes were highlighted in yellow in the manuscript. Thank you for your suggestion.*

Reviewer 1: I believe that there are still many features that should be further reviewed, such the role of advanced oxidation processes in sample pretreatment for trace analysis (not only MW-UV). Other relevant area completely omitted in the review is the speciation analysis. A new section must be included with the most recent advances for sample preparation in speciation analysis. For instance, which green methods are available if I have to determine Cr(VI) and Cr(III), or Hg(II) and methylmercury?

Answer: *The use of advanced oxidation processes in the sample treatment for inorganic determination was reviewed, and it was observed that for the determination of inorganic elements, there are a few studies that cover the AOP application for inorganic analysis. However, it can be observed in the literature that the AOP is extensively applied to organic compounds, either for remediation and/or determination of these substances in several kinds of samples, including waste-waters, dyes, water treatment and others. Then, a few studies that were found in the literature regarding the use of AOP for the determination of inorganics are outside the period evaluated in this review (except the reference (4)), as follows:*

1- A. Correia, M. Galesio, H. Santos, R. Rial-Otero, C. Lodeiro, A. Oehmen, Antonio C.L. Conceição, J.L. Capelo. *Can sample treatments based on advanced oxidation processes assisted by high-intensity*

focused ultrasound be used for toxic arsenic determination in human urine by flow-injection hydride-generation atomic absorption spectrometry? Talanta 72 (2007) 968–975.

2- *J. L. Capelo, C. Maduro and A. M. Mota. Advanced oxidation processes for degradation of organomercurials: determination of inorganic and total mercury in urine FI-CV-AAS. J. Anal. At. Spectrom. , 2004, 19 , 414–416.*

3- *J. L. Capelo, I. Lavilla, and C. Bendicho. Room Temperature Sonolysis-Based Advanced Oxidation Process for Degradation of Organomercurials: Application to Determination of Inorganic and Total Mercury in Waters by Flow Injection-Cold Vapor Atomic Absorption Spectrometry. Anal. Chem. 2000, 72, 4979-4984.*

4- *Carla C. Crispino, Marcos Y. Kamogawa, José R. Ferreira, Elias A.G. Zagatto. Sulphate radical generation through interaction of peroxymonosulphate with Co(II) for in-line sample preparation aiming at spectrophotometric flow-based determination of phosphate and phosphite in fertilizers. (this reference was inserted in the review [reference number 191].*

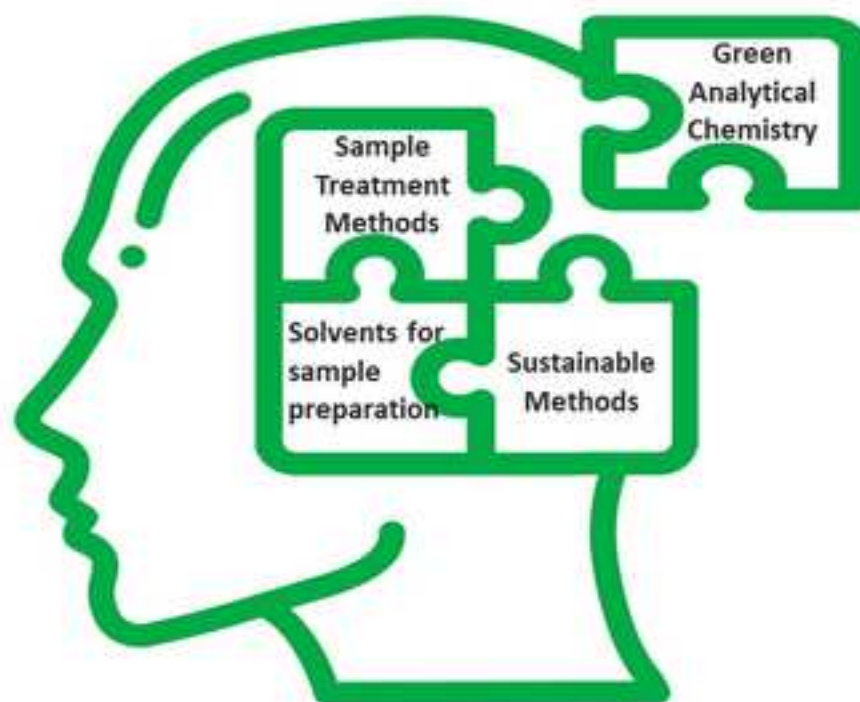
In relation to the speciation analysis in agreement with the GAC principles, some studies were inserted in this review in accordance with the sample treatment strategy employed and to its context/subject addressed in the review.

Reviewer 1: Finally, latest developments in the evolution of the concept of 'green chemistry' should be considered in this review, something that has only mentioned at the end of the manuscript. For instance, the novel concept 'White Analytical Chemistry' (TrAC, 2021, 138, 1162223) should be considered here in more detail. There should be balance between the green attribute and other essential attributes influencing the actual usefulness and functionality of the method, such as the analytical (red) and practical (blue) criteria. How can analytical methods in this review be evaluated according to these criteria?. I recommend to diminish the descriptive character of the review, increasing the criticism having in mind the aforementioned criteria. This should help readers to choose the best analytical approach taking into account not only greenness but also analytical performance and cost-efficiency.

Answer: *Thank you for your suggestion. The concept “White Analytical Chemistry” was described in more detail. This review comprises different areas of analytical chemistry, and the cited works were selected, taking into account the green analytical chemistry principles, providing information about the relevant trends in the elementary analysis for the several matrices employing different analytical techniques. The changes were highlighted in yellow in the manuscript.*

1. The principles of Green Chemistry aiming environmental, health, safety, and economic targets.
2. Sustainable analytical methods have increasingly importance within green chemistry principles.
3. The green analytical chemistry includes developing new solvents for suitable elemental analysis.
4. The use of less toxic, diluted reagents and miniaturized methods are green sample strategies.

THINK GREEN IN INORGANIC ELEMENTAL ANALYSIS



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

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(Re) thinking Towards a Sustainable Analytical Chemistry:

Part I: Inorganic Elemental Sample Treatment

Abstract

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.

Keywords: sample treatment, acid digestion, alkaline solubilization, ultrasound, combustion, direct solid sampling analysis, green analytical chemistry.

Abbreviations

CF-CV-ICP OES: Continuous Flow Cold Vapor coupled to ICP OES; CF-CV-ICP-MS: Continuous Flow Cold Vapor coupled to ICP-MS; CVAAS: Cold Vapor Atomic Absorption Spectrophotometry; CVG-ICP-MS: Cold Vapor Generation coupled to ICP-MS; DRC-ICP-MS: Dynamic Reaction Cell Inductively coupled Plasma Mass Spectrometry; EDTA: Ethylenediaminetetraacetic Acid; FAAS: Flame Atomic Absorption Spectroscopy; FAES: Flame Atomic Emission Spectroscopy; FI-CVG-ICP-MS: Flow Injection Cold Vapor Generation coupled to ICP-MS; FMIC: Focused Microwave-Induced Combustion; GAC: Green Analytical Chemistry; GF AAS: Graphite Furnace Atomic Absorption Spectroscopy; HG-ICP OES: Hydride Generation Inductively Coupled Plasma Optical Emission Spectroscopy; HP-ICP OES: High Performance Inductively Coupled Plasma Optical Emission Spectroscopy; HR-CS-GFAAS: High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry; IC: Ion Chromatography; ICP OES: Inductively Coupled Plasma Optical Emission Spectrometry; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; LIBS: Laser-Induced Breakdown Spectroscopy; LOD: Limit of Detection; LOQ: Limit of Quantification; MAE: Microwave Assisted Extraction; MAWD: Microwave-Assisted Wet Digestion; MAWD-SRC: Microwave-Assisted Wet Digestion equipped with a Single Reaction Chamber; MIC: Microwave-Induced Combustion; MIP OES: Microwave Induced Plasma Optical Emission Spectrometry; MW-UV: Microwave-Assisted Ultraviolet Digestion; NADES: Natural Deep Eutectic Solvents; NIR: Near-Infrared Spectrometry; PVC: Poly(vinylchloride); RCC: Residual Carbon Content; RSD: Relative Standard Deviation; SF-ICP-MS: Sector Field Inductively Coupled Mass Spectrometry; SiO₂-NPs: Synthetic Silica Nanomaterials; SRC: Single Reaction Chamber; TMAH: Tetramethylammonium Hydroxide; TOF-ICP-MS: Inductively Coupled Plasma Orthogonal Acceleration Time-of-Flight Mass Spectrometry; TXRF: Total Reflection X-Ray Fluorescence; UAE: Ultrasound Assisted Extraction; Universol[®]: (40% w v⁻¹) Benzyltrimethylammonium Hydroxide in Water; USN-ICP-MS: ICP-MS with an Ultrasonic Nebulizer; UV-Vis: Ultraviolet–Visible Spectrophotometry; VF-ICP OES: Vapor Generation coupled to ICP OES; VG-ICP-OES: Vapor Generation Inductively Coupled Plasma Optical Emission Spectrometry; XRF: X-ray Fluorescence.

1. Introduction

Sample preparation is considered one of the most critical steps in chemical analysis. Several procedures are required, such as sampling, homogenization (for example, by crushing or grinding), and digestion/extraction, which are often highly labor intensive and time-consuming operations within the analytical procedure. In many cases, the samples need to be converted into solutions, since most analytical instruments are unable to directly analyze solid samples, due to the introduction systems and the difficulty in developing calibration methods for solid sample analysis [1].

For a given chemical analysis, there may be a number of acceptable preparation methods reported in the literature. It is also possible that no sample preparation procedure is required for a planned analysis, if the sample is naturally available in a form suitable for direct analysis. However, in most cases, sample preparation is unavoidable [2].

Microwave-assisted wet digestion (MAWD) is a widely adopted technique applicable for the treatment of many types of samples. It has been used in the mineralization of organic matrices including vegetables [3–6] medicinal foods [7,8], food supplements [9], animal feed [3,10], and biodiesel [11], among others. The procedure for sample preparation can be performed in an open or closed system, applying monomode (focused) radiation, multimode radiation, or hybrid radiation (directed multimode). The closed system has the advantages of allowing high pressures and temperatures above the boiling points of the acids used, providing efficient mineralization of samples, safer analytical procedures, and savings of time, compared to conventional methods such as calcination, water baths, and sand baths, among others. In addition, it minimizes the risks of contamination of the sample and analyte loss. Despite the benefits, the digestion of matrices with high organic contents results in high pressures in the closed vessel, so that the amount of sample mass is limited, which is not a restriction in the case of open systems [11,12].

Microwave-assisted extraction (MAE) can provide efficient extraction of analytes from solid samples such as plants, sediments, and soils, among others [13]. The microwave heating occurs directly in the molecules, due to the transfer of energy according to two mechanisms: the rotation of dipoles and molecular movement. In many applications, the two mechanisms occur simultaneously. In addition to heating, the extraction efficiency of this technique also depends on other factors such as the solvent, extraction time, and solid:liquid ratio. Another

relevant factor in extraction using MAE is the use of closed and pressurized containers, which increases the efficiency of the reactions and minimizes volatilization losses [14].

Another commonly applied sample treatment strategy is the use of ultrasound (frequencies between 20 kHz and 10 MHz). For analytical purposes, a small range from 20 to 50 kHz is used. Ultrasound waves, when propagating through a medium, induce a series of compressions and expansions of the molecules. The process of formation, expansion, and collapse of microbubbles, known as cavitation, is the driving force for the extraction of analytes by ultrasound-assisted extraction (UAE) [15,16]. In addition to the high pressures and temperatures generated at microscopic levels, the phenomenon of cavitation is also responsible for the mechanisms of fragmentation, erosion, ultrasonic capillary effect, sonoporation, and shear interruption. This increases the sample surface area and the speed and depth of penetration of the solvent into the matrix, improving mass transfer and, consequently, providing faster extraction and a shorter process. The extreme conditions of temperature and pressure generated by ultrasound are also responsible for the formation of highly reactive radicals such as $\text{H}\cdot$ and $\text{OH}\cdot$ in aqueous media. These free radicals contribute to degradation of the matrix and release of the analyte into the solution [17].

Microwave-induced combustion (MIC) is another technology reported for use in sample preparation treatments. This technique is based on the decomposition of organic sample masses of up to 700 mg [18], employing combustion in closed vessels pressurized with oxygen, followed by absorption of the analytes in an appropriate solution. A reflux step can be added to remove particles adhered to the flask wall, so that the entire sample is efficiently digested [18,19]. The use of a sample pellet and a paper disc ensures that the ignition process is reproducible [20]. In the decomposition of liquid samples, polycarbonate capsules and polyethylene films can be used to introduce the sample onto the quartz support, while for volatile liquids, glass or quartz wool is also recommended, in order to reduce the contact surface between the fuel and the oxidizer, decreasing the kinetics of the combustion reaction [21].

In recent years, the technologies mentioned above have been used in the development of greener analytical procedures for chemical analysis. These are generally based on the use of diluted reagents, less hazardous solvents, and low volumes of reagents by employing miniaturized systems to digest samples and extract analytes. In this review, an overview is provided concerning analytical method development and sample preparation using sustainable methods. Also discussed the use of the chemometric tools in agreement with the green

analytical chemistry in order to obtain sustainable analytical methods, as well as spectroscopic technologies for direct analysis of solids and chemical inspection of samples.

2. Sample treatment strategies proposed in Analytical Chemistry

2.1. Microwave-assisted wet digestion (MAWD)

When MAWD was first introduced, the use of concentrated acids provided very efficient digestion of organic matrices, being widely used in conventional methods. However, the use of concentrated reagents in digestion procedures poses risks to the analyst, increases the risk of contamination and the amount of waste, and is incompatible with some analytical techniques (such as ICP OES and ICP-MS), increasing the detection limit values. These disadvantages have been overcome using diluted acids [4,6,9].

Taking advantage of the benefits of digestion in closed systems, MAWD has been used with diluted acids in studies aiming at compliance with the principles of green chemistry [4,6,9]. It has been found that the efficiencies of digestion/extraction methods are not impaired using diluted acids [22,23], which could be explained by the regeneration of HNO_3 within the reaction vessel [23].

Mesko *et al.* [24] proposed a method employing MAWD and pressurization of the closed vessel with O_2 to determine P and S in dietary supplements by ion chromatography. The presence of oxygen in the gaseous phase, associated with the temperature gradient between the liquid and gas phases, made it possible to regenerate the diluted nitric acid, promoting oxidation of the organic matter. This strategy enabled the use of diluted acid solutions, making the methods greener. This approach was also effective for digesting animal feed [25] and sports supplements [9]. In another study, conducted by Tarantino *et al.* [6], evaluation was made of the use of diluted acid and H_2O_2 (30% w w⁻¹) as an oxidizing aid in the digestion of rice samples for multi-element determination by ICP OES. The H_2O_2 acted as an O_2 source in the closed vessel, enabling the use of diluted acids, which was highly compatible with the spectrometric techniques. This reagent has also been evaluated in the digestion of food supplements [26] and guaraná seeds [27], achieving recoveries of 80-120% and RSD values <10%.

In the last decade, several advances have been made in MAWD systems, aiming to align this technique with the principles of green chemistry. In the study by Savio *et al.* [28], evaluation was made of a single reaction chamber (SRC) system (UltraWAVE™) in the

development of a greener analytical method, where 4 mL of dilute 7 mol L⁻¹ HNO₃ and 1.5 mL of concentrated H₂O₂ were used to digest up to 500 mg of organic samples (grain and cereal). The use of H₂O₂ as an oxidizing agent is an attractive approach for the development of green analytical methods, since in addition to promoting efficient oxidation of organic matrices, it generates only water and oxygen as reaction byproducts [7,10,28]. Excellent precision and accuracy have been achieved using this reagent and the SRC technology. The system consists of a high pressure reaction chamber pressurized with an inert gas (N₂ or Ar, usually at 40 bar) prior to heating, followed by microwave irradiation of the reaction flasks to achieve operating temperatures and pressures of up to 300 °C and 199 bar, respectively. The high pressures and temperatures allow the use of larger amounts of sample, compared to conventional systems, as well as the digestion of different matrices in a single run. Sample masses of up to 1.25 g were efficiently decomposed using only H₂O₂ [29]. This system represents a major advance in sample preparation in green analytical chemistry (GAC), especially considering the minimal residual acidity of the digest obtained using only H₂O₂, compared to the use of HNO₃ [10,28].

Interestingly, Garitta *et al.* [30] showed that the digestion efficiency is related, among other factors, to the size and shape of the digestion vessel. In this study, two sample types were evaluated using the same heating program in two microwave systems employing vessels of different shapes and sizes. It was found that taller vessels increased the regeneration rate of nitric acid in the presence of H₂O₂, due to the higher temperature gradient formed in the system, improving the efficiency of the method. It was also demonstrated that the great advantage of the SRC system lies in the possibility of applying high temperatures, with low temperatures resulting in inferior performance, compared to systems using longer vessels.

Another approach that can make MAWD a greener preparation strategy is to associate it with ultraviolet irradiation (MW-UV). In this system, a UV lamp is placed in the closed vessel and activated by microwave radiation. Ultraviolet radiation has sufficient energy to break organic chemical bonds, leading to the formation of oxidative radical species (mainly hydroxyl and oxygen radicals) inside the vessel. Successive reactions with organic matter then increase the efficiency of digestion in the presence of diluted acids [31–34].

Microwave-assisted ultraviolet digestion has been applied to several complex matrices resistant to the digestion process. In the work of Oliveira *et al.* [32], this method was used for the digestion of petroleum coke prior to the determination of Ni, V, and S by ICP OES. The association of diluted HNO₃ solution (4 mol L⁻¹) with 3 mL of H₂O₂ (30% w w⁻¹) enabled the

efficient digestion of up to 500 mg of sample. The accuracy of the method was assessed by analysis of petroleum coke certified reference material, achieving recoveries in the range from 96 to 101%, with residual carbon content (RCC) <21%. The developed method presented greater sensitivity, compared to the conventional method recommended by the American Society for Testing and Materials (ASTM, D5600-14). Hartwig *et al.* [35] demonstrated the efficiency of this method in the digestion of 600 mg of chocolate with diluted acid (4 mol L⁻¹ HNO₃), for quantification of As, Cd, Ni, and Pb by ICP-MS. A conventional microwave-assisted digestion method was also applied, in order to compare the digestion efficiencies of the methods. The proposed MW-UV method showed lower RCC values, compared to the conventional method, evidencing that radical formation greatly increased digestion performance, making it possible to reduce the use of concentrated acids or other oxidizing reagents, reducing both blank values and the amount of laboratory waste, according to GAC principles. Other studies in the last six years that have used MAWD to make sample preparation greener are described in Table 1.

[TABLE 1]

2.2. Microwave-assisted extraction (MAE)

Microwave-assisted extraction (MAE) exploits increased diffusion of the extractor solvent in the sample, with desorption of the analyte from the matrix due to exposure to precise and high levels of heating [39,40]. In this case, both the viscosity and surface tension of the solvent decrease at high temperatures, which improve wetting and penetration into the matrix, enhancing extraction of the analyte [41]. The main advantages of using MAE are as follows: i) reduction of the extraction time (due to better thermal transfer); ii) simultaneous extraction of several samples (capacity for several vessels); iii) use of diluted and/or safer reagents; iv) less risk of cross-contamination; and v) energy savings [1,13].

Due to these benefits and compliance with environmentally friendly procedures, the MAE technique has attracted increasing attention in the last decade, especially in recent years. Komorowicz *et al.* [42] used MAE with water as solvent to extract total As and As species from mushroom samples, obtaining 83% extraction efficiency. Despite the long extraction time (~55 min), a satisfactory extraction efficiency was achieved employing a non-aggressive, simple, and inexpensive solvent.

Santana *et al.* [43] studied the applicability of MAE with natural deep eutectic solvents (NADES) for the extraction of As, Cd, Hg, Pb, Se, and V from animal and plant samples. The NADES with a citric acid: malic acid: water molar ratio of 42:13:45, used in the MAE procedure, provided satisfactory results for most of the elements studied, obtaining recoveries in the range from 80 to 120%, together with low detection and quantification limits. The advantages of this method, compared to traditional acid digestion, were reduction of the amount of sample (from 150 to 90 mg) and a shorter digestion time (from 60 to 30 min). Furthermore, the use of NADES, instead of nitric acid, reduces accident risks and follows the principles of green analytical chemistry (in accordance with the Analytical Eco-Scale).

Husáková *et al.* [44] proposed the use of ammonium fluoride (NH_4F) in an extracting solution for analytes (Li, Be, Ni, As, Se, Rb, Sb, Cs, W, Tl, and U) present in samples of fly ash. In this work, 10 mg of sample and 5 mL of 140 g L^{-1} NH_4F were used in an extraction process performed for 10 min at 200°C . The authors proposed the use of NH_4F due to its lower toxicity than the HF commonly used in the preparation of this type of sample. Furthermore, NH_4F is capable of reacting with silicates and alumina, not requiring the addition of a mixture of acids. However, when NH_4F is employed, the ICP-MS analysis requires the use of Pt cones, instead of the usual Ni cones, which increases the analytical costs.

Some other studies have demonstrated the effectiveness of using diluted acids for the extraction of trace elements in different samples, employing MAE. Inorganic elements were satisfactorily extracted from deposited particulates [13], as well as from geological materials including dolomites [45] and sediment [46]. The use of MAE enabled the quantification of Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn in sediment samples by ICP OES, after extracting the analytes using 0.2 g of sample and an extraction solution composed of 12 mL of 1.0 mol L^{-1} H_2O_2 and 400 μL of aqua regia [46]. Given that acid mixtures such as $\text{HCl}/\text{HNO}_3/\text{HF}$ are commonly used for extracting analytes from sediment samples, the use of diluted H_2O_2 could contribute to reduced waste generation, improved analyst safety, and minimization of spectrometric interferences in ICP OES.

Mimura *et al.* [14] used MAE to obtain efficient extraction of Al, As, Cd, Cr, Cu, Fe, Mn, Pb, and Zn from particulate matter, where the extractant was diluted aqua regia. In this study, three methods of sample preparation were compared, as follows: (1) hotplate (conventional acid extraction); (2) ultrasound-assisted extraction; and (3) microwave-assisted extraction. For all methods, 0.12 g of sample was used, while the extraction solutions and

extraction times were different. Method (1) used 5 mL of HNO_3 (65% v v⁻¹), 2.0 mL of HCl (37% v v⁻¹), and 10 mL of H_2O ; method (2) used 5.0 mL of aqua regia ($\text{HCl}:\text{HNO}_3$ 3:1 v v⁻¹); method (3) employed 5.0 mL of diluted aqua regia ($\text{AR}:\text{H}_2\text{O}$ 1:3 v v⁻¹). The extraction times for methods (1), (2), and (3) were 2 h, 10 min, and 11 min, respectively. No significant differences (95% confidence level) were observed among the three methods. Nonetheless, despite the similar results, the use of MAE offered advantages including a shorter extraction time, compared to the conventional method (hotplate), lower consumption of reagents, less waste generation, lower risk of accidents, and higher analyte yield.

Statistical tools have been employed for the purpose of obtaining efficient analytical methodologies in shorter times, in a process involving optimization of the different factors and their interactions. In the study by Mokoena *et al.* [47], response surface methodology (RSM) based on a Box-Behnken design was used for optimization of the factors influencing a microwave-assisted extraction process. Based on the response surface plots and the desirability score of 1, the optimum conditions found were 1.5 mol L⁻¹ HNO_3 , 16 min extraction time, and 15% v v⁻¹ hydrogen peroxide concentration. In agreement with other studies cited here, the advantages of the technique, compared to the classical methods, were considered to include improvements in terms of rapidity, environmental impacts, and safety.

Besides the use of less toxic and/or diluted reagents, the MAE technique can also be miniaturized, in accordance with the second principle of GAC. Flache *et al.* [48] used a miniaturized system in the extraction step, as briefly proposed by Czarnecki and Düring [49], to determine Cd, Cu, Mn, Mo, Pb, and Zn in bat hair, employing 500 μL of 69% w v⁻¹ HNO_3 as the extracting solution. The apparatus (μMAE) enabled the introduction of three 2.0 mL vials (containing sample and extracting solution) in each vessel commonly used for MAE, obtaining satisfactory recovery values in the range from 81 to 120%. Despite the advantage in relation to the reduced amount of sample, it is important to note that for samples with low concentrations of analytes, sensitive analytical techniques are required, such as ICP-MS or others with similar detectability.

Table 2 provides information about several applications of MAE procedures in environmentally friendly sample preparation methods during the last six years.

[TABLE 2]

2.3. Ultrasound-assisted extraction (UAE)

As in MAE, the irradiation during ultrasound-assisted extraction (UAE) contributes to accelerating the process of extracting species of interest from a solid to the liquid medium [50,51]. Due to the suitable interaction between the solid sample and the extraction solution, the chemical bonds between the analytes and the matrix components can be broken by the action of dilute acids. Small volumes of organic solvents and sample masses can be used, making this extraction process even more environmentally friendly. The efficiency of these mechanisms and, consequently, the extraction process depend on the frequency and intensity of the ultrasound radiation, the physicochemical properties of the solvent (viscosity and surface tension), and the particle size of the sample [14,15,52,53].

Given its advantages, UAE can be used for the extraction of inorganic elements from various matrices, with ultrasonication typically using equipment such as baths, probes, and the cup-horn sonoreactor. The choice of equipment to be used should consider the number and size of the samples, the complexity of the matrix, and the operating cost, among other factors. The ultrasound bath is most widely employed, mainly due to the low costs of acquisition and maintenance. Studies have reported the use of ultrasonic baths for the efficient extraction of metals from food [54–57], biological [43], and environmental [58,59] samples, among others, obtaining recovery values between 80 and 120%. In most studies, smaller volumes of reagents and shorter extraction times were required, compared to conventional extraction methods, as observed in the study by Costa *et al.* [60], who used 0.5 mol L⁻¹ HNO₃ and 1.1 mol L⁻¹ HCl, rather than concentrated HNO₃, for the extraction of Cu, Fe, Mn, and Zn from plant samples. In this work, the sample preparation time was reduced to 10 min, compared to 3 h for the usual procedure. In addition to the high analytical efficiency commonly observed in ultrasound-assisted extractions, there is compliance with several principles of green analytical chemistry, such as the elimination or substitution of toxic reagents, reducing the risks for the analyst.

Despite being widely used (Table 3), some authors have highlighted the non-uniform energy distribution in the ultrasonic bath, as a disadvantage of UAE. However, the regions of high cavitation intensity can be mapped, resulting in satisfactory relative standard deviation (RSD) values (<10%) for samples prepared simultaneously [61].

The use of cup-horn sonoreactors or ultrasonic baths allows the simultaneous treatment of multiple samples, with a homogeneous distribution of the ultrasound energy permitting a greater reduction in the volume of extraction solution used, from 1.0 to 0.5 mL. This equipment also allows the use of a small amount of sample (~10 mg), as described by De la Calle *et al.*

[62]. Despite its advantages, the cup-horn sonoreactor has not been used in recent years, except in the studies by Diehl *et al.* [63] and Gatibone *et al.* [58], mainly due to its high price, compared to ultrasonic baths, in addition to lower analytical frequency. Furthermore, for the extraction of a larger quantity of samples (up to 8 samples in vials of up to 2 mL), small quantities of samples and reagents are used, hindering analysis by techniques that require larger volumes, such as ICP OES.

The advantages of UAE were demonstrated in the work of Teixeira *et al.* [64], who achieved efficient extractions of Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn from 0.12 g of organic fertilizers, employing 0.5 mL of a mixture containing HNO₃:HCl:HF (5:3:3) and 0.5 mL of deionized water in the cup-horn sonoreactor for 10 min. The mixture was allowed to rest for 20 min, before the sonication process. Compared to conventional microwave digestion, smaller amounts of sample (0.12 g instead of 0.2 g) and reagents (0.5 mL instead of 6.0 mL) were employed, and the procedures were performed at room temperature. Satisfactory RSD values (<6%) were obtained, even employing small amounts of sample, mainly due to the better homogenization using ultrasound energy in the cup-horn sonoreactor, as mentioned above. The authors reported the requirement for HF, which was due to the presence of silicon oxides in the matrices studied. It is known that HF can solubilize silicon oxides, leading to the fragmentation of solid particles and improving the efficiency of extraction of the metals from the matrix. Furthermore, fluoride ions can form complexes with metallic elements, enabling improved extraction of elements such as Cr, Cu, Ni, and Zn.

The use of ultrasonic probes enables even shorter extraction times, compared to the use of ultrasonic baths and cup-horn sonoreactors, because the probes are immersed directly into the reaction vessels, so the ultrasound energy is completely absorbed by the mixture, consequently improving the sonication efficiency [17]. However, similar extraction times can be obtained when ultrasonic baths are optimized, especially considering homogeneous irradiation in the bath, for which high amplitudes are generally needed. In the work by Ahmed *et al.* [65], Machado *et al.* [66], and Machado *et al.* [50], similar extraction times were obtained when similar reaction conditions were employed, especially considering the sample mass and the volume and concentration of the extracting solution. Ahmed *et al.* [65] evaluated the extraction of Al, As, Cd, Cu, Fe, Mn, Pb, and Zn from *Curcuma longa* L. samples using an ultrasonic bath and a probe, under similar reaction conditions employing 0.5 g of sample and 10 mL of 25% w w⁻¹ HNO₃. As expected, a shorter extraction time was obtained with the

ultrasonic probe, compared to the ultrasonic bath (10 min vs. 25 min). The greater sonication efficiency of the ultrasonic probe results in higher efficiency of extraction of the analyte from the matrix, when the same conditions are applied with the different ultrasonic extraction equipment. Gatibone *et al.* [58] obtained recovery values of 95% using an ultrasonic probe, compared to 90% for an ultrasonic bath and 84% for a cup-horn sonoreactor, in a study of the extraction of rare earth elements from carbonite samples.

However, the use of ultrasonic probes has some disadvantages, compared to the bath and cup-horn sonoreactor, such as the limited sample throughput (only a single sample is processed at a time), higher risk of probe contamination, and higher operational cost associated with the use of acid solutions (especially HF), which can cause corrosion of the probe [67].

Several studies have reported the use of diluted acids in extraction processes assisted by ultrasound, where the H^+ ions present in the solution can displace the metallic species from the surface of the solid structure, solubilizing these elements to the liquid phase. The H^+ ions occupy the sites from which the metal ions were removed from the solid matrix, maintaining the analyte in the solution [68]. The literature reports several ‘green solvents’ that can be applied to extract inorganic analytes. Santana *et al.* [43] obtained satisfactory performance parameters for the extraction of As, Cd, Hg, Pb, Se, and V employing UAE with a natural deep eutectic solvent (NADES) composed of citric acid: xylitol: water at a molar ratio of 42:13:45. In this study, in addition to the use of a green solvent, rather than the commonly used reagent (HNO_3), it was possible to significantly reduce the sample mass, from 150 to 90 mg, achieving reliable results in a shorter procedure. In the same way, Komorowicz *et al.* [42] replaced the acidic solvents commonly used in microwave-assisted digestion by ultrapure water and ultrasonic extraction. The extraction time was reduced 15-fold, compared to the traditional method (MAWD). As can be observed, the methods used in these studies were in agreement with green analytical chemistry, considering reduced environmental risks, safer products and reagents, and efficient analyte extraction, among others.

These studies reported that the composition of the extraction solution should be selected according to the type of sample, the chemical bonds between the analytes and the constituents of the matrix, and the intrinsic properties of the analytes. Evaluation was made of the need to use temperatures higher than room temperature, as well as the compositions of extraction solutions suitable for solubilization of the analytes and their extraction into the solution phase. In the process of extracting rare earth elements (Ce, Dy, Eu, Er, Gd, Ho, La, Lu, Nd, Pr, Sm,

Tb, Tm, Y, and Yb) from carbonate rocks, it was necessary to heat the system to around 70 °C, due to the complexity of these samples. The use of high temperature can assist the cavitation effects, decreasing the surface tension and consequently increasing the vapor pressure of the liquid, leading to the more frequent formation of microbubbles. For the ultrasonic bath, ultrasonic probe, and cup-horn sonoreactor, reaction media containing about 0.2 g of sample and 10 mL of 3.0% v v⁻¹ HNO₃ were employed, with 15 min of sonication [58].

It is possible to combine UAE with other extraction and/or preconcentration methods, in order to make them greener. Altunay *et al.* [69] used ultrasound-assisted cloud point extraction (UA-CPE) for the preconcentration of Zn, Ni, and Co present in food and vegetable samples. Sonication during 5 min provided efficient dispersion of the surfactant into the solution, increasing the extraction yield. Altunay *et al.* [70] also proposed the combination of ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME) using NADES for extracting Cd, Cu, and Pb from honey samples. In this study, the elements were extracted from the aqueous phase to the NADES phase. After centrifugation, the NADES phase was diluted to 2.0 mL with 1.0 mol L⁻¹ HNO₃ in methanol, in order to reduce its viscosity for sample introduction in the FAAS technique. Ultrasonication (for 10 min at 35 °C) was employed to disperse the self-aggregating NADES droplets, in order to accelerate the formation of NADES microspheres in which the metal complexes were easily associated and separated from the aqueous phase.

As demonstrated by these studies, UAE allows the use of small reagent volumes and sample amounts, as well as the use of diluted acids, with shorter extraction times providing energy savings. Furthermore, UAE has the advantages of low contamination risks (except for the probe method) and reduced analyte losses [13,51]. In addition, the use of UAE in the extraction process reduces the risks to the analyst, compared to techniques such as MAE and the use of supercritical fluid (SCF), which employ high temperatures and pressures. For the UAE, the process is performed at atmospheric pressure, and often at room temperature. Other studies employing UAE for the purpose of greener extraction are shown in Table 3.

[TABLE 3]

2.4. Microwave-induced combustion (MIC)

Microwave-induced combustion (MIC) is a sample treatment strategy based on association between MWAD and combustion in a closed system. An advantage of the method

is that the high temperature (above 1000 °C) during the combustion process ensures complete decomposition of the organic matrix, resulting in a low residual carbon content in the digested solution [21,78]. The use of closed vessels also reduces the risks of analyte loss and sample contamination. In addition, an important feature is the possibility of varying the composition of the absorbing solution according to the analytical technique and the physicochemical characteristics of the analytes to be determined [21,79,80]. The ability to vary the chemical composition of the absorbing solution, in conjunction with the use of a closed system, make this technique an excellent option for the digestion and subsequent determination of halogens and sulfur, which are incompatible with conventional wet digestion methods [81,82].

Given these outstanding advantages of MIC technology, it has been widely employed for sample preparation in recent years. For example, MIC has been used for the efficient decomposition of samples of coal [78], powdered milk [18], cereals and vegetables [83], graphene [84], polymeric waste from electrical and electronic equipment [19], and even samples that are hard to digest, such as pitch [85].

Rondan *et al.* [83] applied MIC with 6 mL of water as an absorbing solution for the decomposition of 500 mg samples of cereals and legumes, prior to analysis by ion chromatography (IC). The accuracy of the method was assessed using CRM analysis, obtaining recoveries of 91-101%.

In the MIC procedure, in addition to the water and diluted acids that are commonly used, other chemical compositions can be employed for the absorbing solution. High digestion efficiencies (RCC <1%) have been reported using alkaline absorbing solutions obtained with NH_4OH [18,78,86] and $(\text{NH}_4)_2\text{CO}_3$ [87]. The use of water or dilute solutions of HNO_3 , HCl , and NH_4OH , among others, is highly compatible with atomic spectrometry techniques (such as ICP OES and ICP-MS), reducing waste generation and complying with most of the principles of green chemistry. In the work of Pereira *et al.* [86], analysis was made of inorganic impurities (Ba, Cd, Co, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, V, and Zn) in poly(vinylchloride) (PVC), employing ICP OES. The samples were digested by MIC, MAWD, and MAWD equipped with a single reaction chamber system (MAWD-SRC). The residual carbon contents of the digest solutions were determined, in order to evaluate the digestion efficiencies of the different sample treatment techniques. Sample masses of around 500 mg were digested by the proposed methods, under the following conditions: i) for MAWD, 6 mL of $14.4 \text{ mol L}^{-1} \text{ HNO}_3$ and digestion time of 60 min (RCC = 5%); ii) for MAWD-SRC, 8 mL of $14.4 \text{ mol L}^{-1} \text{ HNO}_3$ and digestion time

of 65 min (RCC = 2%); iii) for MIC, 6 mL of 3 mol L⁻¹ HNO₃ and digestion time of 25 min (RCC < 0.6%). The proposed method using MIC enabled safe combustion of PVC, while consuming a smaller quantity of dilute HNO₃.

Since closed vessels are used in MIC, the amount of sample is limited (<700 mg), due to the high pressure generated by the combustion of organic matter. Mesko *et al.* [88] proposed a digestion method to overcome this disadvantage, using a focused microwave-induced combustion (FMIC) technique that combined the characteristics of MIC and focused microwave-assisted wet digestion (monomode). The proposed sample treatment was performed using a modified flask (semi-open system), with a sufficient flow of oxygen to start the sample combustion process. After starting the ignition process induced by microwave irradiation, the oxygen flow was increased, in order to maintain suitable reaction conditions for complete combustion of the sample. After combustion, the absorbing solution was introduced into the flask and a subsequent reflux step could be performed by microwave irradiation [88]. This system allowed the mineralization of sample masses of up to 3 g of botanical and milk samples [89,90]. However, since this technique was based on the use of modified flasks, it required the development of the equipment, which could hinder its wider use. Table 4 shows some studies in the last decade that have employed MIC or FMIC.

[TABLE 4]

2.5. Alkaline treatment

Although the literature commonly highlights the use of concentrated or diluted acids for sample preparation, it is also reported that the use of alkaline reagents in sample treatment can provide satisfactory results in terms of analyte extraction efficiency. The use of alkaline reagents is suitable for digestions, extractions, and formation of slurries for subsequent quantification of the analytes [94].

The procedure employing alkaline digestion for solubilization of samples offers advantages such as minimal sample manipulation, reduced consumption of reagents and generation of residues, and lower temperatures, compared to acid treatments. These factors

reduce the risk of sample contamination and analyte loss, and are in accordance with the principles of GAC. Low temperature conditions (milder treatments) also make alkaline treatment effective in chemical speciation analyses, avoiding interconversion of species in the reaction medium [95].

One of the most frequently used alkaline reagents is tetramethylammonium hydroxide (TMAH), a strong organic base that is soluble in water and alcohol at room temperature. TMAH is able to complex and stabilize volatile elements, producing homogeneous slurries, and is compatible with spectrometric methods, especially atomic absorption spectrometry (AAS). Aranha *et al.* [94] evaluated the presence of toxic elements in meat samples using alkaline treatment. In this study, prior to the addition of TMAH, the sample was hydrated with ultrapure water, allowing the reagent to more easily penetrate the protein matrix and dissolve the sample, releasing the analyte to the liquid phase. It was noted that this procedure could significantly reduce the duration of the sample preparation step, even at room temperature. According to the authors, the time reduction was 500-fold, requiring treatment for only 10 min, compared to the one week of sample preparation used in previous studies.

In alkaline treatments, the efficiency of sample preparation is influenced by factors including the nature of the matrix and the size of the solid particles. For matrices that are more complex, the effectiveness of alkaline reagents can be enhanced by the application of auxiliary techniques such as microwave irradiation, ultrasonication, or conventional heating. Van Beik *et al.* [96] used a water bath in a procedure for the determination of Cr and Pb in leather samples. The solution containing 0.1 g of sample and 0.5 mL of 2.75 mol L⁻¹ TMAH was heated during 30 min, at 95 °C, in order to improve extraction of the analytes. Subsequently, 0.5 mL of concentrated HNO₃ was added to reduce the risk of co-precipitation of the analytes with proteins present in the matrix. Similar to the study mentioned previously [86], there was a significantly shorter time required for sample preparation, compared to acid digestion, with a decrease from 2 h 30 min to 30 min, as well as decreases of sample mass (from 0.5 to 0.1 g) and reagents (from 4 mL of concentrated HNO₃ to 0.5 mL of 2.75 mol L⁻¹ TMAH). Menezes *et al.* [97] used microwave energy (10 min at 100 °C) to solubilize hemp-based products with TMAH. In this work, a small sample mass (0.01 g) was solubilized with 10 mL of 0.1% w v⁻¹ TMAH and analyzed by GFAAS, in order to evaluate the toxicity profiles of the samples in terms of the concentrations of As, Cd, and Pb. As observed in the studies of Aranha *et al.* [94], and Nascimento *et al.* [98], the developed methods showed similarity between external

(aqueous medium) and internal (alkaline TMAH medium) calibration curves, allowing the application of both analytical curves to quantify the analytes solubilized in the alkaline medium. This contributed to good analytical frequency, while the use of TMAH, instead of acid solution, increased the useful life of the graphite tubes used in the GFAAS technique.

Other reagents have also been used in alkaline solubilization processes. Barros *et al.* [99] proposed a new methodology for determining Si in plant materials. It is well known that the quantification of silicon is particularly difficult, generally requiring the use of hazardous reagents, such as HF, that can chemically attack the glass tubes and other constituents of the analytical equipment. Therefore, the authors proposed the use of NaOH to solubilize the SiO₂ present in these samples. However, the use of NaOH at a higher concentration level (4 mL of 50% w w⁻¹ NaOH) could also harm the equipment, while the element sodium has a very low ionization energy, resulting in interference with the analyte signals. Therefore, this reagent was employed at low concentrations (1.5 mol L⁻¹ NaOH), after acid digestion of the plant samples with dilute HNO₃ (1 mol L⁻¹) assisted by H₂O₂ (30% v v⁻¹), resulting in a simple, safe, and reliable analytical procedure. Bossert *et al.* [100] adapted a method for determining Si in samples of synthetic silica nanomaterials (SiO₂-NPs), with an optimal 1:2 ratio of 0.1 mol L⁻¹ KOH:SiO₂ established for digestion of colloidal SiO₂-NPs. The procedure could be applied at room temperature, for analyses by UV-Vis colorimetry, or with application of microwave irradiation, when ICP OES was employed. Recovery values higher than 84% were reported for all the analytes (Si, Al, B, Ca, Cu, Fe, K, Mg, Mn, Mo, S, and Zn).

Donnici *et al.* [101] employed a patented solubilizing alkaline solvent composed of 40% w v⁻¹ benzyltrimethylammonium hydroxide in water (Universol[®]) for the solubilization of human hair and serum samples for the determination of Fe and Zn by GFAAS. The advantages of this reagent were fast sample solubilization and high stability of the solution. In accordance with the principles of green chemistry [102], the proposed method was simple, fast, inexpensive, and robust for the determination of multiple elements in blood, requiring only small volumes of samples and reagents. In this work, about 0.5 mL of ammoniacal EDTA solution was used to solubilize 0.1 mL of blood sample, followed by vortexing for 5 s. The resulting sludge was made up to 5.0 mL with deionized water and was analyzed by ICP-MS. An advantage of this approach was the short time required for sample treatment, compared to conventional acid digestion. The ability to directly introduce the sample into the ICP-MS provided further savings of time and greater simplicity of the method.

The reported studies show that the use of TMAH, sodium hydroxide, potassium hydroxide, and other alkaline reagents can make the sample preparation step simpler and faster, in addition to reducing the amounts of sample and reagents required, in accordance with some of the GAC principles. Other studies using alkaline reagents for more environmentally friendly treatments in the sample preparation stage are shown in Table 5.

[TABLE 5]

3. Chemometric approaches to assess sustainable conditions

In the field of elemental determination, chemometric tools can be used to find the most sustainable conditions for an analytical methodology. In particular, the use of solvents is one of the most concerning aspects in relation to possible environmental harm. The use of chemometric approaches usually involves the selection of appropriate solvents and amounts of chemical reagents, prediction of the properties of solvents, and optimization of time and energy consumption. The approaches used in chemometric analysis include design of experiments (DoE), response surface methodology (RSM), classification and pattern recognition, and multivariate techniques. This enables the selection of sustainable conditions, experimental optimization, and grouping or classification, for the purpose of quantitative analysis [110,111]. Cluster analysis (CA) and principal component analysis (PCA) are the most common unsupervised techniques used for the dimensional reduction of data. Linear discriminant analysis (LDA), k-nearest neighbors (KNN), and partial least squares (PLS) are techniques that have been applied for classification and prediction analysis, in addition to multiple linear regression (MLR) and principal component regression (PCR) algorithms. Artificial neural network (ANN) and genetic algorithm (GA) methods have recently attracted attention for the modeling or regression of large data sets for classification and prediction purposes [110].

Santana and coworkers [43] employed a constrained mixture design for optimizing the synthesis of three different NADES. A total of 30 different combinations were assessed for the synthesis of NADES, with the best proportions of the components successfully identified using RSM. The synthesized solvents were used in the extraction of samples of biological tissue and plant material by UAE and MAE, for subsequent elemental determination of As, Cd, Hg, Pb, Se, and V by ICP-MS. Acceptable accuracies in the range from 80 to 120% were obtained for most of the elements determined.

Quantitative extraction of Cd, Cu, Cr, Pb, and Zn was achieved in 16 min, using 1.5 mol L⁻¹ HNO₃ and 15% w v⁻¹ H₂O₂, based on RSM and a Box-Behnken design. Romão *et al.* [112] optimized the acid digestion of *Casearia fasciculata* fruits, for determination of inorganic constituents by ICP OES. The digestion using dilute HNO₃ (1.0 mol L⁻¹) was optimized by mixture design, with different approaches being used to evaluate the digestion procedure, including the desirability function and multiple responses. PCA and HCA were also employed for data analysis and interpretation of the results. Andrade *et al.* [113] optimized a MAE procedure using the combination of a factorial design and PCA. Different types of acid solvents (aqua regia, inverted aqua regia, dilute aqua regia, 7 mol L⁻¹ HNO₃ + H₂O₂, and 14 mol L⁻¹ HNO₃) were assessed for determination of the inorganic fraction in electronic waste samples by ICP OES. The most sustainable condition selected was the use of dilute aqua regia (50% v/v), which provided the highest extraction efficiency.

Regarding regression algorithms, Torrecilla *et al.* [114] used an ANN model to predict the properties of ionic liquids (ILs). Prior to the synthesis of ILs, the melting points of 97 imidazolium salts were predicted, with a mean prediction error of 1.30% and regression coefficient of 0.99. Similar methodologies were applied by Valderrama *et al.* [115], Huang *et al.* [116], and Cao *et al.* [117] to correlate and predict the viscosity, density, and electrical conductivity of ILs. All the methods showed high prediction capability and were successfully applied for characterization of the solvents.

3.1. Direct solid sampling analysis with minimal or no sample treatment

As discussed above, chemical measurements using conventional methods require exhaustive sample preparation steps. As most types of samples are in solid form, while many analytical instruments require the use of liquids, various solvents are used to dissolve/digest/extract samples. These sample preparation methods seem to present the greatest challenge in the development of techniques that are more environmentally friendly, requiring solvents that are greener, or even their complete elimination. Although the elimination of sample preparation steps and the use of reagents that are less hazardous would appear to be ideal solutions, these goals are very difficult to achieve for most of the methods currently available [118].

Closer adherence to the criteria of green analytical chemistry necessitates sample preparation methods (when required) that use biodegradable solvents and low volumes of reagents, and that avoid pollution. Additionally, direct analyses of samples can be performed using spectroscopic techniques such as laser-induced breakdown spectroscopy (LIBS) [119,120], laser ablation ICP-MS/OES (LA-ICP-MS/OES) [121], Raman spectrometry [122], near-infrared spectrometry (NIR) [123], and X-ray fluorescence (XRF) [124]. Since sample preparation may be minimal (such as drying, grinding, or polishing) or absent, these are promising green analytical techniques [125]. It is also important to emphasize that the “green” attributes of these techniques are simply concepts. It is not appropriate to label a technique as “green”, if it does not meet the requirements, considering aspects other than only the absence of a requirement for solvents. Furthermore, considering all twelve principles of green chemistry, it would be impossible to make all analytical methodologies compliant with all aspects [118]. Therefore, it should be kept in mind that no method is absolutely benign, although selecting a technique that eliminates the sample preparation steps may be a greener option, compared to other alternatives.

If sample preparation is not required, many advantages can be highlighted, including elimination (or a significant reduction) of the consumption of hazardous reagents, reduction of waste generation, reduced emissions of vapors and gases, and reductions of time, labor, and energy consumption in the analytical procedures [118,125,126]. In addition to consuming a significant amount of solvents, the sample preparation step is a critical process [2,126]. It is in this part of the analytical procedure that more time is spent and more mistakes are made. Due to the existence of several steps during sample preparation, such as sampling, handling, homogenization, and digestion/extraction, there is ample opportunity for the introduction of errors in the analytical procedure, directly affecting the accuracy and measurement precision of the final results [2].

In this context, analytical techniques especially designed for direct analysis offer several advantages that contribute to their compliance with many of the principles of GAC. For instance, technological advances have made it possible to develop simpler instrumentation, including handheld portable devices (such as for LIBS, Raman, XRF, and NIR analyses). *In situ* monitoring has been exploited in the field and in space [127-129], enabling the direct analysis of samples including archaeological materials [130-132], artwork [132-134], explosives [135], forensic items at crime scenes [136,137], and samples that cannot be

transported to the laboratory. From the green chemistry perspective, perhaps the most important methods are those spectroscopic techniques that have been adapted for online/real-time measurements [138-140]. Real-time analysis consisting of continuous sampling of material, using a flow configuration, can also avoid the formation of hazardous substances and the consequent environmental pollution [118,141].

In recent work, Noll *et al.* (2021) reported an advance in the use of LIBS for selective identification of highly enriched fractions obtained from end-of-life products and their components [142]. This system comprised a scanning LIBS device combined with measurements in 2D and 3D geometry, used to develop inverse production lines that could achieve a sustainable circular economy. The proposed LIBS methodology could be successfully applied in the recycling of electronic waste, replacing conventional methods that require laborious procedures and concentrated solvents (usually aqua regia) for acid leaching.

A portable LIBS device has been used in remote analyses to investigate explosives and non-explosive samples [155]. A standoff distance of approximately 6.5 m was used for the analysis of different samples, obtaining excellent classification results by application of PCA and ANN protocols. The findings demonstrated that LIBS was suitable for application in out-of-the-lab investigations requiring the rapid identification of explosives.

Rodriguez *et al.* [133] described the use of portable equipment for non-destructive analysis aiming at the conservation of artwork [133]. Infrared reflectography (IRR) and XRF analyses were performed for the copper painting “Venus with Mars and cupids”, completed between 1606 and 1608 by the Italian painter Carlo Saraceni. These techniques were essential for in-depth analysis to understand the process of creation of the painting and the original painter’s palette, as well as the condition of the painting for conservation of the artwork in the future. Portable XRF (pXRF) was also employed in an out-of-the-lab application for characterizing the geochemistry of soils and sediments [127]. The direct analysis in the field (with the samples dried, ground, and loosely placed in plastic cups) was compared with the laboratory method employing pressed-powder pellets). The pXRF spectrometry showed good performance, with the results being closely aligned to those obtained using benchtop XRF.

Raman spectroscopy is another versatile analytical technology useful for a variety of interesting applications. Forensic science usually requires *in situ* testing methodologies, with hand-held and portable instrumentation having proven extremely important for this purpose. Raman analysis has been investigated for application to real crime scene samples including

serological substances (such as blood, semen, and saliva), gunshot residues, explosives, and drugs [136].

Among the outstanding advantages of these spectroscopy techniques, their use can provide rapid acquisition of chemical information, minimizing errors, costs, time, and sample treatments, while avoiding the use of hazardous reagents and the generation of waste associated with traditional laboratory-based analyses [143]. Furthermore, few green analytical methods combine these advantages with multi-elemental analysis, high throughput, and microanalysis with little or no requirement for sample preparation.

However, other green alternatives analytical methodologies have been proposed in the literature, employing environmentally friendly solvents and greener analytical strategies. Over the course of the last couple of decades, the growth of analytical methods compliant with the principles of green chemistry has demonstrated how fundamental scientific approaches can be developed to meet combined environmental, health and safety, and economic targets. The studies that bring this concept and its applications are reported in Part II of this review.

Conclusions

As reported in this review, very many sample treatments have been proposed, depending on the nature of the sample matrix, the intrinsic properties of the analytes, and the characteristics of the determination methods. Selection of a suitable sample treatment should consider all of these aspects related to the samples and the analytical technique, acknowledging that all sample treatment strategies have their advantages and limitations. The sample treatment should deliver the analyte in a suitable chemical form for its determination, while aiming at promoting the use of sustainable analytical methods that comply with the principles of green chemistry, without ignoring the need for efficient and accurate analysis, which is one of the purposes of analytical chemistry. The literature now reports several analytical methods employing miniaturization strategies, diluted reagents, and smaller amounts of samples, as a result of the increasing awareness of the need to ensure minimal waste generation, while at the same time providing high analytical throughput. Most of the sample treatments employ auxiliary energy sources, such as microwaves or ultrasound irradiation, to improve the extraction/digestion/solubilization of the analytes present in the sample matrix. In addition, direct analysis has increasingly gained attention in chemical analysis, since the intrinsic properties of such analytical techniques can enable accurate, precise, and rapid determination of analytes, even in complex matrices, with

minimal or no requirement for sample pretreatment. There has been a remarkable increase in the application of greener advanced technologies for chemical analysis, providing analyses with adequate accuracy and high analytical throughput, free from laborious sample preparation steps, which has revolutionized the area of sustainable analytical chemistry.

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Table 1. Applications of microwave-assisted wet digestion methods in sample preparation.

Applications of microwave-assisted wet digestion using diluted nitric acid							
Analyte	Sample	Digestion conditions	Heating program	Determination technique	Recovery	LOD	References
As, Cd, Hg, Pb	Medicinal plants	500 mg, 6 mL 4 mol L ⁻¹ HNO ₃	20 min up to 1400 W, 20 min at 1400 W, 20 min at 0 W	ICP-MS and FI-CVG-ICP-MS	96-107%	0.004-0.020 µg g ⁻¹	[8]
Applications of microwave-assisted wet digestion using diluted nitric acid and oxygen pressure/hydrogen peroxide							
Analyte	Sample	Digestion conditions	Heating program	Determination technique	Recovery	LOD	References
K, Ca, Mg, S, P, Cu, Fe, Mn, Zn	Guaraná seeds	250 mg, 1 mL 9 mol L ⁻¹ HNO ₃ + 3 mL H ₂ O ₂ (30%) + 6 mL H ₂ O	2 min up to 120 °C, 8 min at 120 °C, 5 min up to 180 °C, 15 min at	ICP OES	94-108%	0.02-7.2 µg g ⁻¹	[27]

				180 °C, 15 min of cooling			
Ba, Cr, Cu, Mn, Mo, Ni, Pb, Sr, V, Zn	Biodiesel	700 mg, 4 mL 7 mol L ⁻¹ HNO ₃ + 2 mL H ₂ O ₂ (30%)	20 min up to 900 W, 20 min at 900 W, 20 min at 0 W	SF-ICP-MS	94-109%	1-239 ng g ⁻¹	[11]
Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Se, Zn	Rice	250 mg, 7 mL 4.8 mol L ⁻¹ HNO ₃ + 1 mL H ₂ O ₂ (30%)	4 min up to 90 °C, 2 min at 90 °C, 10 min up to 200 °C, 21 min at 208 °C	ICP OES and ICP-MS	80-102%	0.002-2.3 µg g ⁻¹	[6]
As, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, Sr, V, Zn	Soybean-based edible products	250 mg, 7 mL 2.1 mol L ⁻¹ HNO ₃ + 1 mL H ₂ O ₂ (30%)	5 min up to 120 °C, 2 min at 120 °C, 10 min up to 210 °C, 15 min at 210 °C, cooling to 25 °C	ICP OES and ICP-MS	90-116%	0.0021-2.90 µg g ⁻¹	[36]
Ca, Cu, Fe, K, Mg, Mn, Na, Zn, P, S	Sports supplements	1350 mg, 6 mL 5 mol L ⁻¹ HNO ₃ , 5 bar oxygen pressure	5 min up to 1000 W, 10 min at 1000 W, 20 min at 0 W	ICP OES	86-108%	0.006-1.85 µg g ⁻¹	[9]

Applications of microwave-assisted wet digestion using dilute nitric acid and SRC technology

Analyte	Sample	Digestion conditions	Heating program	Determination technique	Recovery	LOD	References
As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, P, Pb, Zn	Medical foods	1 g, 6 mL H ₂ O ₂ (50%) 130 mL H ₂ O + 5 mL 14 mol L ⁻¹ HNO ₃ into the SRC chamber, 40 bar of Ar	15 min up to 250 °C, 10 min at 250 °C, cooling	ICP OES	80-120%	0.01-88 µg g ⁻¹	[7]
As, Cd, Hg, Pb	Dietary supplements	200 mg, 5 mL 3.75 mol L ⁻¹ HNO ₃ + 0.5 mL H ₂ O ₂ (30%) 150 mL H ₂ O + 5 mL 14 mol L ⁻¹ HNO ₃ into the SRC chamber, 40 bar of N ₂	2.5 min up to 180 °C, 2.5 min at 180 °C, 2.5 min up to 210 °C, 2.5 min at 210 °C, 10 min up to 220 °C, 10 min at 220 °C	ICP-MS	82-125%	*0.0048-0.37 µg g ⁻¹	[26]

Ca, Co, Cu, Fe, K, Mg, Mn, Mo, Na, P, Sr, Zn	Grains and cereals used in swine feed	500 mg, 4 mL 7 mol L ⁻¹ HNO ₃ + 1.5 mL H ₂ O ₂ (30%) 150 mL H ₂ O + 5 mL 14 mol L ⁻¹ HNO ₃ into the SRC chamber, 40 bar of N ₂	5 min up to 150 °C, 2 min at 150 °C, 5 min up to 220 °C, 25 min at 220 °C, cooling to 60 °C	ICP OES and ICP-MS	80-120%	0.05-58 µg g ⁻¹ [5]
As, Ba, Cd, Co, Cu, Mn, Mo, Pb, Sr, Zn, Ca, Fe, Mg, Na	Honey and flours	0.75 g flour or 1.25 g honey, 8 mL H ₂ O ₂ (50%) 120 mL H ₂ O + 5 mL 18.4 mol L ⁻¹ H ₂ SO ₄ into the SRC chamber, 40 bar of Ar	20 min up to 250 °C, 10 min at 250 °C, cooling	ICP OES and ICP-MS	-	0.0001-30 µg g ⁻¹ [29]
C, Ca, Fe, K, Mg, Na, Ba, Cd, Cu, Mn, Mo, Pb, Sr, Zn	Milk powder	500 mg, 8 mL H ₂ O ₂ (50%) 120 mL H ₂ O + 5 mL 18.4 mol L ⁻¹ H ₂ SO ₄	10 min up to 250 °C, 20 min at 250 °C, cooling to 65 °C	ICP OES and ICP-MS	-	0.0001-30 µg g ⁻¹ [10]

into the SRC
chamber, 40 bar of Ar

Applications of microwave-assisted wet digestion using dilute nitric acid and ultraviolet radiation

Analyte	Sample	Digestion conditions	Heating program	Determination technique	Recovery	LOD	References
Ba, Co, Cr, Cu, Mn, Ni, Pb, Sr, V	Biodiesel	950 mg, 10 mL 7 mol L ⁻¹ HNO ₃ (MW-UV)	20 min up to 900 W, 20 min at 900 W, 20 min at 0 W	SF-ICP-MS	95-108%	0.12-6.9 ng g ⁻¹	[37]
As, Cd, Cu, Mn, Mo, Ni, Pb, V, Zn	Macroalgae	700 mg, 10 mL 2 mol L ⁻¹ HNO ₃ (MW-UV)	-	ICP-MS	94-106%	<0.580 µg g ⁻¹	[4]
Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, Zn	Produced water from crude oil extraction	8 g, 0.8 mol L ⁻¹ HNO ₃ 0.4 mL H ₂ O ₂ (30%) (MW-UV)	5 min up to 700 W, 10 min at 700 W, 20 min at 0 W	ICP OES	90-102%	*0.004-0.462 µg g ⁻¹	[38]

As, Cd, Ni, Pb	Chocolate	600 mg, 10 mL 4 mol L ⁻¹ HNO ₃	20 min up to 550 W, 40 min at 550 W, 15 min at 0 W	ICP-MS	95-104%	0.87-29.7 ng g ⁻¹	[35]
As, Cd, Pb	Antarctic seaweeds	700 mg, 10 mL 2 mol L ⁻¹ HNO ₃	10 min at 900 W, 20 min at 0 W	ICP-MS	96-106%	0.001-0.012 µg g ⁻¹	[31]
Ni, V, S	Petroleum coke	500 mg, 15 mL 4 mol L ⁻¹ HNO ₃ + 4.9 mol L ⁻¹ H ₂ O ₂ (MW-UV)	10 min up to 400 W, 10 min at 400 W, 10 min up to 1000 W, 10 min at 1000 W, 20 min at 0 W	ICP OES	96-101%	0.12-8.7 µg g ⁻¹	[32]

* LOQ value.

Table 2. Applications of microwave-assisted extraction methods in green analytical chemistry.

Analyte	Sample	Sample mass and reagents	Power or temperature	Extraction time	Recovery	LOQ	References
Ba, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn	Sediments	0.2 g / 12 mL 1.0 mol L ⁻¹ H ₂ O ₂ + 400 µL AR	180 °C	30 min	74-124%	0.1-2.0 mg kg ⁻¹ (ICP OES)	[46]
Cd, Cu, Mn, Mo, Pb, Zn	Bat hair	0.005 g / 500 µL concentrated HNO ₃	200 W 300 W	10 min	81-120%	0.0002-0.15 mg kg ⁻¹ (ICP OES)	[48]
As, Be, Cs, Li, Ni, Rb, Sb, Se, Tl, U, W	Fly ash	10.0 mg sample / 5.0 mL 140 g L ⁻¹ NH ₄ F	200 °C	10 min	91-104%	0.3-1587 µg kg ⁻¹ (TOF-ICP-MS)	[44]
Al, As, Cd, Cr, Cu, Fe, Mn, Pb, Zn	Deposited particulate matter	0.12 g / 5.0 ml AR:H ₂ O (1:3vv ⁻¹)	150 °C	11 min	87-114%	0.015-333 mg kg ⁻¹ (FAAS and GFAAS)	[13]

Pb	Geological	0.5 g / 0.3 mol L ⁻¹ HCl or HNO ₃ or CH ₃ COOH	350 W	15 min	92-114%	*3.4-6.8 µg L ⁻¹ [45] (HG-ICP OES)
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*LOD value / method limit of quantification.

Table 3. Applications of ultrasound-assisted extraction methods (ultrasonic bath, probe and cup-horn sonoreactor) in green analytical chemistry.

Analyte	Sample	Sample mass and reagents	Ultrasound equipment and temperature	Extraction and time	Recovery	LOQ	References
Al, As, Cd, Cu, Fe, Mn, Pb, Zn	Plant	0.5 g / 10.0 mL 25% w w ⁻¹ HNO ₃	Probe	10 min	99-100%	0.034-0.065 mg kg ⁻¹	[71] (FAAS and ICP OES)
			Bath	25 min	99-100%		
				60 min	82-107%	0.78 mg g ⁻¹ of Al and 4.34-24.5 µg g ⁻¹ (FAAS)	
Al, Cd, Cu, Ni, Zn	Soils	0.1 g / 2.0 mL 3.0 mol L ⁻¹ HCl, or 3.60 mol L ⁻¹ HNO ₃ , or 3.0 mol L ⁻¹ HF	Bath / 50 ± 5 °C				
Hg	Inorganic fertilizers	0.15 g / 4.0 mL 3.6 mol L ⁻¹ HCl	Bath	5 min	100%	-	[61] (CV AAS and MIP OES)

Al, Ba, Cd, Cu, Fe, Mn, Mo, Ni, Ti, V, Zn	Edible oils	3.0 g / 1.0 mL 1.0% lipase	Bath	10 min	88-111%	*0.007-0.67 $\mu\text{g kg}^{-1}$ (ICP-MS)	[72]
Fe, Zn	Milk-based infant formula	0.5 g / 25 mL 15% w w ⁻¹ HNO ₃	Bath Probe	5 min	99-101% 101-109%	(FAAS)	[67]
Ca, Cu, Mg, Mn	Oilseed crops	0.3 g / 10 mL 1.4 mol L ⁻¹ HNO ₃	Bath	10 min	89-106%	*3.5 mg g ⁻¹ Mg and 333.4-666.7 $\mu\text{g g}^{-1}$ (FAAS)	[73]
Cd, Cu, Ni, Pb, Zn	Artichoke leaves, soybean seeds	0.5 g / 10.0 mL 3.5 mol L ⁻¹ HNO ₃	Probe Bath	10 min 25 min	79-103% 79-107%	- -	[50]
Cd, Cu, Ni, Pb, Zn	Globe artichoke	0.5 g / 10.0 mL 25% w w ⁻¹ HNO ₃	Probe Bath	10 min 25 min	99-100% 97-99%	*0.006-0.54 mg kg ⁻¹ (FAAS and ET AAS)	[66]
			Bath	15 min	90-118%		[54]

Ba, Ca, Cu, Fe, K, Mg, Mn, P, Sr, Zn	Green coffee beans	0.2 g / 1.0 mL 0.6 mol L ⁻¹ HNO ₃				*0.1-300 µg g ⁻¹ (ICP OES)	
I	Food	0.1 g / 10 mL H ₂ O	Bath	5 min	80-118%	0.164 mg L ⁻¹	[74]
Cd, Cr, Cu, Fe, Mn, Pb, Zn	Edible oils	1.0 g / 2.5 mL 25% w v ⁻¹ TMAH and 1.5 mL 0.06 mol L ⁻¹ EDTA	Bath	30 min	87-100%	0.016-0.80 ng mL ⁻¹ (GFAAS)	[56]
Al, Ca, Cd, Cu, Mg, Mn, Ni, Ti, V, Zn	Edible oils	3.0 g / 2.0 mL 0.01 mol L ⁻¹ EDTA	Bath	20 min	83-118%	*0.013-2.81 µg kg ⁻¹ (ICP-MS)	[55]
Na	Pet foods	100 mL H ₂ O for each 1.0 g of sample	Bath	20 min	98-104%	0.90 mg L ⁻¹ (flame photometry)	[75]

As, Cr, Mo, Sb, Se, V	Agricultural soil	0.1 g / 5.0 mL 2.0 mol L ⁻¹ HNO ₃ and 10 mL DES ^a	Bath	5 min + 5 min at 120 °C in digester block	98-102%	0.03-0.3 µg g ⁻¹ (ICP OES)	[59]
Ca, Mg, P	Swine feed	0.1 g / 20 mL 0.1 mol L ⁻¹ HCl	Probe	50 s	99-113%	53-70 µg L ⁻¹ (FAAS and UV-Vis)	[57]
Cd, Pb	Coconut water and milk	1.0 g / 20.0 mL 1.0 mol L ⁻¹ HNO ₃	Bath	10 min	102-108%	0.06-0.7 µg L ⁻¹ (water) 0.10-0.85 ng g ⁻¹ (milk) (HR-CS GF AAS)	[76]
Ce, Dy, Eu, Er, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb	Carbonatite rock	0.2 g / 10 mL 3.0% v v ⁻¹ HNO ₃	Probe: 70 °C Cup-horn: 70 °C Bath: 70 °C	15 min	80-95%	0.001-0.013 µg g ⁻¹ (ICP-MS)	[58]

Ca, Cu, Mg, Mn, Na, Zn	Hardaliye beverages	3.0 mL / 1.0 mL 5.0% v v ⁻¹ HNO ₃	Probe	1 h rest before 2min extraction	95-110%	0.008-0.013 mg L ⁻¹ [77] (FAAS)
Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, Pb, Se and Zn.	Milk-based infant formulas	0.5 g / 10 mL 25% w w ⁻¹ HNO ₃	Probe Bath	10 min 25 min	99-100% 99-103%	0.007-0.098 µg mL ⁻¹ [65] ¹ (FAAS and ICP OES)

* LOD values. ^a Choline chloride: oxalic acid ratio of 1:2.

Table 4. Applications of microwave-induced combustion (MIC) methods in sample preparation.

Applications of microwave-induced combustion in closed vessels							
Analyte	Sample	Digestion conditions	Heating program	Determination technique	Recovery	LOD	References
Ba, Ca, Fe, K, Li, Mg, Na, Zn	Graphite powder	600 mg as powder (acted as self-ignition aid), 6 mL 4 mol L ⁻¹ HNO ₃ (absorbing solution), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP OES	100-101%	*0.48-1.95 µg g ⁻¹	[20]
S	Coal	250 mg as pellet, 6 mL 2 mol L ⁻¹ HNO ₃ (for ICP OES) or 6 mL 50 mmol L ⁻¹ NH ₄ OH (for IC) (absorbing solution) + 50 µL 6 mol L ⁻¹	1 min at 1400 W (without reflux), 5 min at 0 W	ICP OES and IC	87%	2.5 µg g ⁻¹	[78]

		NH ₄ NO ₃ (igniter), 20 bar oxygen pressure						
Ba, Cd, Co, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sr, V, Zn	Poly(vinyl chloride) (PVC)	500 mg as pellet, 6 mL 3 mol L ⁻¹ HNO ₃ (absorbing solution) + 50 µL 6 mol L ⁻¹ NH ₄ NO ₃ (igniter), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP OES	>94%	>0.1 µg g ⁻¹	[91]	
Ba, Ca, Cd, Fe, Mg, Pb, Sr, V, Zn	Pitch	400 mg as pellet, 6 mL 3 mol L ⁻¹ HNO ₃ (absorbing solution) + 50 µL 6 mol L ⁻¹ NH ₄ NO ₃ (igniter), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP OES and XRF	97-106%	1.3-20.8 µg g ⁻¹	[85]	
Br, I	Milk powder	700 mg as pellet, 6 mL 25 mmol L ⁻¹ NH ₄ OH (absorbing solution) + 50 µL 6 mol L ⁻¹	5 min at 1400 W (optional reflux), 20 min at 0 W	ICP OES and ICP-MS	97-106%	0.003-0.007 µg g ⁻¹	[18]	

		NH ₄ NO ₃ (igniter), 20 bar oxygen pressure					
Ba, Co, Fe, Mg, Mn, Ni, S, V	Crude oil distillation residues	500 mg in polyethylene film, 6 mL 3 mol L ⁻¹ HNO ₃ (absorbing solution) + 50 µL 6 mol L ⁻¹ NH ₄ NO ₃ (igniter), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP OES	94-105%	0.02-12.7 µg g ⁻¹	[79]
Cd, Co, Cr, Cu, Mn, Ni, Pb, V	Diesel	400 mg on 100 mg of quartz wool in polyethylene film, 6 mL 4 mol L ⁻¹ HNO ₃ (absorbing solution) + 50 µL 6 mol L ⁻¹ NH ₄ NO ₃ (igniter), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP-MS	90-102%	*0.001-0.20 µg g ⁻¹	[21]
Cl, S	Rice, maize, wheat,	500 mg in low-density polyethylene film, 6 mL ultrapure H ₂ O	5 min at 1400 W (with reflux), 20 min at 0 W	IC	91-101%	9-10 µg g ⁻¹	[83]

	beans, lentils, soybeans	(absorbing solution) + 50 μL 6 mol L^{-1} NH_4NO_3 (igniter), 20 bar oxygen pressure					
S	Diesel	400 mg on 100 mg of glass wool in polyethylene film, 6 mL 2 mol L^{-1} HNO_3 5 min at 1400 W (with (absorbing solution) + reflux), 20 min at 0 W 50 μL 6 mol L^{-1} NH_4NO_3 (igniter), 20 bar oxygen pressure	ICP OES	>97%	2 $\mu\text{g g}^{-1}$	[92]	
Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Sr, V, Zn	Graphite powder	400 mg as pellet, 6 mL 4 mol L^{-1} HNO_3 (absorbing solution) + 5 min at 1400 W (with 50 μL 6 mol L^{-1} reflux), 20 min at 0 W NH_4NO_3 (igniter), 20 bar oxygen pressure	ICP OES and ICP-MS	>95%	*0.03-6.54 $\mu\text{g g}^{-1}$	[93]	

Br, Cl, F, I	Soil	100 mg + 400 mg of microcrystalline cellulose as pellet, 6 mL	100 mmol L ⁻¹ NH ₄ OH (absorbing solution) + 50 μL 6 mol L ⁻¹ NH ₄ NO ₃ (igniter), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP-MS and IC	83-103%	*0.06-60 g ⁻¹ μg	[86]
As, Br, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Zn	Electric and electronic equipment waste	400 mg + 200 mg of microcrystalline cellulose as pellet, 5 mL	2 mol L ⁻¹ HNO ₃ + 1 mL 2 mol L ⁻¹ HCl (absorbing solution) + 50 μL 6 mol L ⁻¹ NH ₄ NO ₃ (igniter), 20 bar oxygen pressure	5 min at 1400 W (with reflux), 20 min at 0 W	ICP OES, ICP-MS, FI-CVG-ICP-MS, and DRC-ICP-MS	95-107%	0.005-3.12 g ⁻¹ μg	[87]

For Br determination, 6
mL 50 mmol L⁻¹
NH₄OH was used as
absorbing solution

For Cr, a mass ratio of
1:1 of CRM:NH₄Cl was
used as additive

* LOQ value.

Table 5. Environmentally friendly alkaline treatments used in the sample preparation step.

Analyte	Sample	Amounts of sample and reagents	Procedure	Recovery	LOQ	References
Cr(III), Cr(VI)	Soil (total content analysis)	1 g / 20 mL Milli-Q water or 20 mL 0.1 mol L ⁻¹ NaOH	Shaking for 2 h at 150 rpm, at room temperature, centrifugation for 15 min at 3000 rpm, filtration	91-106%.	2 mg kg ⁻¹ (FAAS) 25 µg kg ⁻¹ (ETAAS)	[95]

	Soil (speciation analysis)	Appropriate volume (from 1 to 5 mL) ^a + Milli-Q water to 10 mL + 2.00 mL of 2% Aliquat 336 in xylene	Up and down shaking for 8 min			
		^a 1 mL of 0.1 mol L ⁻¹ NaOH was added to the filtrate, before dilution with water				
Cu, Fe, Mn, Zn	Bovine testis	0.3 g / 1 mL 25% w v ⁻¹ TMAH and 0.5 mL H ₂ O	1 h in a digester block at 60 °C	99-102%	0.41-2.50 mg kg ⁻¹ (FAAS)	[103]
Cr, Pb	Leather	0.1 g / 0.5 mL 2.75 mol L ⁻¹ TMAH	30 min in a water bath at 95 °C	100-110%	*4.0-9.0 µg g ⁻¹ (FAAS)	[104]

0.5 mL of HNO ₃ added after heating							
Br, I	Milk powder	0.7 g / 6 mL 0.11 mol L ⁻¹ TMAH	Microwave at 1400 W for 50 min, 20 min cooling	85-102% in relation to the MIC	0.4-0.2 µg g ⁻¹ (ICP-MS)	[18]	
		0.7 g / 6 mL 25 mmol L ⁻¹ NH ₄ OH		87-108% in relation to the MIC			
Cd	Meat	0.5 g / 8 mL H ₂ O and 0.5 mL 25% w v ⁻¹ TMAH	4 min in contact with water, followed by addition of TMAH and 10 min of solubilization at room temperature	100%	3.0 µg kg ⁻¹ (GFAAS)	[105]	
Cr, Cu, Fe, K, Mg, Mn, Zn	Shrimp, crab	0.25 g / 1 mL 25% w v ⁻¹ TMAH, 1 mL 14 mol L ⁻¹ HNO ₃	Ultrasonic bath for 30 min, thermostatic water bath at 70 °C for 10 min at 250 rpm,	91-106%	0.22-2.86 µg g ⁻¹ (MIP OES)	[106]	

			cooling to room temperature			
As, Cd, Pb	Hemp products	0.01 g / 10 mL 0.1% w v ⁻¹ TMAH	Microwave for 10 min at 100 °C, cooling for 12 min	87-99%	0.04-0.61 µg g ⁻¹ (GFAAS)	[97]
As, Cd, Pb	Cannabidiol extracts	0.1 g / 5 mL 0.1% w v ⁻¹ TMAH	Solubilization at 100 °C for 15 min in a water bath	96-109%	0.011-0.26 µg g ⁻¹ (GFAAS)	[98]
Si, Al, B, Ca, Cu, Fe, K, Mg, Mn, Mo, S, Zn	Sugar cane leaves, soy leaves, corn leaves and roots	0.1 g / (1) 5 mL 1 mol L ⁻¹ HNO ₃ + 5 mL 30% v v ⁻¹ H ₂ O ₂ (2) 5 mL 1.5 mol L ⁻¹ NaOH, then 750 µL 14 mol L ⁻¹ HNO ₃	Microwave: (1) 5 min up to 120 °C, 5 min at 120 °C, 5 min up to 160 °C, 5 min at 160 °C, 3 min up to 230 °C, 5 min at 230 °C (2) 5 min up to 150 °C, 5 min at 150 °C, 5 min up to 230 °C, 10 min at 230 °C	91-115%.	1.0-8615 µg g ⁻¹ (ICP OES)	[99]

Si	Synthetic silica nanomaterials (SiO ₂ -NPs)	1:2 ratio of 0.1 mol L ⁻¹ KOH:SiO ₂	Microwave for 14 min at 1500 W or Overnight at room temperature	>84%	80.1-430 µg L ⁻¹ (ICP OES and UV-Vis)	[100]
Fe, Zn	Human serum and hair samples	500 µL / 500 µL Universol [®] 0.1 g dried hair, 500 µL Universol [®]	Dilution of the resulting solutions to 10 mL with ultrapure water	93-103%	1.7-2.3 µg L ⁻¹ (serum), 0.3-1.0 ng g ⁻¹ (hair) (GFAAS)	[101]
Cd, Pb	Fish, shrimp	4 g / 4 mL deionized water, 4 mL 25% w v ⁻¹ TMAH	Left to stand for at least 2 h at room temperature, then making up to 25 mL with deionized water	84-107%	6.25-31.25 µg kg ⁻¹ (GFAAS)	[107]
Ca, Fe, Zn, Mg	Milk samples	0.2 g or 1 mL / 1 mL ultrapure water, 650 µL 25% w v ⁻¹ TMAH	Ultrasonic bath for 32 min	94-98%	0.029-1.07 mg L ⁻¹ (FAAS)	[108]

Cu, Mo, Zn	Beef samples	0.25 g / 5 mL	60 min at 85 °C in a	87-106%	0.048-2.11 mg kg ⁻¹ [109]
		ultrapure water, 1.5 mL 25% w v ⁻¹	water bath		(FAAS and ICP-MS)
		TMAH			

* LOD values; ° Method LOQ.

(Re) thinking Towards a Sustainable Analytical Chemistry:

Part II: Alternative Solvents and Extraction Techniques

Abbreviations

3R's: Reduce, Reuse, Recycle; 5-Br-PADAP: 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol; 5-BrPADAP-TPB: 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol-tetraphenylborate; 8-HQ: 8-hydroxyquinoline; μ SI-LOV: micro sequential injection lab-on-valve; AA-DLLME: air-assisted dispersive liquid-liquid microextraction; Aliquat 336: methyl trioctyl ammonium chloride; AOH⁺: acridine orange; AuNPs: gold nanoparticles; C₂H₆O: ethanol; [C₄MIM]PF₆: 1-butyl-3-methylimidazolium hexafluorophosphate; [C₆MIM]PF₆: 1-hexyl-3-methylimidazolium tetrafluoroborate; ChCl: choline chloride; CHCl₃: chloroform; CM-HFLPME: carrier-mediated hollow fiber liquid phase microextraction; CPB: cetylpyridinium bromide; CPC: cetylpyridinium chloride; CPE: cloud point extraction; CPT: cloud point temperature; CRM: certified reference material; CRM No. 12-2-02: certified reference material for essential and toxic elements in green algae; CRM IAEA-336: certified reference material for trace and minor elements in lichen; CTAB: cationic surfactants such as cetrimonium bromide; CV-AAS: cold vapor atomic absorption spectrometry; CYPHOS[®] IL 101: tetradecyl(trihexyl)phosphonium chloride; DA: decanoic acid; D-CPE: displacement cloud point extraction; d-CPE: dual cloud point extraction; DES: deep eutectic solvent; DES-DLLME : deep eutectic solvent-assisted dispersive liquid-liquid microextraction; DES-MNF: deep eutectic solvent-based magnetic nanofluid-linked; DI-SDME: direct immersion single drop microextraction; DLLME: dispersive liquid-liquid microextraction; Dpkbh: di-2-pyridylketone benzoylhydrazone; **DPX: disposable pipette extraction**; DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy; EDXRF: energy dispersive X-ray fluorescence spectrometry; **EME: electromembrane extraction**; [EMIM]Tf₂N: 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethyl sulfonyl)imide); ETAAS: electrothermal atomic absorption spectrometry; FAAS: flame atomic absorption spectrometry; FIA: flow injection analysis; FIA-CPE: flow-based cloud point extraction; **G-EME: gel electromembrane microextraction**; GAC: green analytical chemistry; GAPI: Green Analytical Procedure Index; GFAAS: graphite furnace atomic absorption spectrometry; GHS: Globally Harmonized

System; GO-Gly: glycine modified graphene oxide; GO-silica: graphene oxide-silica; HBA: hydrogen acceptor compound; HBD: hydrogen donor compound; HDES: hydrophobic deep eutectic solvents; HF-LPME: hollow fiber liquid phase microextraction; [HMIM]PF₆: (1-hexyl-3-methylimidazolium hexafluorophosphate); HPLC-ICP-MS: high performance liquid chromatography inductively coupled plasma mass spectrometry; H₂Se: hydrogen selenide; HS-SDME: drop microextraction in headspace analysis; HTAR: (6-hexyl-4-(2-thiazolylazo)-resorcinol); ICP-MS: inductively coupled plasma mass spectrometry; ICP OES: inductively coupled plasma atomic emission spectroscopy; IL: ionic liquid; IL-DLLME: ionic liquid-assisted dispersive liquid-liquid microextraction; IL-MgGO: ionic liquid graphene oxide nanoparticles; KClO₄: potassium perchlorate; KH₂PO₄: potassium dihydrogen phosphate; KBH₄: potassium borohydride; LDS-DLLME: low density solvent dispersive liquid-liquid microextraction; LLE: liquid-liquid extraction; LLME: liquid-liquid microextraction; LOC: lab-on-chip; LOD: limit of detection; LOV: lab-on-valve; LPME: liquid-phase microextraction; MAE: microwave-assisted extraction; MCDA: multi-criteria decision analysis; MeHg: methylmercury; MGO@SiO₂-APTES-IL: ionic liquid-coated amino silanized magnetic graphene oxide; MILLE: membrane-based inverted liquid-liquid extraction; MIP-OES: microwave induced plasma-optical emission spectrometry; MNPs: magnetic nanoparticles; MS-FAAS: microsample injection system coupled with flame atomic absorption spectrometry; MSPE: magnetic solid phase extraction; MSPME: magnetic-based dispersive micro-solid phase extraction; MW-CPE: microwave assisted cloud point extraction; MW-SWE: microwave-assisted subcritical water extraction; NaDDTC: sodium diethyldithiocarbamate; NADES: natural deep eutectic solvent; NEMI: National Environmental Methods Index; NMIJ-7402a: certified reference material for cold fish tissue; PAN: 1-(2-pyridylazo)-2-naphthol; PAR: 4-(2-pyridylazo)resorcinol; Ph: phenol; PDMS: polydimethylsiloxane; PHWE: pressurized hot water extraction; PLE: pressurized liquid extraction; RS-CPE: rapidly synergistic cloud point extraction; SBME: stir bar microextraction; SBSE: stir bar sorptive microextraction; SCI-E: expanded science citation index; SDS: sodium dodecyl sulfate; SHS: switchable-hydrophilicity solvents; SIA: sequential injection analysis; SPE: solid phase extraction; SPLE: selective pressurized liquid extraction; SPME: solid phase micro-extraction; SRM 1084a: standard reference material for lubricating oil; ST-DLLME: solvent-terminated dispersive liquid-liquid microextraction; SUPRAS: supramolecular solvents; SWE: subcritical water extraction; TAN: 1-(2-thiazoylazo)-2-naphthol; TBAC: tetrabutylammonium chloride; TBACl:

tetrabutylammonium chloride; THF: tetrahydrofuran; TiO₂-PPHF: titania immobilized polypropylene hollow fiber; TOACl: trioctyl ammonium chloride; TOMAS: methyltrioctylammonium thiosalicylate; TORT-2: certified reference material for lobster hepatopancreas; Triton X-100: polyoxyethylene-9.5-octylphenoxy ether; Triton X-114: polyoxyethylene-7.5-octylphenoxy ether; Tween 60: polyoxyethylene sorbitan monostearate; Tween 80: polyethylene glycol sorbitan; UA-CPE: ultrasound-assisted cloud point extraction; UA-DLLME: ultrasound-assisted dispersive liquid-liquid microextraction; UAE: ultrasound-assisted extraction; UA-ELPME: ultrasound-assisted deep eutectic solvent-based emulsification liquid phase microextraction; UA-DES-ELPME: ultrasound assisted-deep eutectic solvent based emulsification liquid phase microextractyion; UALPME-DES: ultrasonic assisted dispersive liquid-liquid microextraction based on deep eutectic solvent; US-DLLME: ultrasound-assisted dispersive liquid-liquid microextraction; USAE: Ultrasound-assisted emulsification; USA-TILDLM: ultrasound-assisted temperature-controlled ionic liquid dispersive liquid-liquid microextraction; UV-Vis: ultraviolet-visible spectroscopy; VA-DLLME: vortex-assisted dispersive liquid-liquid microextraction; VA-LLME: vortex-assisted supramolecular solvent liquid-liquid microextraction; VA-ELL_μE: vortex-assisted emulsification liquid-liquid microextraction; WAC: White Analytical Chemistry; WoS: Web of Science[®].

1. Introduction

Increasing awareness of environmental responsibilities has inevitably posed many challenges for chemists involved in designing products and processes that should minimize environmental impacts [1]. Efforts have been made towards the development of new approaches that are effective, efficient, and more environmentally benign. Green chemistry has set out to reduce or eliminate damage to health and the environment, by reducing the use and release of dangerous substances. This has resulted in a new and more successful greener chemistry in practice, as well as innovative research and applications [2,3].

It is evident that analytical procedures play a key role in environmental monitoring [3,4]. However, an unfortunate irony is that analytical methods often contribute to causing environmental impacts, due to overuse of chemicals and generation of waste. Many analytical procedures require sample preparation, calibration solutions, and equipment cleaning, where the chemicals employed may have greater toxicity than the sample analyzed [5,6].

The principles of green chemistry target analytical methods, many of which present problems related to the sample preparation step. Since the extraction, digestion, separation, or chemical modification of samples often require the use of large amounts of solvents, sample preparation is a central concern of green analytical chemistry (GAC) [7,8]. Therefore, reduction (or elimination) of the use of traditional hazardous solvents, together with their substitution by less toxic alternatives in analytical procedures, are topics of particular research interest in GAC [3,9].

Since the introduction of the green chemistry concept in 1998 by Anastas [10], many scientific studies have been reported concerning greener sample preparation in analytical chemistry. These publications related to sample preparation were identified using the Expanded Science Citation Index (SCI-E) in the Clarivate Analytics Web of Science® (WoS) database. Using the combination of “green* chemistry*” and “sample* preparation*” keywords, a total of 134 academic articles were found addressing this topic in the last seven years, from 2015 to 2022 (searched on 26th February 2022). The number of records per year and the five main WoS categories related to these publications are shown in Figure 1.

[FIGURE 1]

The numbers of studies addressing green sample preparation procedures have increased considerably over the last **seven years** (see Figure 1). Most of these publications were related to WoS category *Analytical chemistry*, followed by *Biochemical research methods*, *Multidisciplinary chemistry*, *Food science technology*, and *Spectroscopy*. The numbers of publications reached two peaks, in **2016 and 2022**. The main research topics in these years were microextraction techniques, greener chromatographic methods, and extraction/digestion using environmentally friendly solvents, with subsequent spectroscopic analysis.

All the papers retrieved were evaluated using a bibliometric map for co-occurrence analysis of all author keywords. This analysis was carried out using VOSviewer software (version 1.6.14; www.vosviewer.com) to visualize and understand how green sample preparation research topics from different authors were organized around this central theme. For this purpose, bibliometric mapping is a valuable research tool [11], since it allows the visualization of indicators in the form of networks [12]. The statistical analysis revealed **1068 author keywords** from the total papers retrieved. Figure 2 shows the top 60 author keywords, which presented the highest co-occurrence among the articles. This bibliometric map shows a set of links connecting a list of terms, where the size of the node is proportional to the number of citations, while the colors indicate to which cluster of topics the keywords belong. The most frequent topics were “extraction/digestion techniques (e.g., **ultrasound-assisted extraction (UAE), microwave-assisted digestion, and digestion**) prior to elemental analysis” (**red cluster**); “extraction and microextraction approaches (e.g., **liquid-liquid microextraction, solid-phase microextraction, bar sorptive extraction, cloud point extraction and single-drop microextraction**) towards sustainable chromatography techniques” (**yellow, purple and green clusters**); “synthesis and use of greener solvents (e.g., **ionic liquids, deep eutectic solvents, natural deep eutectic solvent**) (purple and green clusters).

[FIGURE 2]

The growth of analytical methods aiming at green chemistry during the last couple of decades has demonstrated how fundamental scientific approaches can be developed that combine environmental, health and safety, and economic targets. In addition, some studies that use naturally green or possibly green analytical methods do not convey the concept of “green”.

The development of sample preparation methods that enable reductions in the use of reagents and solvents, or their replacement, minimal sample handling, the use of more efficient

energy sources, and lower risks to the operator and the environment, are all issues addressed by GAC [10].

This part of the review addresses the state-of-art of methods for inorganic elemental analysis that comply with green analytical principles, in order to improve the literature on this subject. The main focus concerns the application of alternative solvents, as well as miniaturized and automated analytical strategies, highlighting the innovations and analytical details that green analytical methods have contributed to the further development of analytical chemistry. The advantages and limitations of these strategies applied in GAC are also considered, and the different green metrics were mentioned. It should be highlighted that relatively few studies were found in the literature concerning green techniques applied for elemental analysis.

2. Solvents for sample preparation in inorganic analysis

Solvents play fundamental roles in sample preparation steps [13]. Conventional solvents with low molecular weight and high volatility have potential for greater exposures, increasing risk when they also have toxic properties [14]. For these reasons, minimization and substitution of solvent use has been an active area in green chemistry [3,13-15]. Solvent extraction is one of the main unit operations in the sample preparation step [15]. The objective of an extraction is to isolate the analyte of interest from the matrix and preconcentrate it [14]. The extraction methods for solid samples are based on the mechanisms of desorption, solvation, and diffusion of the analyte from the matrix, enabling its transfer to the liquid phase [16]. In the case of liquid samples with complex matrices (saline water, body fluids, and juices, for example), transfer to a new liquid phase is necessary, using an immiscible extractor solvent suitable for the extraction [14].

One of the main issues relates to the definition of a green solvent, which often only considers its origin, disregarding the chemistry necessary for its synthesis [17]. It is very difficult for any solvent to comply with all the green chemistry requirements, such as prevention of wastes, energy efficiency, renewable feedstock, low toxicity, and biodegradability [18]. Many solvents were introduced based on the premise of being green because they originated from natural materials, but this is not a correct assumption [18]. There are factors such as the concentration and volume of a solvent that must be considered in determining whether an analytical procedure is green [17]. In addition, the term “green solvent” is relative. Green

chemistry was defined by Anastas and Warner [10] as processes that reduce harm, rather than as processes that cause no harm. Therefore, a new solvent can be termed green when it is “greener”, compared to the other solvent that should be replaced, and when clear evidence can be given for this assumption [19]. Over the course of the last couple of decades, the growth of analytical methods aiming at green chemistry has demonstrated how fundamental scientific approaches can be developed that combine environmental, health and safety, and economic targets.

Due to the fundamental role of solvents in the sample preparation stage, together with the interest in studying and developing new green solvents, this overview is focused on strategies based on new extraction media that can replace conventional solvents, employing environmentally friendly reagents in analytical methodologies targeting inorganic analysis.

2.1. Ionic liquids (ILs)

Ionic liquids (ILs) have been widely studied as alternatives to replace organic solvents [20,21]. These substances are salts at room temperature, with melting points below 100 °C, formed from the combination of an organic cation with an organic or inorganic anion (Figure 3) [20]. They have characteristics such as negligible volatility, high thermal stability, and high solubilization power [20-22].

[FIGURE 3]

The possibility of adjusting the physicochemical properties of ILs by means of different combinations of cations and anions has aroused great interest, especially in relation to their applications as extraction solvents in various techniques [20-22]. However, studies have shown that despite their non-volatility (reduced air pollution), non-flammability (process safety), and excellent stability (recycling and reuse potential), some classes of ionic liquids are toxic and non-biodegradable [22]. In addition, the synthesis of an ionic liquid is expensive and requires the use of substantial amounts of reagents, resulting in the generation of large quantities of byproducts in the form of waste [23].

The toxicity of ILs is much more affected by the structure of the cation than the anion [16,24]. Although studies have shown the efficiency of fluoride-based ILs for liquid-phase microextraction and extraction [25,26], ILs containing fluorine present greater threats to the environment, compared to those that are fluorine-free [22,24]. In addition, the presence of long

alkyl groups in imidazolium-based ILs increases toxicity, because it intensifies the lipophilic character of ILs, resulting in higher affinity for viable cells [20,27].

The biodegradation of ILs is strongly influenced by factors such as the length of the alkyl side chain, the core ring structure, and the functional groups present [22,28-30]. The influence of the anion structure is less pronounced [24]. However, there is a scarcity of studies examining the toxicity of metabolic products after degradation of ILs. Metabolization may not always result in less toxic products. Research is needed to investigate the types of microorganisms capable of degrading ILs [24].

The compound tetradecyl(trihexyl)phosphonium chloride (CYPHOS[®] IL 101) was used in dispersive liquid-liquid microextraction (DLLME) of Co present in water, parenteral samples, and ophthalmic solutions [31]. ILs based on the phosphonium ion were also used for liquid-phase microextraction of Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Pt, Sn, and Zn, applied to industrial and domestic wastewater samples [32]. In comparison of a wide range of ILs with different cations, anions, and alkyl chain lengths, phosphonium-based ILs with long alkyl chains were found to be least toxic towards four microorganisms [33].

Rapid and simple ultrasound-assisted dispersive liquid-liquid microextraction (UA-DLLME) was used for extraction of tellurium from water samples, employing the IL methyl trioctyl ammonium chloride (Aliquat 336) [34]. Aliquat 336 was nontoxic in a mixed culture of facultatively anaerobic, acid-producing bacteria [35]. In addition, Aliquat 336 showed no growth inhibition of the bacterium *Pseudomonas putida*, at least with respect to molecular toxicity [36].

The IL 1-octyl-3-methylimidazolium salicylate was found to enable selective extraction of Cr(III) using aqueous biphasic systems applied to water (tap and underground) and urine (non-diabetic human) samples [37]. The UA-DLLME method was employed for extraction of mercury in water samples (tap, river, lake, and seawater). The IL methyltrioctylammonium thiosalicylate (TOMAS) was used as a dispersive and extraction solvent [38]. Vraneš *et al.* [39] observed that oxygenation of the alkyl substituent could reduce the toxicity of imidazolium-based ionic liquids towards the aquatic microorganism *Artemia salina* and a human non-tumor cell line. The introduction of the oxygen in the alkyl substituent increased the polarity of the ion, while the lipophilicity decreased. This weakened the interactions between cell membrane lipids and the ionic liquid, which significantly reduced the toxicity [39].

It is important to note that ILs are not intrinsically greener than traditional solvents, given that their production and disposal are usually more resource-intensive, compared to traditional solvents [3]. However, if the 3R's (Reduce, Reuse, and Recycle) strategy is applied [40], ILs can be more environmentally friendly. Majidi and Shemirani [41] used the IL 1-hexyl-3-methylimidazolium tetrafluoroborate ($[C_6MIM]PF_6$), at low acidity, for the extraction of Au^{3+} by ultrasound-assisted temperature-controlled ionic liquid dispersive liquid-liquid microextraction (USA-TILDLM), during at least 10 cycles of the extraction-stripping process.

Studies of the environmental fate and toxicity of ILs have shown that their toxicities vary considerably across organisms and trophic levels [24]. The future application of ILs in sample preparation requires them to be less toxic and more biodegradable. Furthermore, it is important that future developments should incorporate the recycling and reutilization of IL wastes [42].

2.2. Deep eutectic solvents (DES) and subclasses

Deep eutectic solvents (DES) subsequently emerged as a viable alternative to ILs. These solvents are formed using combinations of organic compounds that result in a eutectic mixture with a melting point below those of the individual precursors [43]. When the DES precursors are amino acids, organic acids, sugars, or choline derivatives originating from natural sources, the compounds are called natural deep eutectic solvents (NADES) [44]. Both DES and NADES are formed by hydrogen bonds between an acceptor compound (HBA) and a donor compound (HBD), in conjunction with other intermolecular interactions, such as van der Waals and electrostatic forces [45].

These solvents have physicochemical properties (such as density and viscosity) that are very close to those of common ILs. In addition, they consist of inexpensive compounds that make them favorable candidates from the economic perspective [46]. It is possible to adjust their properties (including viscosity and density) by varying the proportions of the precursors used, enabling various approaches for their use in extraction methods [47].

Despite their sustainability advantages when used as reaction media, in order to consider DES as environmentally friendly solvents, it is first necessary to evaluate their potential toxicity and biodegradability [48]. There is still controversy about their potential toxicity [49,50]. Several reports support the notion that DES are nontoxic, eco-friendly, biodegradable, and benign solvents, while others demonstrate the opposite [51,52]. It has generally been assumed that they are not toxic and are environmentally friendly, because most of the DES components are naturally occurring and biodegradable [51,53].

Choline chloride-based DES and NADES are among those most studied and applied in extraction techniques [47]. A NADES based on choline chloride and oxalic acid (1:2) was used for determination of As, Cr, Mo, Sb, Se, and V in soil samples by inductively coupled plasma optical emission spectrometry (ICP OES), in which the procedure for optimization of factors affecting the extraction procedure employed a 2³ full factorial design [54]. A NADES formed by the combination of choline chloride and lactic acid (1:1) was used by Yilmaz and Soylak [55], in an ultrasonic bath, for the extraction of Fe from sheep, bovine, and chicken liver samples, prior to determination by flame atomic absorption spectrometry (FAAS), achieving recoveries higher than 95 %.

The number of combinations is practically unlimited, while the properties of DES and NADES are determined by their composition [56,57]. The extraction potential of a NADES is related to its ability to form hydrogen bonds with analytes. Hence, the optimization of parameters such as heating time and temperature, proportions of components, and volume of water, as well as use of the solvent under green extraction conditions, are essential for obtaining satisfactory results [56]. The results of some studies using DES and NADES as extractor solvents for elemental analysis are shown in Table 1. Additionally, when the NADES contains ingredients such as sugars, amines, and amino acids, it is essential to avoid the use of high temperatures [57].

[TABLE 1]

Due to the intense electrostatic interactions of DES and NADES, these solvents have high viscosity and density, which can decrease the efficiency of mass transport, hence affecting the extraction efficiency [66]. Therefore, strategies such as adding water to the NADES composition have been used to decrease their viscosity and density, consequently improving their extraction efficiency. NADES obtained with the same precursors (including water), but in

different proportions, were used for the extraction of As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, P, and Zn from plant samples [67]. The extraction of methylmercury (MeHg) and total mercury from fish samples was performed with a NADES (betaine/sorbitol, 1:3) containing 10 % (v v⁻¹) water [68].

Mixture design was performed for the synthesis of three different NADES using citric acid, malic acid, xylitol, and water, for extraction of As, Cd, Hg, Pb, Se, and V from biological tissue and plant material samples [69]. This strategy enables the study of different combinations of precursors for the preparation of NADES, with faster optimization and lower consumption of reagents.

NADES cannot be considered as universal solvents; in fact, they are highly selective solvents [57]. Therefore, the use of DES and NADES as speciation solvents is being studied. The speciation of selenium species (Se(IV) and Se(VI)) found in water and food samples was performed with DES synthesized using the combinations choline chloride/phenol (ChCl/Ph), trioctyl ammonium chloride/decanoic acid (TOACl/DA), and tetrabutylammonium chloride/decanoic acid (TBACl/DA) [70]. ChCl-based DES were used for speciation of Cr(III) and Cr(VI) in water samples [71]. The speciation of MeHg and total mercury in fish samples was performed with NADES synthesized using the combination betaine/sorbitol [68].

Most of the synthesized DES are miscible with aqueous media and hydrophilic organic solvents, restricting their applications in water or with lipophilic samples. Therefore, hydrophobic deep eutectic solvents (HDES) emerged as a new option to increase the range of applications [72]. The high thermal stability, negligible vapor pressure, wide liquid range, and incombustibility of HDES are in accordance with green chemistry [72,73].

HDES were synthesized using menthol, sorbitol, and mandelic acid, for use in the extraction of Cd, Cu, Pb, and Zn from milk and juice samples. The synthesis was fast (4 minutes). The ligand-less air-assisted liquid-liquid microextraction procedure, based on solidification of a ternary deep eutectic solvent, was simple, rapid, efficient, and green [74]. HDES based on menthol and different biodegradable terpenes and fatty acids were synthesized for use as solvents in the extraction and separation of Cu(II) from other transition metals present in mildly acidic solutions [75].

Although this class of solvents is relatively new (especially HDES), the study of their reuse and recycling has been gaining ground. This is important for complying with the metrics of green solvents and sustainable development [72]. The few studies reporting the recycling or reuse of these solvents have concerned their use in the extraction of organic analytes.

DES and their subclasses are attractive as promising environmentally friendly materials, with excellent extraction properties, easy preparation, and low cost. Their high viscosity can be a significant disadvantage, although there are cases where this problem has been overcome.

2.3. Water

Water is the safest and most environmentally friendly solvent that can be considered for use in different procedures. Besides being nontoxic, non-flammable, inexpensive, and widely available, it is capable of hydrogen bonding, dissolving polar compounds and solvating ionic compounds under environmental conditions, while less polar compounds can be dissolved at higher temperatures. Another important characteristic is that water maintains the liquid state in a wide temperature range (0 to 100 °C) at atmospheric pressure [76].

Water can be used alone or mixed with another solvent to improve the solvation of less polar analytes. However, the waste generated needs to be treated to ensure avoidance of contamination of water resources. The dielectric constant, polarizability, and degree of hydrogen bonding of water decrease with increase of the temperature, together with decreases of viscosity and surface tension. These changes result in alteration of the solvent properties of the water, enabling their adjustment by only changing the temperature [76].

Pressurized hot water extraction (PHWE), also called subcritical water extraction (SWE), is one of the methods of using water as an extractor solvent [77]. PHWE employs pressurized water under controlled conditions of elevated temperature and pressure [78]. When the water is in the liquid phase, in the temperature range from 100 °C (the boiling point of water) to 374 °C (the critical point of water), the term “pressurized hot water” is used [79]. Other common terms such as “superheated water”, “near-critical water”, “subcritical water”, “high temperature extraction” and “extraction using hot compressed water”

have also been used [78,79]. During the extraction, moderate pressures are needed to conserve a condensed phase of water, such as 15 bar at 200 °C or 85 bar at 300 °C [78,80].

PHWE has been used for the extraction of Cr, Mn, Ni, Cd, and V from mineral samples. The use of superheated water increased the solubility of the metals, with even the organically bound metals in sediments being more amenable to extraction. However, acid digestion showed better results for vanadium [81].

Microwave-assisted subcritical water extraction (MW-SWE) was used for the analysis of metals in certified reference materials [82]. Approximately 0.1 g of the certified reference materials IAEA-336 (Trace and Minor Elements in Lichen) and CRM No. 12-2-02 (Essential and Toxic Elements in Green Algae) were added to a microwave digestion vessel, together with 5 mL of water and 100 µL of HNO₃. The extraction was performed for 10 min at 280 °C and 90 bar. After the extraction with acidified subcritical water, the elements present in the liquid phase (Ba, Ca, Cu, Fe, Mg, Mn, Na, Pb, Sr, and Zn) were determined by microwave-induced plasma optical emission spectrometry (MIP-OES). The measured contents of the elements in the reference materials were in agreement with the certified values [82].

Pressurized liquid extraction (PLE) uses solvent at high pressure and/or high temperature, without reaching the critical point. One of the main difficulties in the analysis of lubricating oil is due to its high viscosity and complex matrix. To overcome this, Carballo-Paradelo *et al.* [83] used PLE with acidified water to extract Ag, Al, Cu, Mg, Pb, Sn and Ti from samples of lubricating oils. Acceptable recoveries (80-118 %) were generally achieved when a lubricating oil standard reference material (SRM 1084a) was analyzed. However, low recoveries (< 20 %) were obtained for Ag [83].

Selective pressurized liquid extraction (SPLE) was used for the extraction of arsenic from seafood samples [84]. This procedure is commonly considered environmentally friendly, due to the mild temperature and pH conditions, as well as the absence of polluting or toxic reagents [84]. Selenium was extracted from fish, algae, and seafood samples by PHWE using pure water at a temperature of 180-220 °C and high pressure. Application of the method using the certified reference materials (CRMs) NMIJ-7402a (Cod Fish Tissue) and TORT-2 (Lobster Hepatopancreas) resulted in satisfactory recoveries [85].

PHWE was used for the extraction of arsenic in hair samples with water acidified with acetic acid, at a temperature of 100 °C and pressure of 1500 psi, during 5 min [86]. Acetic acid was used as a modifier to improve the solubility of the analyte in water and/or to increase interactions of the water with the analyte.

PHWE and other extraction methods with water as solvent are generally used for extracting organic analytes. There are few studies reporting the use of water as an extraction solvent for elemental analysis [76,79,80].

2.4. Alternative solvents

The switchable-hydrophilicity solvents (SHS) are tertiary amines with hydrophobic character when in contact with air and hydrophilic character when in contact with a CO₂ atmosphere [87,88]. They are less flammable and volatile than classical organic solvents, and their synthesis is simpler and cheaper, compared to ILs [89]. Furthermore, the CO₂ is benign and can be easily removed without the need for distillation [89].

Zhang *et al.* [90] used triethylamine as SHS in liquid-liquid microextraction (LLME) of Pb and Cd from water, tea, and hair samples. The extraction time was 3 minutes, using 1 mL of extracting solvent. Triethylamine was used as SHS in LLME for the extraction of Cd, Ni, Pb, and Co from water, urine, and tea samples, in 6 minutes, using 450 µL of extracting solvent [91]. SHS were also used for elemental extraction from different matrices such as water, hair, sediment, soil, and food [87,89].

Medium-chain fatty acids (e.g., hexanoic, octanoic, and decanoic acids) have also been considered as SHS [87]. However, the formation of their hydrophilic form requires the addition of sodium carbonate, followed by the use of sulfuric acid to transform them into their hydrophobic form [87,89]. Therefore, amine-based SHS are still the best alternative as extraction solvents, with a large number of suitable compounds available [87,89].

The supramolecular solvents (SUPRAS) are a new class of alternative solvents for the extraction of a wide variety of analytes in different sample matrices, and have been extensively used in liquid-phase microextraction (LPME) [92]. The preparation of SUPRAS involves two steps (molecular and nano) [92,93]. The first step is self-aggregation of amphiphiles, while in the second step there is the formation of nanostructured aggregates [93]. SUPRAS are

considered as green solvents due to their physical properties including non-volatility and non-flammability, which enables safer management [94].

A SUPRAS prepared from a solution of reverse micelles of decanoic acid in tetrahydrofuran was used in selective ultrasound-assisted microextraction of arsenic from water samples [95]. In other work, the components 1-decanol and tetrahydrofuran were used to prepare a SUPRAS used in a vortex-assisted supramolecular solvent liquid-liquid microextraction (VA-LLME) method for the determination of mercury in different environmental and biological samples [96].

There are still few studies reported in the literature regarding the use of SHS and SUPRAS as solvents in elemental analysis. Therefore, the use of alternative solvents for this purpose needs to be further explored.

3. Extraction approaches for inorganic elements

Miniaturized and automated methods are important features of a green analytical procedure, in order to reduce both the use of reagents and the generation of chemical residues [97]. These techniques can accelerate the extraction process and improve the separation of the analyte, using smaller amounts of samples and solvents [98]. Current trends are the development of microextraction techniques with minimal amounts of organic solvents and fewer steps during sample preparation. In addition, there is a focus on the development of these extraction techniques using alternative solvents that present less risk to health and the environment.

The conventional liquid-liquid extraction (LLE) and solid-phase extraction (SPE) techniques used for sample preparation are characterized by long procedures and the use of large masses or volumes of samples and organic solvents, in addition to difficulties in automation [99]. Miniaturization techniques using these conventional methods as a basis have been developed with the aim of improving the sustainability of chemical analyses, as well as to enhance the effectiveness and precision of the methods [100].

Microextraction and other techniques considered to comply with the principles of GAC have been applied in the preparation of samples for the analysis of inorganic elements [101]. Recent studies have described the miniaturization of processes, with low consumption of

organic reagents, use of environmentally friendly extraction solvents such as ILs and DES, and analysis by multi-element detection techniques such as ICP OES and inductively coupled plasma mass spectrometry (ICP-MS) [101,102].

The main green analytical chemistry techniques employed in the preparation of samples for the extraction or preconcentration of inorganic analytes are LPME, dispersive liquid-liquid microextraction (DLLME), solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), stir bar microextraction (SBME), and cloud point extraction (CPE). Table 2 lists studies reported in the literature over the last 6 years, where these techniques have been applied to determine inorganic elements.

[TABLE 2]

The liquid phase-based and solid phase-based microextraction techniques have been shown to be promising for elemental analysis of complex environmental matrices. In combination with other sample pretreatments, they are excellent options in the elemental analysis of solid environmental and biological materials [117].

3.1. Liquid phase microextraction

LLE is a technique based on sequential treatment of the aqueous sample with portions of a solvent or with the use of various solvents of increasing polarity, promoting transfer of the analyte phase to a water-immiscible solvent [118]. This is one of the oldest extraction techniques, with several disadvantages such as formation of emulsions, the use of large volumes of samples and toxic organic solvents, time-consuming procedures, and the need for a skilled analyst [118].

To overcome such disadvantages, LPME strategies were developed that require only a few microliters (μL) of a water-immiscible solvent, acting as an acceptor phase, in an aqueous sample containing the analytes (donor phase) [99]. The single drop microextraction (SDME) method and its derivations emerged as initial alternatives to the LLE technique [119]. Direct immersion single drop microextraction (DI-SDME) is performed by suspending a drop of extraction solvent (acceptor phase) at the tip of a micro-syringe needle, which is directly immersed in the donor phase (sample) [119]. After a certain contact time, the drop is retracted into the micro-syringe and then immediately injected for analysis [119]. The transition of the

analyte from the aqueous sample to the single drop system is generally limited by the slow rate of diffusion, requiring control of the temperature and the solvent viscosity, and the samples are usually agitated by magnetic stirring [120]. The mechanical vibration or movement of the syringe plunger increases the contact area between the phases, consequently increasing the diffusion rate [120].

The selection of the solvent to be used in SDME is important, since it must have low (or no) solubility in water, preventing dissolution in the aqueous phase, and be of low volatility, avoiding loss of the organic phase during the extraction procedure and ensuring satisfactory solubilization of the analyte [121]. Nunes *et al.* [122] used DI-SDME to extract Mn from samples of tonic drinks and seafood, employing 10 μL of 1-(2-pyridylazo)-2-naphthol (PAN) chelating agent and 5 μL of the IL 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_4\text{MIM}]\text{PF}_6$) as extraction solvent. A micro-drop formed using a micro-syringe was immersed in the sample, maintaining the system under magnetic stirring for 7 min, after which the micro-drop was retracted and directly inserted for analysis using graphite furnace atomic absorption spectroscopy (GFAAS). The method was efficient, with recoveries from 92 to 112 % and limit of detection (LOD) of 3.9 ng L^{-1} .

Sen *et al.* [123] optimized a DI-SDME procedure for preconcentration of Se present in water samples, with evaluation of the organic solvent according to its density, as well as the influence of pH on the complexation process using N-hydroxy-N-phenyl-N'-(o-tolyl) benzimidamide as a complexing agent. It was found that acid conditions were more favorable for the reaction. Evaluation was also made of the extraction time and the influence of the volume of the micro-drop suspended on the tip of the needle, since its surface area affected transfer of the analyte from the donor phase to the extractor solvent (acceptor phase) [121]. The organic solvent selected for the extraction was 1,2-dichloroethane, based on its high efficiency. The other conditions employed were pH 3.0, 5 μL drop volume (larger volumes were not stable at the tip of the needle), and extraction time of 15 min. Subsequently, the drop was removed from the micro-syringe and analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS).

In the early 2000s, the use of SDME was extended to headspace analysis (HS-SDME) of volatile analytes, employing a microliter droplet of solvent suspended in the headspace above the sample. This technique was considered to provide greater stability and lower contamination,

compared to DI-SDME [123]. Magnetic nanoparticles are commonly used in conjunction with the HS-SDME method for the determination of trace elements, combining in a single phase the extractor dispersion procedure and magnetic separation [124].

Bagheri and Saraji [125] used HS-SDME to determine Se in an animal supplement, employing gold nanoparticles (AuNPs) as an adsorption agent under the surface of the single drop. Potassium borohydride (KBH_4) at 0.5 % w v⁻¹ was used as a reducing agent, acidified with 3 mol L⁻¹ HCl, resulting in the reduction of Se(IV) to hydrogen selenide (H_2Se). This highly volatile species was rapidly transferred from the sample to the headspace and then to the micro-drop, where Se⁰ was oxidized and adsorbed by the AuNPs, with a total extraction time of only 3 min. After the adsorption of Se⁰, citrate ions at the surfaces of the AuNPs were released to the solution, causing aggregation of the nanoparticles. This caused the color of the single drop to change from red to blue, enabling analysis by digital imaging, which provided the analytical signal for determination of the concentration of the analyte in the sample. A similar procedure was performed for Te speciation in natural water samples, using sodium borohydride (NaBH_4) as a reducing agent, which proved to be efficient for generating volatile species only from Te(IV). A 4 μL microdrop containing Au(III) was exposed for 3 min to retain the $\text{H}_2\text{Te}_{(\text{g})}$ species, which was retracted into the syringe and immediately analyzed by GFAAS, presenting a detection limit of 0.13 $\mu\text{g L}^{-1}$ and recoveries between 95 and 116 % for Te(IV) [126].

Although SDME drastically reduces the consumption of solvents, the suspended drop formed has low stability and may be lost in the sample during the extraction [120]. To circumvent this stability problem, the hollow fiber liquid-phase microextraction (HF-LPME) technique was developed, where the extraction phase is added inside a porous hydrophobic hollow fiber [120]. The method is based on the extraction of an analyte present in an aqueous sample to a thin layer of organic solvent immobilized in the pores of a hollow and porous fiber [127]. From there, the analyte is transferred to an acceptor solution (aqueous or organic) present within the lumen of the hollow fiber, which is directly analyzed after the extraction procedure [127].

This extraction can occur in two different modes: two-phase or three-phase. In the two-phase extraction mode, the same organic solvent, or different solvents that are miscible, can be used in the acceptor phase and be added to the hollow fiber pores, with octanol and toluene

being the most widely used organic solvents [120]. The three-phase system involves the use of an organic solvent or aqueous solution that is immiscible with the organic solvent immobilized in the pores, typically employing octanol and dihexyl ether, as well as hexane, octane, nonane, dichloromethane, butyl acetate, 2-octanone, and diamyl ether [120].

As a further contribution to GAC, Liu *et al.* [128] developed a three-phase HF-LPME procedure employing a 5.3 cm hollow fiber soaked in the ionic liquid [HMIM]PF₆ (1-hexyl-3-methylimidazolium hexafluorophosphate), for the extraction of Pb from water samples and tea drinks. The optimized extraction procedure was agitation at 450 rpm, at room temperature (25 °C), for a total period of 20 min. The acceptor phase was retained and immediately injected for analysis by GFAAS. The method presented high analytical efficiency, with a detection limit of 0.004 ng mL⁻¹ and recoveries in the range 94-105 %.

Alavi *et al.* [129] used an acceptor phase consisting of a mixture of the DES Chcl-urea and KClO₄ (0.06 g mL⁻¹) in an innovative carrier-mediated method (CM-HFLPME) for the determination of Pb in blood samples. The procedure was performed by connecting medical needles to the ends of the filled 8 cm hollow fiber, which was immediately inserted into the sample solution. After 30 min of extraction, the hollow fiber and needles were removed and the extract was transferred to a micro-vial by air pressure, using a medical syringe. Finally, the extract was diluted with ultrapure water (1:1) and injected for analysis by ETAAS. The analytical method presented a detection limit of 0.1 ng mL⁻¹ and recoveries between 88 and 105 %. Due to the high viscosity of the DES, the dilution provided several repeated injections for each extract, enabling greater accuracy of the analytical responses.

In further development of new LPME methods, the DLLME technique was introduced in 2006 [130]. This procedure is based on a ternary system in which the extraction and dispersing solvents are injected rapidly into the aqueous sample in a conical tube, generating high turbulence among the components. Centrifugation then enables removal of the solvent at the bottom of the tube, which can be directly injected for analysis [130]. Figure 4 shows schematic representations of the SDME, HF-LPME, and DLLME methods.

In order to obtain more accurate and reliable analytical results, derivative DLLME methods have been presented, classified into two distinct types [131]. The first type consists of procedures that employ mixtures of extracting and dispersing solvents. These methods include ultrasound-assisted DLLME (US-DLLME), vortex-assisted DLLME (VA-DLME), and air-

assisted DLLME (AA-DLLME), which have been used for the determination of Cd, Cu, Co, Ni, and Pb in food, environmental, and vegetable samples [132-136]. The second type includes procedures using an extracting solvent in the absence of a dispersing solvent. Examples are low density solvent DLLME (LDS-DLLME, usually employing chloroform, tetrachloroethylene, hexane, or cyclohexane), ionic liquid-assisted DLLME (IL-DLLME), deep eutectic solvent-assisted DLLME (DES-DLLME), and solvent-terminated DLLME (ST-DLLME), which have been used for the determination of Cr, Cu, Pb, and Se in environmental samples such as water and sewage [137-139].

[FIGURE 4]

The membrane-based microextraction systems such HF-LPME, electromembrane extraction (EME), gel electromembrane microextraction (G-EME) were reported in the literature as a sample preparation method for elemental analysis [140].

The EME consists of applying a voltage to enhance the mass transportation of charged or ionisable species, providing faster extraction of charged species. The EME has been introduced as a rapid alternative to liquid-phase microextraction [140]. The EME is greener than HF-LPME because it uses a very small volume of organic solvent [140]. When the organic solvent is replaced by a membrane, the technique is called gem electromembrane microextraction (G-EME). The aim of this replacement is to comply with the principles of green chemistry [140]. Recently there are reports of the use of EME and G-EME for extraction and preconcentration of chromium species [140].

An ultrasound assisted-deep eutectic solvent based on the emulsification, in an ultrasound assisted-deep eutectic solvent liquid phase microextraction method (UA-DES-ELPME) combined with microsample injection flame atomic absorption spectrometry, was developed for speciation, preconcentration and determination of chromium Cr(VI) and Cr(III) species in several water samples. The method provides some advantages, such as simplicity of experimental steps, use of low cost and low toxicity extraction solvents, since most of DESs can be prepared from readily accessible chemicals. In particular, for the DESs derived from ChCl and renewable chemicals, relatively high speed of sample preparation is required. These notable advantages of the developed microextraction method and DESs now open alternative routes for the analytical applications [141].

An UALPME-DES method was developed for preconcentration and speciation of Se(IV) and Se(VI) combined with ETAAS. The ultrasonic energy was applied to obtain the fine drops of DES, improving the extraction efficiency of Se ions. The developed procedure showed simplicity, employing non-toxic solvents, whereas, most of the DESs could be synthesized from common available chemicals. The selected DES did not interfere in the determination of the analyte by ETAAS. The robust method is sensitive and relatively easy to be applied [142].

3.2. Solid-phase microextraction (SPME)

The SPE procedure was introduced to overcome the disadvantages of LLE, especially in relation to the problems of high solvent consumption and the need for a skilled analyst [143]. SPE is based on partitioning of the analyte between a liquid phase and a solid phase (solid sorbent) that has the ability to retain the analyte during removal of the aqueous phase and the subsequent washings, consequently enriching it in the sorbent phase [143]. Hence, it is essential to select a suitable sorbent material, which should have high selectivity and sorption capacity for the analyte, as well as to consider the interactions with the solvent and the sample matrix [144].

The sorbents used in traditional SPE include modified silica chemically linked to functional groups such as thiol moieties, forming thiolated silica, as well as carbon-based polymers, polyurethane foams, natural polymers such as cellulose, and chelating resins such as 8-hydroxyquinoline, p-dimethylaminobenzaldehyde, 5-formyl-3-(1'-carboxyphenylazo) salicylic acid, and aminothioamidoanthraquinone [138]. However, the use of these sorbents has some restrictions, such as limitations to use at high or low pH, as well as low ability to reuse the materials [144].

Although SPE is an excellent alternative to traditional LLE, it still requires the use of solvents for desorption of the analyte and subsequent washings [143]. In order to address this problem, solid-phase microextraction (SPME) emerged, with the main objective of completely eliminating the use of an eluent solvent, since the analytes are thermally desorbed from the SPME fiber, with the sampling, extraction, and analysis procedures carried out in a single step [143].

Like SPE, SPME is based on partitioning of the analyte between the sample, a liquid or gaseous phase, and a solid polymeric coating on fused silica [97]. Selection of the solid coating must consider parameters such as stability, polarity, and thickness, because these physical properties affect the distribution coefficient between these two phases (the solid coating and the sample), consequently influencing the extraction efficiency of the method [97,145]. With the objective of innovation and avoiding the problems usually associated with SPE, manganese dioxide-coated magnetite was presented, in 1996, for use in a magnetic solid phase extraction (MSPE) procedure, with phase separation being promoted by magnetic decantation [146]. Since then, magnetic nanomaterials such as Fe_2O_3 , MnO_2 , Al_2O_3 , ZnO_2 , and other nanoparticles and nanocomposites [147-151] have been described, together with reinforcement materials such as graphene oxides [152-154], carbon nanotubes [155], metal organic frameworks [156], and biological materials (cellulose, moss and chitosan) [157-159]. These systems have been successfully applied for the extraction of rare earth elements, Au, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, and Zn from environmental, food, and geological matrices.

Filik and Avan [160] performed the preconcentration of Co ions present in water samples by microextraction using the DLLME and SPME methods. For this, a reddish Co-5-Br-PADAP (2-(5-bromo-2-pyridylazo)-5-diethylaminophenol) complex was initially formed, followed by injection of 200 μL of acetone as dispersing solvent and 100 μL of the IL 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonylimide) ([EMIM]Tf₂N) as extraction solvent. This resulted in the immediate formation of a cloudy solution, which was allowed to stabilize for 1 min, followed by addition of 30 mg of Fe_3O_4 nanoparticles (Fe_3O_4 NPs) and keeping in an ultrasonic bath for 2 min at 50 kHz. The IL was immobilized on the Fe_3O_4 NPs, forming an IL/ Fe_3O_4 NPs phase that could be easily separated with a strong magnet, obtaining a clear phase that was directly injected into a flame atomic absorption spectrometer (FAAS). This development of DLLME in conjunction with dispersive magnetic solid-phase microextraction (MSPME) provided a low detection limit of 0.05 $\mu\text{g L}^{-1}$ and recoveries in the range 97-102 %.

A dispersive SPME method was employed for Hg separation and preconcentration using the IL [BMIM]Cys modified with magnetic reduced graphene oxide nanoparticles (IL-MgGO) as a sorbent [161]. For this, 2 mg of the sorbent were added to a tube containing deionized water, with sonication for 5 min. A syringe was then used to inject the IL-MrGO solution into 20 mL of sample solution. After stabilization, the IL-MrGO was isolated by magnetic

decanting. Treatment using HNO₃, thiourea, and sonication for 4 min resulted in complete desorption of Hg, which was then determined by cold vapor atomic absorption spectrometry (CV-AAS). The method was applied to real water samples, resulting in recoveries of 97-100 %.

In addition, the disposable pipette extraction (DPX) has gained prominence due to its advantages such as fast extraction, low sample consumption, reduced amount of solvents and the possibility of automation [162, 163]. This technique can be adapted using micropipette tips and natural adsorbents (such as husk and seeds) [162, 164]. Despite its advantages, the DPX procedure is still little explored for the extraction of inorganic analytes, in particular, metal ions [162]. Tomasin *et al.* [162] developed DPX for extraction of Cu(II) ions in hemodialysis water, using a homemade device with *Moringa oleifera* seeds powder as a solid phase with recoveries ranged from 96.8 to 100.4 %

3.3. Stir bar sorptive extraction (SBSE)

Despite the advantages of SPME, limitations of the technique may include low specificity, fiber degradation, and contamination, which were overcome with the development of the stir bar sorptive extraction (SBSE) method.

SBSE was introduced in 1999 and is considered a derivation of SPME, with the difference being the use of a greater volume of extraction solvent as the sorbent phase, leading to higher analyte enrichment factors, greater sensitivity, and high recovery percentages [165]. The principle of this technique is based on the partitioning equilibrium of the analyte between the extraction phase coated on the stir bar and the sample matrix [165]. The method was used for the extraction and preconcentration of analytes present in aqueous solution, using a magnetic stir bar coated with the polydimethylsiloxane (PDMS) polymer, which adsorbed the compounds to be extracted as the bar was used for stirring the sample [165].

The nature of the polymer used to coat the stir bar determines whether analyte extraction occurs by absorption and/or adsorption. Homogeneous polymers, such as PDMS, are used as absorbent coatings, because they have glass transition temperatures below the external temperature, forming a pseudo-liquid phase [166]. The extraction process is based on the

diffusion of analytes between the sample and the polymeric phase, with dissolution of the analytes in the coating, without formation of chemical bonds [166].

Adsorbent coatings, on the other hand, are multiphase polymers that present porous structures and functional groups, where chemical or physical adsorption can take place [166]. The chemical adsorption process occurs by means of hydrogen interactions, whereas physical adsorption mainly involves van der Waals forces, with hydrophobic interactions between the nonpolar polymeric phase and the analyte [165,166]. After sorption, the analyte must be desorbed, with the process employed depending on the strength of the interaction between the analyte and the coating. Liquid desorption is used to disrupt strong interactions, such as electrostatic interactions and chelation, while thermal desorption can be used to break weak interactions, such as van der Waals forces [166]. Hence, control of the experimental parameters is essential to obtain the maximum efficiency of the method. Kinetic parameters (equilibrium time and agitation speed) influence the rate of mass transfer of the analyte towards the polymeric phase, while thermodynamic parameters (pH, polarity, and ionic strength) affect the interaction between the analyte and the polymeric phase [155].

SBSE is considered an environmentally friendly extraction procedure and is normally applied for sorption extraction of organic analytes, although modification of the chemical structure of the coating material can enable its use for the extraction of inorganic ions. The PDMS polymer is only suitable for extraction of nonpolar analytes, so new approaches have been developed using other coatings with affinity for polar analytes [165]. The application of sol-gel technology was the first approach adopted to prepare stir bar coatings that presented selectivity for the extraction of polar analytes, employing the incorporation of different chemical groups in the PDMS network [165].

The advantages of SBSE include ease of automation and application, as well as the possibility of applying it to samples containing analytes with different properties and/or chemical structures [165]. In order to better comply with the principles of GAC, stir bar microextraction (SBME) has emerged as a new technique, including for the analysis of polar compounds, presenting good performance and high sensitivity for trace analysis [165]. However, there are few works that have addressed the application of SBSE in inorganic analyte extraction methodologies. It has mainly been employed for monitoring nonpolar or medium

polarity compounds, typically using a multi-residue approach that complies with the principles of GAC [165].

López-Lopez *et al.* [167] prepared an SBSE microextraction bar filled with two solvents as the accepting solution. The IL tri-octylmethylammonium was used for the extraction of Ag from seawater samples, where the species AgCl_2^- and AgCl_3^{2-} are present, which can be ionically exchanged for Cl^- ions, with 1-dodecanol as a matrix modifier. This system was inserted into the sample matrix, with constant stirring at 800 rpm for 60 min. After the extraction procedure, the acceptor phase was recovered and analyzed by GFAAS, obtaining recoveries in the range 83-120 % and LOD of 0.09 ng L^{-1} .

In work by Herce-Sesa *et al.* [168], the IL CYPHOS[®] 101 was used as an extractor solvent, employing a hollow fiber with a stir bar configuration, for the extraction of Pd, Cd, and Ag from water samples. Stirring was performed at 800 rpm for 30 min, with subsequent analysis by FAAS, resulting in recoveries higher than 90 % for Pd, around 100 % for Cd, and between 93 and 95 % for Ag.

3.4. Cloud point extraction (CPE)

Cloud point extraction is a reliable technique for quantifying inorganic elements at trace levels, which can be used in extraction, separation, and preconcentration procedures [169]. It is based on the use of surfactants, with micelle formation in a cloudy aqueous solution after heating to a certain temperature, known as the cloud point temperature (CPT) [169]. When the CPT is exceeded, the solution separates into two phases: a surfactant-rich phase and a diluted aqueous phase [169]. For the preconcentration of inorganic analytes, normally applied to metals, a complexing agent capable of forming hydrophobic chelates that remain in the nucleus of the micelles present in the surfactant-rich phase is added to the solution, resulting in the extraction and preconcentration of the analyte in a residual aqueous phase (Figure 5) [169]. Currently, the most used chelating agents are dithiocarbamates, dithizone, 8- hydroxyquinoline, diethyldithiophosphate, and Schiff bases [170].

[FIGURE 5]

In conventional CPE, a phase rich in highly viscous surfactant is obtained, requiring dilution with an organic solvent before the analysis is carried out [171]. Therefore, alternative

CPE-based methods have been developed to avoid problems associated with the injection of organic solvents in the detection equipment, in addition to speeding up and simplifying the procedure. These techniques include displacement CPE (D-CPE), rapidly synergistic CPE (RS-CPE), ultrasound-assisted CPE (UA-CPE), microwave-assisted CPE (MW-CPE), flow-based CPE (FIA-CPE), and dual CPE (d-CPE).

The use of surfactant is crucial in the CPE process, with the most widely used non-ionic surfactants being polyoxyethylene sorbitan monostearate (Tween 60), polyethylene glycol sorbitan (Tween 80), polyoxyethylene-9.5-octylphenoxy ether (Triton X-100), and polyoxyethylene-7.5-octylphenoxy ether (Triton X-114) [169]. Cationic surfactants such as cetrimonium bromide (CTAB), cetylpyridinium bromide (CPB), and cetylpyridinium chloride (CPC), as well as mixtures between non-ionic and ionic surfactants, can also be used in CPE [170].

The extraction of metal ions using CPE involves the use of chelating agents capable of forming complexes that are insoluble or sparingly soluble in water. The efficiency of the process is governed by the hydrophobicity of the ligand and the complex, considering their equilibrium constants, the kinetics of complex formation, and their transfer between phases [170]. The organic binders PAN, 1-(2-thiazolylazo)-2-naphthol (TAN), 4-(2-pyridylazo)resorcinol (PAR), and 5-Br-PADAP are pyridylazo and thiazolylazo derivatives that are widely employed, since they feature low water solubility and high capacity for complexation with various metals [172].

Milcheva *et al.* [173] developed a new CPE method for the determination of V in water samples prior to ultraviolet-visible spectroscopy (UV-Vis) analysis, using Triton X-100 as surfactant and a mixture of H₂O₂ and HTAR (6-hexyl-4-(2-thiazolylazo)-resorcinol) as complexing agent. The system was heated at 85 °C for 25-30 min and cooled in a refrigerator for 45-60 min, to separate the liquid phase. The method proved to be simple and low cost, using only common laboratory equipment, with no requirement for any organic solvent. The complexing agent mixture acted to increase the absorbance of the analyte of interest, obtaining high sensitivity (LOD = 0.8 ng mL⁻¹) and accuracy (recovery = 99-100 %). Akl and Hegazy [174] synthesized a novel tetra-cationic surfactant IL based on tetraazonia-trycyclo[3.3.1.1^{3,7}]decane. This IL was used in a conventional CPE method, together with Triton X-100, for the extraction of Th(IV) ions from water samples, which resulted in a more

selective, sensitive, simple, and GAC-compliant procedure, with a detection limit of only 77.10^{-2} ng mL⁻¹ and recoveries from 98 to 101 %.

CPE is a versatile technique that is inexpensive and highly efficient, standing out from conventional liquid-liquid techniques that use water to form the phases, while avoiding the use of any organic solvent. In addition, it employs chelating agents of low water solubility that are capable of forming complexes with inorganic analytes, which makes this technique useful for elemental analysis [170]. The future prospects of the technique include the use of these chelating agents combined with nanomaterials, especially those that have magnetic properties, such as nanomaterials functionalized with SiO₂, Al₂O₃, and Fe₂O₃, nanocomposites, as well as graphene, with the main goal of increasing the preconcentration factor [175].

3.5. Alternative techniques for sample preparation

In addition to the sample preparation methods presented above, other techniques have been developed in recent years that comply with GAC, while also increasing sensitivity and accuracy, although few studies have applied them for the determination of inorganic analytes. Among these methods, membrane-based extraction employs a chemically inert membrane layer, situated between an acceptor phase, which contains the analyte and a donor phase, which retains and accumulates the analyte [176]. The technique proved to be highly efficient, with high enrichment factors, the use of micro-volumes of solvent, and the need for only small sample volumes [176]. A membrane-based inverted liquid-liquid extraction (MILLE) method was performed employing a small heat-sealed bag containing 2 mL of seawater and only 200 µL of chelating agent, which was stirred for 10 min in chloroform to form Cd, Co, Cu, Mo, Ni, Pb, V, and Zn chelates. The chelates were heated to dryness, digested, and analyzed by ICP OES, obtaining recoveries between 75 and 94 %, showing the efficiency of this innovative method [177].

Emulsification procedures coupled with ultrasound-assisted extraction (ultrasound-assisted emulsification, USAE), followed by agitation, offer low electricity consumption, small surfactant volumes, and production of stable and homogeneous emulsions, with a trend towards the use of alternative and sustainable solvents [178]. Junior *et al.* [179] used a biosurfactant based on corn, molasses, canola oil, and water to extract Cu, Pb, and Zn from soil samples.

Vortex-assisted emulsification liquid-liquid microextraction (VA-ELL μ E) was used for Se speciation in water samples, using the choline chloride-phenol DES as extractant, achieving enrichment factor and detection limit values of 81.8 and 0.036 $\mu\text{g L}^{-1}$, respectively [180].

In the study conducted by Lukjok *et al.* [181] the new miniaturized mercapto-functionalized silica/cellulose membranes were developed for highly selective adsorption and determination of inorganic arsenic species, As(III) and As(V). The excellent adsorption capacity and high affinity of mercapto groups to As(III) indicate that membranes can be applied in preconcentration and/or separation of trace and ultratrace arsenic ions and determination by EDXRF. The batch adsorption experiments show that the cellulose/SiO₂/MPTMS membranes are characterized by high selectivity toward As(III) in the presence of As(V), heavy metals and anions that usually exist in natural waters. The great advantage of the method is that it can be successfully applied in analysis of high salinity water, which is difficult to analyze by using other spectroscopy techniques. The method is a solvent-free approach based on miniaturized membranes and very low-power instruments without gas consumption. It can be considered as environmentally friendly and meets the standards of green analytical chemistry principles.

The automation of analytical procedures has been gaining prominence in GAC, with the main objectives of minimizing the consumption of samples, reagents, and analytical standard solutions, increasing the speed of analysis, reducing operator participation, and enabling the processing of large numbers of samples in a highly controlled way [182]. Several methodologies have been described for the determination of inorganic analytes. Among these, analytical techniques based on continuous flow were applied for the determination of As, Cd, Se, and Te in food and environmental samples, for example [183-186]. Flow injection analysis (FIA) is based on inserting liquid samples into a solution flow that transports them directly to the detector [182]. This technique is widely applied for elemental determination and was used by Llaver *et al.* [187] for simultaneous determination of Se and Te in environmental samples, in just 8 min, using a hydrophobic IL formed directly in the sample stream, increasing the sensitivity factors and obtaining low detection limits in the range from 1.8 to 3.2 ng L⁻¹.

Sequential injection analysis (SIA) is an FIA-based method that has been successfully employed for the determination of Hg in water samples and Se in wastewater [188,189]. This method is based on sample and reagent insertion zones, followed by reversal of the flow direction, which allows mixing between the components. This reduces the consumption of

reagents and the production of waste, in addition to being a method fully controlled by computer, enabling accurate timing of connection of the zones and automatic regulation of the flow rates [181].

The speciation analysis is crucial for the information in aspects of environmental mobility, toxicological, bioavailability and nutritional studies, and the alignment with the principles of the green and sustainable chemistry should be considered. The green chemistry concept as miniaturization methods, employing microvolumes of ecological solvents, and avoiding the generation of significant amounts of waste, when applied in the sample preparation step, makes the method greener.

The speciation of metalloids (As, Sb, Se, and Te), and metals (Cr, Cu, Fe, Gd, Hg, Mn, Pb, Sn, Tl and V), were performed employing different kind of solvent and sorbent in the extraction methods in environmental samples. Recent trends in elemental speciation analysis have been described taking into account the principles of green analytical chemistry, e.g., direct analysis; replacement or elimination of toxic reagents; reduced waste generation; power efficiency; miniaturization and automation of analytical apparatus; the greenness of analytical methods [190].

Considering the relevance of the phosphate and phosphite determinations in fertilizers, the favorable characteristics of the flow-batch analyzer, a flow-based procedure for in-line sample preparation and sequential determination of these analytes in fertilizers was studied. The advanced oxidative comply to employ the Co(II) as a catalyst, activating the peroxymonosulphate (PMS), establishing the Co/PMS system, and generating the $\text{SO}_4^{\bullet-}$ radicals in the flow analysis process. Then, as this process can be accomplished in-line, this sample preparation improves the spectrophotometric determinations of phosphate and phosphite in liquid foliar fertilizers. Phosphite was determined as being the difference in the analytical signals corresponding to the sample handling with and without the oxidation step. The oxidation time was reduced from some hours to a few minutes, and the analytical frequency reached was about 24 samples can be run per hour, obtaining reliable results. The procedure can be applied to the speciation analysis of P_2O_5 in liquid fertilizers by relating it to phosphorus source added to the commercial formulation, as suggested by the authors [191].

The development of environmental-friendly methodologies based on biological substrates in elemental preconcentration and speciation analysis, employing several types of biological substrates classes, as well as, the mechanisms involved in elemental extraction, and methods for elemental preconcentration analysis were described in the work conducted by Smichowski *et al.* [192]. Most of the methodologies reported are in agreement with the green chemistry principles, reducing the consumption of organic solvents or even not using, are safe, inexpensive, being considered environmental friendly alternatives.

The latest trends in the automation and miniaturization of continuous flow methods for the determination of inorganic analytes are related to the application of lab-on-chip (LOC) and lab-on-valve (LOV) techniques, where the flow rates are only μL per minute [182]. The LOC technique employs microfluidic chips that use small sample volumes and are capable of performing various chemical analysis functions, characterized by fluidic, electronic, optical, and sensory integration [193]. In the LOV methodology, the various steps of an analytical method can be integrated into a miniaturized device coupled to a selector valve [194]. Both methods are excellent alternatives to traditional chemical analysis, increasing the repeatability, reliability, and robustness of the method, and allowing *in situ* analysis [195]. The LOC methodology has been little explored for the determination of inorganic analytes, but Geißler *et al.* [196] reported efficient determination of Mn in seawater using a device that required 63 μL of sample, obtaining recoveries greater than 99 %. Mattio *et al.* [194] developed a LOV device for the determination of Cd and Pb in water, with detection limits between 0.17 and 0.20 $\mu\text{g L}^{-1}$. Miranda *et al.* [197] applied a micro-sequential injection lab-on-valve ($\mu\text{SI-LOV}$) method for determination of Fe in fresh and marine waters, characterized by the consumption of only 30 μg of reagent and production of 2.5 mL of waste, obtaining a detection limit of 0.13 $\mu\text{mol L}^{-1}$.

4. Metrics for green analytical chemistry

Although GAC is not a new concept, there is no single green metrics system. Efforts have been made to develop metrics for chemical analysis, with some being simple to use, but not covering all the environmental aspects of analytical methods. Others are more comprehensive, but can be difficult to apply [198].

One of the oldest tools is the National Environmental Methods Index (NEMI), which consists of a circle in four fields [198]. Each field reflects a different aspect of the analytical methodology, with the field being filled in green when: (i) none of the chemicals is present on the persistent, bioaccumulative, and toxic chemicals list; (ii) none of the chemicals applied in the procedure is listed on hazardous wastes lists; (iii) the pH of the sample is within the range 2-12, to avoid a highly corrosive environment; and (iv) the process produces less than 50 g of waste [199]. The NEMI is easy to read, but the result of the analysis is only qualitative, with no information about the quantity of reagents. In addition, there is a lengthy search for reagents [199,200].

Another metric is the Analytical Eco-Scale, which uses penalty points associated with the type and quantity of reagents, energy consumption, waste production, and conditions of the sample preparation treatment [201]. The penalty points for reagents are calculated by multiplying the number of GHS hazard pictograms by the degree of hazard (multiplication by 1 for “warning”, and by 2 for “danger”) [200,201]. The closer the value to 100, the greener the process is considered to be [201]. It is easy to calculate (Globally Harmonized System (GHS) pictograms are found on reagent labels), considering the volumes of reagents used in the processes [198,200]. However, no information about the structure of the hazards is obtained, and the calculation does not inform about the causes of environmental impacts of analytical procedures, considering aspects such as the use of solvents, other reagents, occupational hazards, or generation of wastes [198,200].

Multi-criteria decision analysis (MCDA) is used in the selection of analytical procedures with low environmental impact [198,200]. Criteria are selected and assigned weights (economic and environmental), with ranking performed using a suitable algorithm [198,200,202]. MCDA enables evaluation of many similar criteria using a single score, with easy interpretation and the possibility of simultaneously evaluating several analytical procedures [198,200,202]. An advantage is the ability to obtain a complete ranking of the procedures, while a disadvantage is that preparation of the dataset is difficult and requires some analytical knowledge and experience [200].

The Green Analytical Procedure Index (GAPI) is a metric based on NEMI and Analytical Eco-Scale that measures the green character of a methodology from sample collection to final determination [203]. It takes account of the reagents (amount, health hazard,

and safety hazard), instrumentation (occupational hazard, waste, and waste treatment), sample collection and transport, and sample preparation (direct or indirect method, scale of extraction, reagents used, and additional treatments). The results are expressed by means of a pictogram in red (high impact), yellow (medium impact), and green (low impact) colors. The GAPI provides general and semi-quantitative information that is easily interpreted, with the colors indicating weak and strong points in the procedures [204].

Pena-Pereira *et al.* [204] proposed a new metric, the Analytical GREEnness calculator, based on the criteria of the 12 principles of GAC. The score ranges from 0 to 1, where the closer to 1, the more environmentally correct the analytical procedure is considered to be. The method is comprehensive (incorporating the 12 GAC principles), flexible (with the ability to assign weights), easy to interpret (color pictogram with weak and strong points), and fast (software available) [204].

Nowak *et al.* [205] recently proposed a new approach called White Analytical Chemistry (WAC), which is inspired by the Red-Green-Blue (RGB) model [206]. This metric extends the concept of green chemistry using other primary colors such as Red and Blue. In this case, red refers to validation criteria of the analytical method (accuracy, precision, LOD, LOQ), green is assigned to environmental impact (well known GAC principles), and blue relies on economic aspects, productivity and practical efficiency. The WAC model is also based on an available Excel spreadsheet that must be filled out covering 12 WAC principles to assess the parameter called “whiteness” of the method, i.e. degree of sustainability. To validate the applicability of this model, the authors assessed many bioanalytical methods based on different sample preparation methods also reported in the present review (i.e. SPE, LLE, MAE, DI-SPME, Micro-Extraction on Packed Sorbents - MEPS) prior to HPLC analysis using two different detection systems (DAD and MS). This described applicability helps the analytical chemistry community to use the WAC metric for evaluating sustainability of newly developed methods as well as compare new and known methods such as those mentioned in the present review. According to the authors, the other metric tools mentioned earlier do not take into account analytical efficiency (sensitivity, recovery, and precision) and functionality (practical and economic criteria). The WAC technique fits into sustainable development because it takes into account other attributes that influence the actual use and functionality of the method [205].

Conclusions

The chemical analysis considered as ideal should be direct analysis, without the need for a sample preparation step or the use of solvents. However, in most cases, this is still not realistically feasible, so the analysis of substances present at low concentrations in samples requires techniques for their prior isolation and enrichment.

In this step, solvents play a fundamental role, so current research concerning analytical practices aims at the development and use of environmentally friendly and benign solvents, replacing organic and toxic solvents. For a solvent to be classified as green, in addition to its origin, factors such as synthesis method, toxicity, and biodegradation must be considered, since “green” is a relative term that can be used to compare different solvents. Attractive candidate solvents are ionic liquids, eutectic solvents (DES and NADES), and superheated water.

In addition to the use of environmentally friendly solvents, green analytical chemistry envisages the development of extraction and microextraction techniques that require minimal amounts of solvent and sample, in procedures that are easy to perform, safe for the analyst, fast, and with little or no need for electrical energy. Furthermore, these techniques must provide high levels of sensitivity and efficiency.

Combining these factors, the future perspectives for green analytical chemistry should include continued efforts to develop new solvents for use in green extraction procedures, as well as improved microextraction techniques, including those suitable for elemental analysis, for which there are still relatively few published works in the literature. There is also a need for further research concerning the use of these solvents and techniques for the purpose of chemical speciation.

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Table 1. Applications of deep eutectic solvents (DES) and natural deep eutectic solvents (NADES) in sample preparation for elemental analysis, published from 2010 to the present time.

Analytes	Samples	Sample volume or mass	Extraction technique	Conditions	Extraction time	Determination technique	Recovery (%)	LOD	Ref.
Cu	Liver	10 mg	UA-ELPME	2 mL TBAC-decanoic acid DES, 80 °C, pH 6.0, and centrifugation at 4000 rpm for 5 min.	2 min	MS-FAAS	92-101	4.00 µg L ⁻¹	[58]
Cd, Pb, Cu, and As	Food and non-alcoholic beverages	2 g	DLLME	40 µL DES-MNF ChCl-thiourea, pH 6.5, and separation using a magnet.	10 s	ETAAS	94-101	3.0-4.2 ng L ⁻¹	[59]
Pb	Whole blood	17 mL	HF-LPME	The fiber lumen was filled with a mixture of ChCl-urea DES and KClO ₄ , and the extract was diluted with ultrapure water.	10 s	ETAAS	88-105	0.1 ng mL ⁻¹	[60]
Co	Pharmaceutical supplement and tea	0.5 g	LPME	0.5 mL ChCl-phenol DES, 1 mL 1-nitroso-2-naphthol (0.1%), 0.5 mL tetrahydrofuran, and pH 6.0.	2 min	MS-FAAS	97-105	1.10 µg L ⁻¹	[61]

Pb, Cd, and Hg	Soil and vegetables	1-2 g	DLLME	50 μ L imidazolium chloride-1-undecanol DES, 400 mg NaCl, 55 $^{\circ}$ C, and centrifugation at 5000 rpm for 4 min.	4 min	GFAAS	91-110	0.01-0.03 μ g kg ⁻¹ [62]
Pb and Cd	Edible oils	28 g	LPME	160 μ L ChCl/urea DES, 40 μ L HNO ₃ , 50 $^{\circ}$ C, and centrifugation at 5000 rpm for 5 min.	5 min	ETAAS	96-105	8 and 0.2 ng kg ⁻¹ [63]
Pb and Cd	Soil, hair, and water	0.2-1.0 g	SPE	200 μ L DES-MNF ChCl-urea as the sorbent, pH 6.0.	10 min	FAAS	96-105	0.4 and 0.1 μ g L ⁻¹ [64]
Cu and Ni	Water, human urine, and serum	50 mL	SPME modified with DES	5 mL ChCl-urea DES and 15 mL of methanol were used as an immobilizer on the surface of cotton fibers.	Flow rate of 7 mL min ⁻¹	FAAS	95-104	0.05 and 0.60 μ g L ⁻¹ [65]

Table 2. Some applications of different green sample preparation methods for elemental analysis.

Analyte	Samples	Sample volume or mass	Extraction technique	Conditions	Extraction time	Determination technique	Recovery (%)	LOD	Ref.
Hg	Water and freshwater fish	10 mL and 100 mg	LPME	100 μ L of 0.1% (w v ⁻¹) dithizone as chelating reagent, 500 μ L DES (ChCl/phenol and urea/glycerol) as extractor solvent, and use of an ultrasonic bath.	2 min	ETAAS	80-114	0.073 μ g L ⁻¹	[103]
Cr(III) and Cr(VI)	Water and chromium plating factory wastewater	10 mL	LPME	0.4 mL of 0.25% (w v ⁻¹) NaDDTC as chelating agent, 450 μ L DES (ChCl/phenol), 450 μ L THF, and use of an ultrasonic bath.	2 min	FAAS	95-110	5.5 μ g L ⁻¹	[71]
Mn	Water and coffee	50 mL	LPME	1.5 mL of 0.02% (w v ⁻¹) 3-[[[2-hydroxyphenyl]imino]methyl]-2-naphthalenol as chelating reagent, 500 μ L DES (ChCl/phenol) as	90 s	FAAS	87-109	0.52 μ g L ⁻¹	[104]

				solvent extractor, and vortex stirring.					
Ag	Water	100 mL	DLLME	1600 μL of $\text{C}_2\text{H}_6\text{O}$, 400 μL CHCl_3 , 500 μL 8-HQ chelating agent, and centrifugation at 3000 rpm.	10 min	FAAS	97-102	$2.0 \mu\text{g L}^{-1}$	[105]
Pb, Cu, and Cd	Shellfish	30 mL	MSPE	25 mg of $\text{MGO@SiO}_2\text{-APTES-IL}$ as sorbent, sonication for 3 min, and vortexing for 6.3 min.	6.3 min	ICP-MS	95-99	2.42, 3.36, and 3.75 ng L^{-1}	[106]
Cr, Zn, and Cu	Water	50 mL	MSPE	0.5 mL of GO-Gly as sorbent, stirring at 700 rpm, and vacuum filtration.	10 min	EDXRF	97-99	0.15, 0.07, and 0.08 ng mL^{-1}	[107]
Pd	Soil	1 g	SPME	50 mg MNPs, vortexing, and desorption with 150 μL HNO_3 .	30 s	FAAS	90-101	6.4 ng mL^{-1}	[108]
Mn, Co, Ni, Cu, Cd, and Pb	Water	1 mL	SPME	Hollow fiber coated with GO-silica as adsorbent, desorption with 100 μL of 0.5 mol L^{-1} HNO_3 .	6 min	ICP-MS	85-119	7.5, 0.39, 20, 23, 6.7, and 28 ng L^{-1}	[109]
As(III) and As(V)	Chicken meat / liver	1.0 g	SBSE	Bar coating of $\text{TiO}_2\text{-PPHF}$, stirring at 600 rpm, 100 μL of 1 mol L^{-1}	25 min	HPLC-ICP-MS	78-120	$11.4\text{-}64.6 \text{ ng L}^{-1}$	[110]

				KH ₂ PO ₄ as eluent, and 15 min in an ultrasonic bath.					
Cu	Seawater	35 mL	SBME	Hollow fiber bar coated with Dpkbh, stirring at 800 rpm, and 95 µL of 0.5 mol L ⁻¹ HNO ₃ as eluent.	120 min	GFAAS	94-95	0.62 nmol L ⁻¹	[111]
Cd	Water	25 mL	SBME	Neodyme bar coated with MNPs, stirring at 800 rpm, and 1 mL of 1.5 mol L ⁻¹ HNO ₃ as eluent.	15 min	FAAS	95-103	0.37 ng mL ⁻¹	[112]
I	Milk	5 mL	UA-CPE	Triton X-114 as surfactant, AOH ⁺ as chelating agent, and sonication at 40 °C.	10 min	UV-Vis	94-98	0.4-1.5 µg L ⁻¹	[113]
Ag	Beer and wine	25 mL	UA-CPE	Triton X-114 plus Triton X-100 as surfactant, SDS as chelating agent, and sonication at 45 °C.	12 min	UV-Vis	91-98	0.85 µg L ⁻¹	[114]
Cu, Zn, and Fe	Water	30 mL		Triton X-114 as surfactant, 5-BrPADAP-TPB as chelating agent, and thermostatic bath at 40 °C.	15 min	FAAS	95-105	0.44, 0.14, and 0.78 µg L ⁻¹	[115]

Cu	Water, plasma, and urine	50 mL	Triton X-114 as surfactant, 4-(2- chloroacetamido-salicylic acid as complexing agent, centrifugation for 3 min, and ice bath for 10 min to separate the surfactant- rich phase.	13 min	FAAS	95-100	0.25 µg L ⁻¹	[116]
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Figure 1. Numbers of publications in the last 7 years addressing “green chemistry” and “sample preparation”, and their WoS categories.

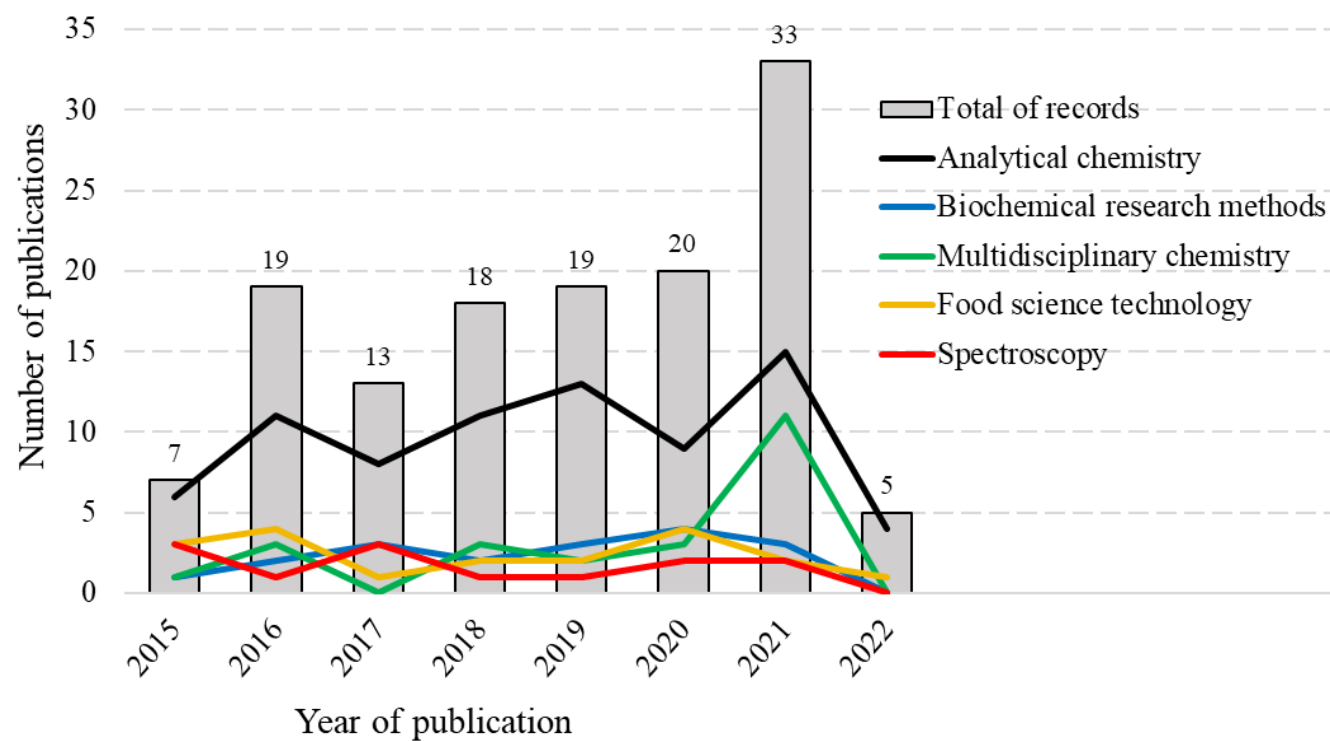


Figure 2. Bibliometric map obtained the top 60 author keywords for all papers retrieved.

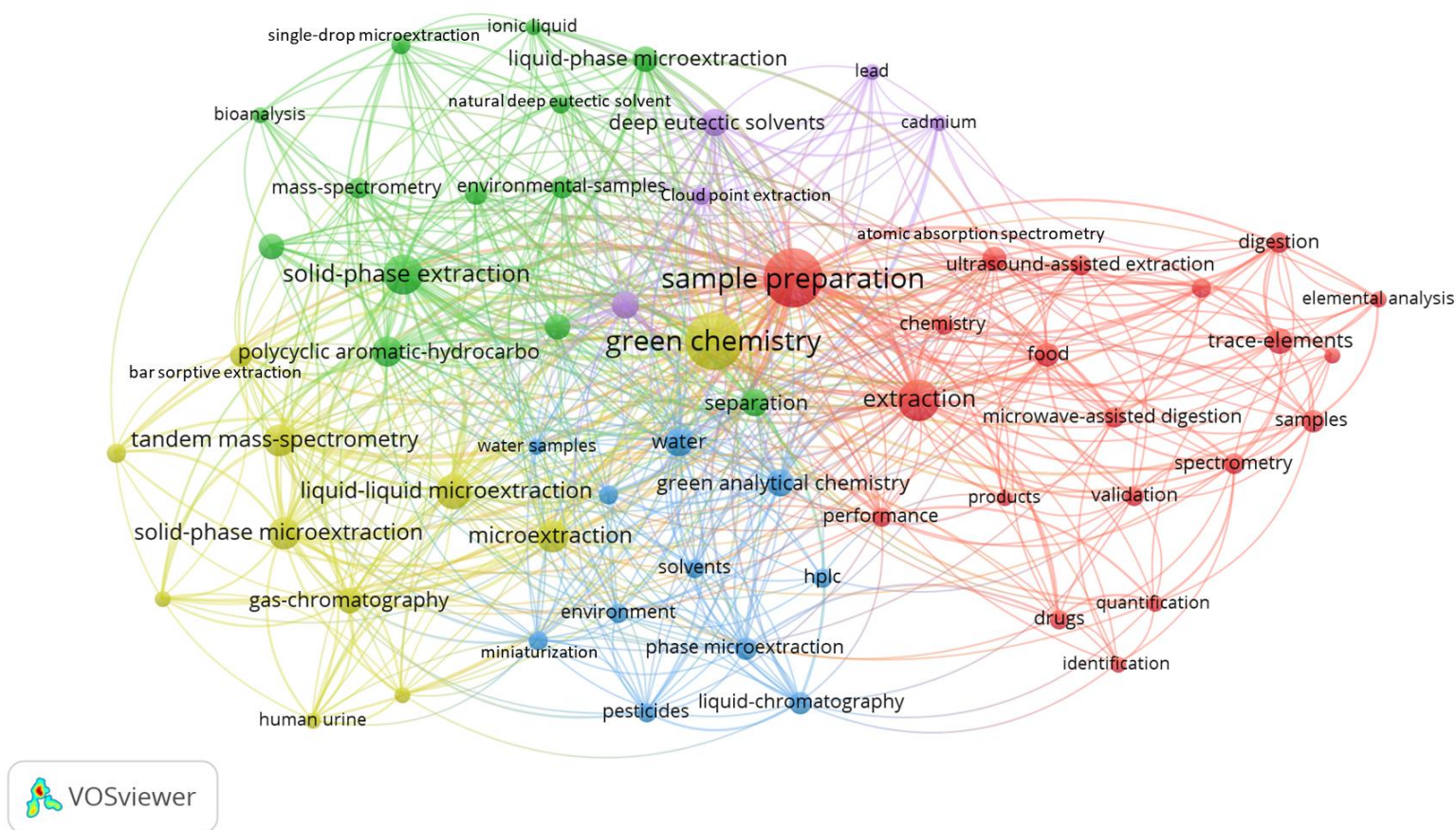


Figure 3. Cations and anions commonly used in ILs synthesis.

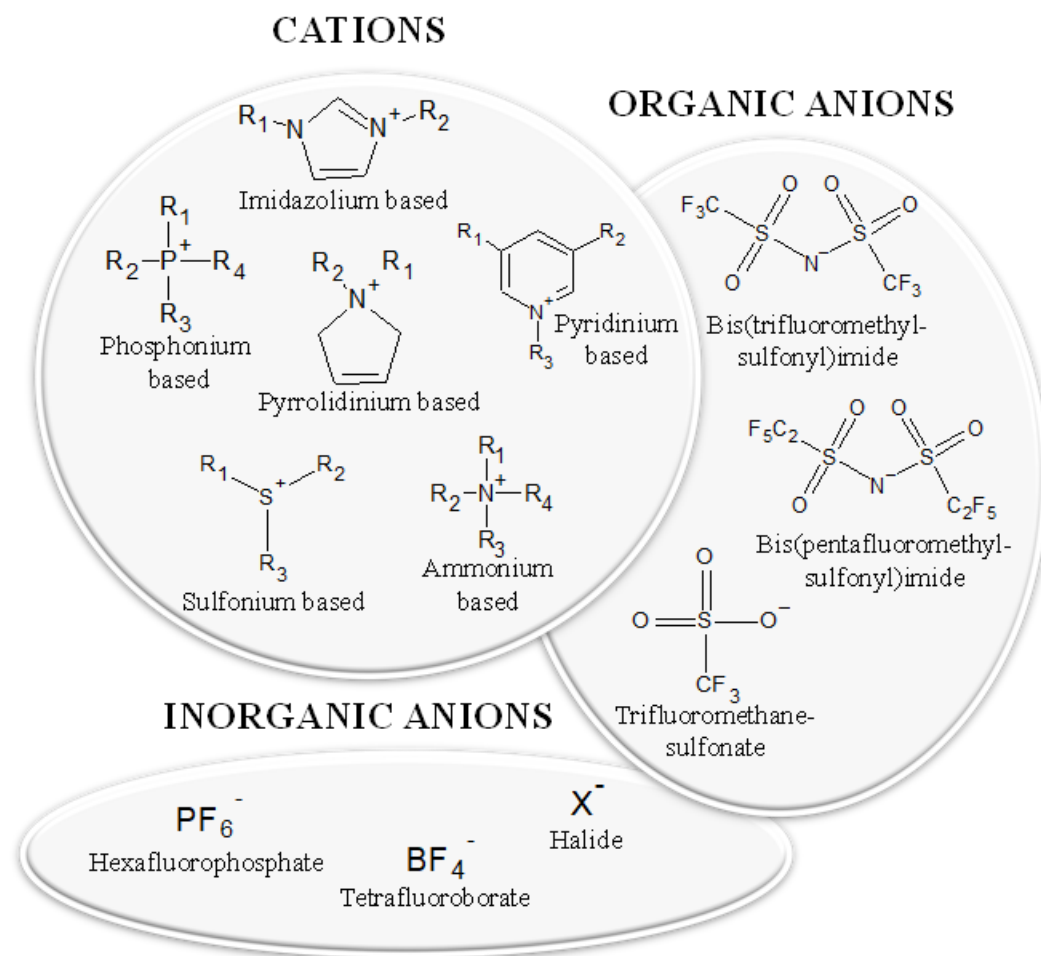


Figure 4. Schematic illustration of LPME methods. a) Different modes of SDME: DI-SDME, and HS-SDME; b) Two-phase and three-phase modes of HF-LPME; c) DLLME process steps.

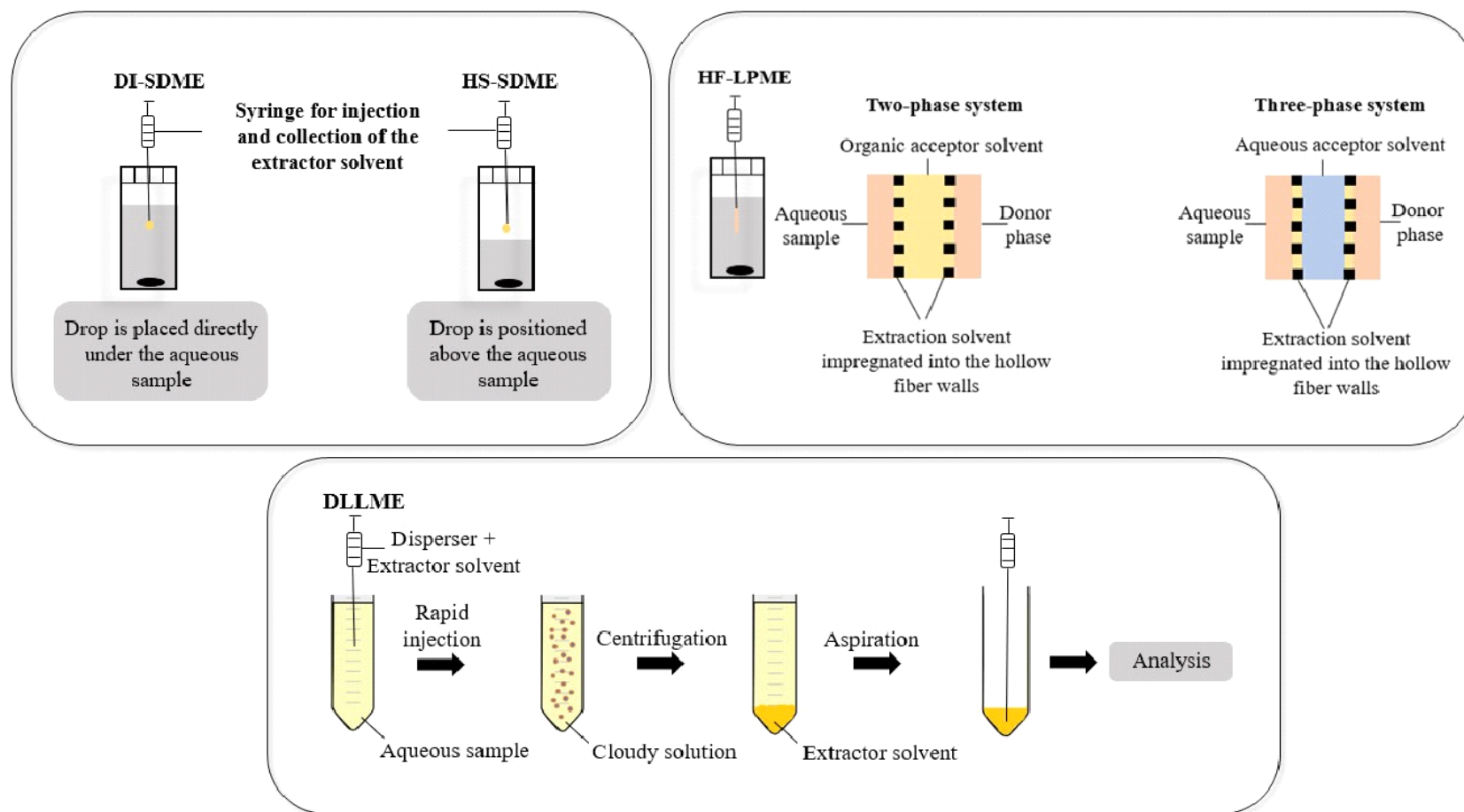
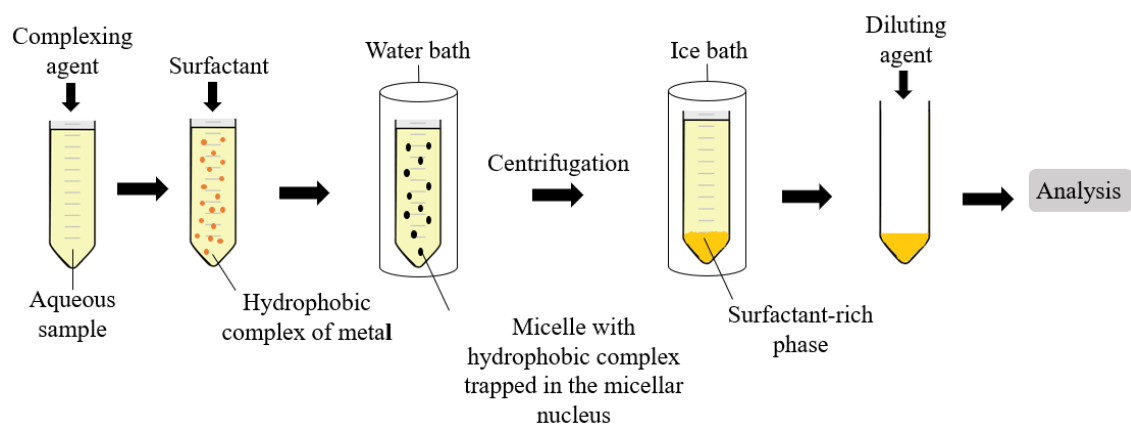


Figure 5. Schematic illustration of the conventional cloud point extraction (CPE) procedure.



Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: