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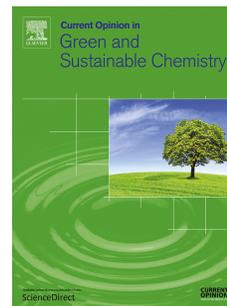
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Green sample preparation strategies for organic/inorganic compounds in environmental samples

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Abstract

A rigorous evaluation of environmental contamination requires constant innovation in analytical approaches to gain early identification and accurate quantification of every substance able to compromise health and well-being. Particularly, when trace analysis of organic and inorganic contaminants, and their species, in complex environmental samples is required. The analytical process comprises several steps, above all sample treatment, involving isolation of analytes, purification of extracts and preconcentration, often constitute the most time and labor consuming part. This review provides an overview in sample-treatment procedures applied for the analysis of organic and inorganic compounds in environmental samples in recent years. The current state of the art is emphasized on those techniques and approaches that have already demonstrated their sufficient analytical performance.

Keywords: Sample preparation; Sustainable strategies; Organic compounds; Trace elemental analysis; Speciation.

1. Introduction

Environmental analysis is one of the most demanding areas in terms of improvement of the overall analytical process, which has led to the introduction and development of new technologies and, in particular, a new generation of sample-preparation procedures. Given the great complexity of air, soil, and water matrices, sample preparation is quite an arduous task [1].

Sample-preparation step largely determines the quality of the results obtained and is the main source of systematic errors and random lack of precision of analytical methodologies. This analytical stage is, perhaps, the one that has received more attention in developing greener approaches for the determination of environmental pollutants, and numerous reviews and articles have been published on the subject [2]. This fact is not surprising since sample pretreatment is considered the most polluting step. The use of organic solvents is required for removing interferents and for concentrating the target compounds, which are generally present at very low concentrations, and the most frequent methods for pollutant determination are chromatographic, which generally require rigorous clean-up and extraction processes of the environmental samples [6, 8, 9]. Moreover, in most analytical methodologies, sample treatment is an unavoidable step, accounting in average for 61% of the total time required to perform analytical tasks [1, 3]. A comparison of green and classic sample treatment strategies is given in **Table 1**.

2. Sustainable sample treatment strategies in the analysis of organic contaminants

Thousands of chemicals have the potential to enter the environment, thus the NORMAN network has identified at least 700 organic substances categorized into 20 classes in the European surface waters. Their inevitable entry into the environment affects all compartments and, by extension, the related ecosystems. Pesticides, pharmaceuticals, disinfection by-products, wood preservation and industrial chemicals are the prominent classes [4-6]. Additionally, transformation products and metabolites contribute to increase the number of compounds to be monitored [1, 3, 7, 8].

For these reasons, one of the latest trends is to expand analytical strategies to monitor a number of chemicals as large as possible and investigate their fate in the environment. Nevertheless, the wide variety of compounds, their different physicochemical properties, and morphologically unstructured matrices with an elevated degree of sample-to-sample variability, complicate the development of sample cleanup and preconcentration steps [3, 6], which has become mandatory and is required by environmental legislations and health authorities. On the other hand, any assessment of efficiency of environmental protection policy needs relevant and reliable data on concentration levels of pollutants (particularly trace-pollutants and emerging pollutants) [6].

There is no universal sample-preparation technique suitable for all types of sample; trace analysis of organic contaminants in environmental samples is always challenging [5]. Typical sample-treatment methods include homogenization, filtration, centrifugation, clean-up, analyte extraction, preconcentration and/or derivatization. During the last years, a great effort has been made towards the development of more efficient extraction and clean-up approaches. The most recent tendencies are focus on environmental friendliness, avoiding

the use of toxic reagents, with strong reductions in consumption of energy and reagents, waste generation), low cost, miniaturization, automation and simplicity [9, 10]. The application of advanced sorbents (such as restricted access materials (RAMs), molecularly imprinted polymers (MIPs), adsorbents based on nanomaterials and immuno-sorbents; among others) and greener approaches (solvent reduced techniques) [5] is highly considered.

In this way, a great variety of extraction techniques used for environmental applications have been developed. These can be classified as solvent-based (liquid-liquid extraction, LLE and variants to Soxhlet extraction such as pressurized assisted extraction (PLE), also named accelerated solvent extraction (ASE)) and sorbent-based extractions (solid-phase extraction, SPE). These strategies have evolved to their miniaturized variants (such as LPME (i.e. deep and natural eutectic solvents, DES and NADES; respectively [11-14] and SPME), and are often combined with microwave-assisted extraction (MAE) or ultrasound assisted extraction (UAME), with a dramatic reduction in time and temperature and solvent requirements [15]. A summary of the milestones in this field are shown in **Figure 1** as well as a classification of sample treatment techniques used for elemental and organic analysis is given in **Figure 2**.

2.1 Liquid phase-based microextraction techniques

These pools of strategies have high potential in sample preparation due to their inherent advantages over any conventional LLE procedure. These include simple operation, low cost, low solvent consumption, speed, the potential for automation and high enrichment factors [10]. However, the extraction solvents used in these techniques are usually chlorinated solvents, which are undesirable for human and environmental health; to

overcome this, low density organic solvents and ionic liquids have been proposed [16]. In this way, different LLE miniaturization strategies for environmental pollutants have been presented in the literature [17-19], i.e. based on the single-drop extraction, dispersive liquid-liquid microextraction (DLLME), hollow-fiber liquid-phase microextraction (HF-LPME), continuous flow microextraction (CFME), and directly-suspended droplet microextraction technique (DSDME). Although different designs, these methods are simple, inexpensive, use micro-volumes of organic solvent, and are employed for a great variety of pollutants.

Nowadays, an interesting alternative is the use of membrane-mediated extraction techniques (electromembrane extraction (EME), stir-membrane liquid-liquid microextraction (SM-LLME, with different formats, i.e. the three-phase and the solid-liquid-liquid designs), which can favor analyte-extraction processes and move it from the original sample to an accepting solution ready to be employed for analyte measurement [20, 21]. Easy automatization of some of the mentioned procedures can be achieved, which can be relatively based on flow-injection analysis (FIA), sequential injection analysis (SIA) or the use of automated syringe systems [22, 23].

2.2 Solid phase-based microextraction techniques

On the other hand, SPE is probably the best option to improve analyte concentration and to separate it from a complex environmental matrix [10]. As known, any SPE procedure consists of column conditioning; sample loading, which implies analyte retention into the solid phase; column post-wash; and, analyte elution from the solid phase using an appropriate solvent. In solid-phase microextraction techniques a little volume of the extraction phase (μL) relative to the sample volume is used [24]. The configuration of

SPME can be classified into dynamic and static techniques. The static techniques are carried out in stirred sample mode. These include thin-film, fiber microextraction, and rotating disk sorptive extraction (RDSE). On the other hand, methods such as in-tube SPME, in-tip and in needle microextraction and capillary microextraction are classified as dynamic techniques [10]. The SPME method has the advantage over other extraction strategies because it requires less manipulation (simplicity) and is not tedious and time consuming [25]. The advantages of SPME also include small sample volumes, analyte concentration from liquid, gaseous and solid samples. In addition it can be considered as an almost solvent free extraction technique, which can be easily automated (sample-preparation step can be performed off-line, at-line or on-line) to allow high throughput analysis [26-28]. At-line procedures are performed with a robotic system or autosampler and no manual preparation is required. Recent developments on microfluidic systems and on-chip μ SPE include the use of disposable sorbents using mesofluidic platforms, which open new possibilities to green analytical methodologies [22, 23].

2.3 Recent advances in the design of extracting solvents

Several solvents have been developed and introduced in analytical practice, in particular in sample preparation process. Ionic liquids, surface-active agents, other organized media (e.g., crown and crypta ethers, and calixarenes) and lipidic structures (e.g., liposomes and vesicles), superheated water, supercritical fluids, deep eutectic solvents, natural deep eutectic solvents or bio-derived solvents have been found to be greener and cleaner alternatives to the use of classical organic solvents [11]. Some of the aforementioned solvents are well understood; however, there are still some aspects that need further studies

and must be taken into account in order to identify clearly the strengths, the weakness, the opportunities and the threats of the alternative extraction processes.

Recent advances in SPE extraction involve the evolution of formats, sorbent types and modes of interaction [11]. In addition to miniaturization, selectivity, online modes and reusability [29]. New selective sorbents for environmental applications include molecularly imprinted polymers, nanosorbents, composite materials, mixed mode ion exchange polymeric sorbents and polymeric ionic liquids (PILs). An alternative to SPE is the quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction method [22], which involves the extraction of analytes from a homogenized sample using an acetonitrile and salt solution and the clean-up of the supernatant using a dispersive SPE (dSPE) technique.

Novel designs for the SPME include also several membrane-based procedures (polymer-coated hollow-fiber membrane (PC-HFM), membrane extraction with sorbent interface (MESI), electrochemically-aided SPME, electrosorption-enhanced SPME (EE-SPME)). Advances in electrochemically-assisted solid-based extraction techniques (EA-SPME), with different electrochemical setups, have been recently reviewed [30]. Positive effects in selectivity and sample cleanup as well as extraction recovery and speed and offers the possibility of having precise control over the beginning and termination of the extraction process are listed as advantages of this new technique. Another interesting field in electrical field stimulated extraction techniques is their application in designing microchip-based devices; however, this technology is still emerging. Special attention must be paid to developments in solvent-free extraction methods for sample preparation and analyte separation, avoiding the isolation of compounds that are easily degraded and/or transformed into others [31, 32]. The use of thermal desorption systems is a good option for the elution

of analytes retained on solid phases. Thus, matrix solid-phase dispersion (MSPD) creates a unique mixture between the target material and a suitable solid sorbent that guarantees a large contact surface, and consequently, an extraction efficiency comparable to that of the classical and assisted extraction techniques without the use of elevated temperature and/or pressure. Analysis of agrochemicals, such as pesticides, herbicides, insecticides and fungicides, is an important research area with significant MSPD activity [32].

3. Green methods for total elemental analysis

Trace elemental analysis (TEA) deals with the determination of metals, metalloids and nonmetals at sub ppm levels [33]. In biological or environmental samples, the concentrations of trace elements are far below those achieved directly by most conventional atomic techniques and often, the detection capability needs to be enhanced. In addition, the field of elemental speciation has been widened in the last few years owing to developments in instrumentation that can determine the molecular form of elements in real samples, leading to a new discipline, namely metallomics [34].

Sample decomposition by acid digestion is common when atomic spectrometric techniques are used. It implies the application of concentrated acids and high temperatures and pressures. Solid sampling can be considered especially green for samples that are difficult to digest even with very drastic conditions, and for elements whose levels are usually very low. The advantages of solid sampling (SS) from the perspective of GAC over acid digestion or other sample pre-treatments (e.g., dry ashing, fusion) were discussed in deep in the article of M. Tobiszewski *et.al.* [35]. A number of contributions have been made by the Welz's group to this matter in the field of SS coupled to ETAAS [36].

As mentioned earlier, sample treatment is also one of the most energy consuming and contaminating analytical steps in TEA due to the large amounts of inorganic acids or bases needed to dissolve, extract, or digest samples under study and the thermal sample treatment required in many cases [37]. Among the most used sample treatment strategies, the listed below are considered to contribute more to Green Analytical Chemistry concepts: (i) extraction techniques: different variants of solid and liquid phase extraction, (ii) direct solid sampling (through sample ablation or by means of slurry formation), (iii) green solvents and reagents (surfactants in micellar-mediated extraction) and, (iv) flow analysis in atomic spectrometry.

Undoubtedly, major developments made in most atomic spectrometric techniques have run in parallel with improvements of green features [38, 39]. As an example, implementation of efficient background correction systems in the early atomic absorption spectrometers made it possible to carry out many requests with a significant saving in procedures such as matrix elimination by classic procedures, which in turn, conveyed a decrease in errors [40, 41]. In this context, in the field of elemental mass spectrometry, the development of efficient collision and reaction cells for elimination of background interferences has simplified the application of quadrupolar ICP-MS to complex matrices [42, 43].

In the last years, new developments in X-ray Fluorescence (XRF) instrumentation [44, 45] and Laser Induced Breakdown Spectroscopy (LIBS) [46] have gained attention due to the possibility of performing *in-situ* analysis thanks to its portability. These techniques are essentially non-destructive, fast and they provide instantaneous multi-element analysis, avoiding sample preparation, reagents and wastes. Apart from LIBS, lasers can be used for sample ablation (LA) in ICP based techniques (OES, MS), which constitutes an excellent

approach for green analytical chemistry, joining features of solid sampling with preconcentration and isotopic resolution ability [47, 48].

4. Green sample preparation strategies in speciation analysis

In nature, the same element can exist in different chemical forms (different isotopic compositions, oxidation state, or type of binding ligand), and each one can have different toxicity, mobility, and bioavailability. Thus, it is more important to determine the concentration of each one rather than to determine the total concentration of an element in a sample. In this context, sample preparation needs to reach an important paramount: avoid species inter-conversion. For this reason, extraction methods are preferred over digestion methods. Extraction methods can involve solid and liquid sorbents. They contribute to green chemistry mainly by miniaturization, decreasing the reagents consumption, and no use of organic solvents and carrier gases (**Figure 3**).

4.1 Liquid-solid phase extraction

Different solids have been introduced as sorbents for the extraction of elemental species from different samples. These include nanomaterials, polymers and carbon-based sorbents.

4.1.1 Nanomaterials

In comparison with conventional sorbents, nanomaterials possess high specific surface area and sorption capacity as well as fast sorption kinetics. Ahmad *et al.* [49] introduced the magnetic nanoparticle Fe₃O₄@Poly-Methacrylic acid (M-PMA) for speciation and preconcentration of As(III) and As(V) from water samples. Speciation was reached by pH modification. The application of this magnetic sorbent reduced the use of organic solvents,

and thus the generation of toxic and dangerous wastes. Another organic reagent-free technique involved a cation exchange reaction (CER) in Cd-Te ionic nanocrystals (NCs) for speciation analysis of Ag⁺ and Ag-nanoparticles. Nanoclusters (NCs) were “bombarded-and-exploded” (exchanged) by mixing the nanocrystals with Ag⁺ solution at room temperature, while this cation exchange reaction did not occur when only silver nanoparticles were present [50]. Nanomaterials can facilitate chemical speciation by selective sorption of chemical species. Another solvent-free methodology introduced alumina supported on graphene oxide (Al₂O₃/GO) nanocomposite for selective retention of As(V) and Cr(III) [51].

As mentioned earlier, miniaturization and low sample consumption are principles of Green Chemistry. In this sense a simple, rapid and miniaturized portable micropipette tip-syringe solid phase microextraction method was developed for speciation of vanadium in water and food samples. Tetra ethylene pentamine functionalized multiwalled carbon nanotubes were synthesized and packed in micropipette tip-syringe system. The V(V) could be adsorbed on the modified adsorbent surface, while V(IV) could not be retained [52]. Chromatographic methods usually requires organic solvents for their mobile phase. In this sense, reduction of reagents consumption is desirable. A solid sampling platform using multi-wall carbon nanotubes (MWCNTs) assisted matrix solid phase dispersion (MSPD) was constructed for online coupling to high performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) for mercury speciation in fish samples. The proposed method reduced usage of solid supports and minimized contamination [53].

4.1.2 Polymers

Polymers can be introduced for extraction of elemental species as membranes and capillaries in miniaturized systems. New miniaturized membranes, which are prepared by synthesis of amorphous silica coating on cellulose fibers followed by the modification with (3-mercaptopropyl)-trimethoxysilane retained arsenite. This membrane was directly analyzed by energy-dispersive X-ray fluorescence spectrometry, avoiding elution step usually required in other spectroscopy techniques. In addition the method is solvent-free, based on miniaturized membranes with very low-power instruments without gas consumption [54]. Ethylenediamine modified poly(glycidyl methacrylate-ethylene dimethacrylate) (poly(GMA-EDMANH₂)) was introduced for polymer monolithic capillary microextraction (CME). This sorbent is highly selective for Se(VI). CME shows encompass Green Chemistry features like low sample and reagent consumption and solvent-free [55].

4.1.3 Carbon based-materials

Graphene and Graphene oxide (GO) have excellent adsorptive properties, becoming materials with increased interest for solid-liquid extraction of elemental species. These properties are results of a huge specific surface area and the hexagonal arrays of carbon atoms that are ideal for strong interactions with other molecules due to the very large delocalized π -electron system. Moreover, GO possesses large quantities of oxygen atoms as epoxy, hydroxyl, and carboxyl groups. In consequence, GO can efficiently bind a metal ion through sharing lone electron pair present in functional groups containing oxygen atoms. A novel adsorbent synthesized by grafting 3-mercaptopropyl trimethoxysilane on a graphene oxide surface was reported. This adsorbent was selective toward arsenite, the most toxic arsenic specie. This material was introduced for dispersive microsolid phase extraction (DMSPE) and total-reflection X-ray fluorescence spectrometry (TXRF), being a

solvent-free and elution-free methodology [56]. Other GO-SH was introduced in cloud point extraction for enrichment of divalent mercury (IHg) and monomethylmercury (MMHg) in the water samples [57]. Another study modified (GO) with amino silanes, becoming sorbents highly selective for Cr(VI) in the presence of Cr(III) [58]; both of them are free solvent methods.

4.2 Liquid-liquid extraction

As stated, after the introduction of Green Chemistry principles, typical liquid-liquid extractions with organic solvents have been replaced by environmentally-friendly natural solvents. Selectivity towards chemical species is reached by addition of complexing reagents. Thus, Fe(II) was concentrated with the aid of the 1,10-phenanthroline (phen) extractant, in a aqueous biphasic systems (ABS), being one phase a polymer-rich phase. This methodology is solvent-free, being some components recyclable [59]. A greener analytical method was also reported, in terms of sample preparation and derivatization, and use of small-scale instrumentation. A single reagent, formic acid, was used for extraction of Hg^{2+} and CH_3Hg^+ in an eco-scale method based on UV-Vis photochemical vapor generation and detection in a capacitive coupled plasma microtorch by optical emission measurement with a low resolution microspectrometer [60].

4.2.1 Dispersive liquid-liquid microextraction

Dispersive liquid-liquid microextraction (DLLME) has also been used in speciation approaches. Speciation is achieved by introduction of an elemental specie-selective reagent, soluble in the non-polar phase. Ammonium pyrrolidine dithiocarbamate was introduced for

Cr (VI) retention at pH 2.0. Reduced volumes of 1-undecanol and ethanol and non-chloride solvents were used for the non-polar phase [61]. As mentioned before TXRF represents advantages for Green Chemistry since no eluents and carrier gases are needed. A DLLME-TXRF technique for preconcentration of inorganic Cr species (Cr(VI) and Cr(III)) in water samples was developed. To TXRF green characteristics were added those DLLME advantages [62].

4.2.2 Ionic liquids

Aqueous biphasic systems are a new promising liquid-liquid extraction method that usually composed of an aqueous phase and a hydrophobic phase. The hydrophobic phase can be composed of polymers, a polymer and a salt, or surfactants, named ILs. IN this sense, ABS is considered an environmentally friendly method, because volatile organic solvents are not used. IL can be task-specific, this mean they can be designed to extract individual chemical species. Recently 1-alkyl-3-methylimidazolium based ionic liquids combined with salicylate or thiosalicylate anions were used to form a stable ionic liquids (IL)/aqueous biphasic. It was found that the 1-octyl-3-methylimidazoliumsalicylate was selective to extract Cr(III) [63]. Another alternative was reported by Wang *et al.* [64], introducing a magnetic IL to an effervescent tablet for separation of As (V), by chelation with ammonium molybdate. Reduced reagents consumption was reported, along with ABS green-characteristics.

4.2.3 Deep eutectic solvents

Deep eutectic solvents are also used to reach elemental speciation, where a complexing reagent is added. In this context, sodium diethyldithiocarbamate (DDTC) was employed for

As (III) extraction with a DES composed of phenol and choline chloride [65]. DESs of different composition and 3,3'-diaminobenzidine were introduced for hydrophobic chelate of Se (IV) [66]. Complex matrix such as blood can also be prepared with DESs by agitation and freezing. A green solvent consisting of 1-octyl-3-methylimidazolium chloride and 1-undecanol was used for extraction of organic mercury (R-Hg) and inorganic mercury (Hg^{2+}) [67]. Ultrasound radiation can be introduced for extraction along with DESs to extract Hg^{2+} and CH_3Hg^+ . In this methodology, choline-phenol based DES was employed [68].

4.3 Gas-solid extraction

An alternative to typical liquid-solid extraction is gas-solid extraction. The latest avoid typical clogging and counter pressure problems of liquid-solid extractions, especially when NPs are used as sorbents. Speciation is reached by forming specific volatile species of the analyzed element. Mercury species were derivatized to their volatile species with NaBPH_4 and preconcentrated by headspace solid phase microextraction using porous carbons [69]. The system could be miniaturized, with low power, reagents and gases consumption. Another miniaturized system was described by Maratta *et al.* [70], by introduction of hybrid NPs (oxidized multiwall carbon nanotubes- TiO_2) in a needle trap device to preconcentrate Sb hydride. Besides miniaturization and low reagents consumption, this methodology does not requires gas carrier. The green sample preparation techniques described in this section are resumed in **Table 2**. The application of green chemistry metrics, based on the calculation of penalty points, as reported by different authors [71-74], is also added in the mentioned table.

5. Conclusions

The complete elimination of the sample preparation step from the analytical process would be always the ideal situation. However, this instance is still not feasible. Concepts like miniaturization, integration and simplification and automation are effective concepts that have contributed to solve some of the drawbacks of conventional sample preparation methods. Concerning the reagents used in the extraction steps, efforts should continue to be directed towards the evaluation of new solvents.

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References

- [1] E.A. Souza-Silva, R. Jiang, A. Rodríguez-Lafuente, E. Gionfriddo, J. Pawliszyn, A critical review of the state of the art of solid-phase microextraction of complex matrices I. Environmental analysis, *Trends Anal. Chem.* 71 (2015) 224–235.
- [2] R.L. Perez, G.M. Escandar, Experimental and chemometric strategies for the development of Green Analytical Chemistry (GAC) spectroscopic methods for the determination of organic pollutants in natural waters, *Sust. Chem. Pharm.* 4 (2016) 1-12.
- [3] A. Andrade-Eiroa, M. Canle, V. Leroy-Cancellieri, V. Cerdà, Solid-phase extraction of organic compounds: A critical review (Part I), *Trends Anal. Chem.* 80 (2016) 641–654.
- [4] NORMAN Network. Network of Reference Laboratories, Research Centers and Related Organizations for Monitoring of Emerging Environmental Substances. <http://www.norman-network.net/>, 2019 (accessed on February 2019).
- [5] M. Farré, L. Kantiani, M. Petrovic, S. Pérez, D. Barceló, Achievements and future trends in the analysis of emerging organic contaminants in environmental samples by mass spectrometry and bioanalytical techniques, *J. Chromatogr. A* 1259 (2012) 86– 99.
- [6] V. Pérez-Fernández, L. Mainero Rocca, P. Tomai, S. Fanali, A. Gentili, Recent advancements and future trends in environmental analysis: Sample preparation, liquid chromatography and mass spectrometry, *Anal. Chim. Acta* 983 (2017) 9-41.
- [7] A.A. Bletsou, J. Jeon, J. Hollender, E. Archontaki, N.S. Thomaidis, Targeted and non-targeted liquid chromatography-mass spectrometric workflows for identification of transformation products of emerging pollutants in the aquatic environment, *Trends Anal. Chem.* 66 (2015) 32-44.

[8] M. La Farré, Y. Picó, D. Barceló, Application of ultra-high pressure liquid chromatography linear ion-trap orbitrap to qualitative and quantitative assessment of pesticide residues, *J. Chromatogr. A* 1328 (2014) 66-79.

[9] F.R.P. Rocha, L.S.G. Teixeira, J.A. Nóbrega, Green Strategies in Trace Analysis: A Glimpse of Simple Alternatives for Sample Pretreatment and Analyte Determination, *Spectrosc Lett.* 42 (2009) 418-429.

*[10] K.M. Dimpe, P.N. Nomngongo, Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices, *Trends Anal. Chem.* 82 (2016) 199–207.

A revision of new strategies for the determination of emerging pollutants in environmental matrices is detailed. Advantages and drawbacks of the different strategies are given.

*[11] J. Płotka-Wasyłka, M. Rutkowska, K. Owczarek, M. Tobiszewski, J. Namiesnik, Extraction with environmentally friendly solvents, *Trends Anal. Chem.* 91 (2017) 12-25.

A complete summary of the most promising and most widely used green extraction solvents for compounds at trace levels is described in this review.

[12] D. Ge, Y. Zhang, Y. Dai, S. Yang, Air-assisted dispersive liquid-liquid microextraction based on a new hydrophobic deep eutectic solvent for the preconcentration of benzophenone-type UV filters from aqueous samples, *J. Separ. Sci.* 41 (2018) 1635-1643.

[13] H. Zeng, K. Qiao, X. Li, M. Yang, S. Zhang, R. Lu, J. Li, H. Gao, W. Zhou, Dispersive liquid-liquid microextraction based on the solidification of deep eutectic solvent for the determination of benzoylureas in environmental water samples, *J. Separ. Sci.* 40 (2017) 4563-4570.

[14] M. Vian, C. Breil, L. Vernes, E. Chaabani, F. Chemat, Green solvents for sample preparation in analytical chemistry, *Curr. Opin. Green Sustain. Chem.* 5 (2017) 44-48.

[15] S.C. Cunha, J.O. Fernandes, Extraction techniques with deep eutectic solvents, *Trends Anal. Chem.* 105 (2018) 225-239.

[16] I. Rykowska, J. Ziemblińska, I. Nowak, Modern approaches in dispersive liquid-liquid microextraction (DLLME) based on ionic liquids: A review, *J. Mol. Liq.* 259 (2018) 319-339.

[17] B. Hashemi, P. Zohrabi, K-H. Kim, M. Shamsipur, A. Deep, J. Hong, Recent advances in liquid-phase microextraction techniques for the analysis of environmental pollutants, *Trends Anal. Chem.* 97 (2017) 83-95.

*[18] M. Guíñez, C. Bazán, L.D. Martinez, S. Cerutti, Determination of nitrated and oxygenated polycyclic aromatic hydrocarbons in water samples by a liquid-liquid phase microextraction procedure based on the solidification of a floating organic drop followed by solvent assisted back-extraction and liquid chromatography-tandem mass spectrometry, *Microchem. J.* 139 (2018) 164-173.

An original DLLME-SFO-SBE strategy for extraction/enrichment of nitro and oxy-PAHs present in drinking and lake water samples was developed. A simple methodology consisting in a minimum volume of extracting solvent, short time, efficient recoveries and quantitative enrichment factors was presented.

[19] R. Canales, M. Guíñez, C. Bazán, M. Reta, S. Cerutti, Determining heterocyclic aromatic amines in aqueous samples: A novel dispersive liquid-liquid micro-extraction method based on solidification of floating organic drop and ultrasound assisted back extraction followed by UPLC-MS/MS, *Talanta* 174 (2017) 548-555.

- [20] H. Qian, L. Hu, C. Liu, H. Wang, H. Gao, W. Zhou, Determination of four pyrethroid insecticides in water samples through membrane emulsification-assisted liquid–liquid microextraction based on solidification of floating organic droplets, *J. Chromatogr. A* 1559 (2018) 86–94.
- [21] J. Płotka-Wasyłka, K. Owczarek, J. Namieśnik, Modern solutions in the field of microextraction using liquid as a medium of extraction, *Trends Anal. Chem.* 85 (2016) 46–64.
- [22] S. Armenta, S. Garrigues, M. de la Guardia, The role of green extraction techniques in Green Analytical Chemistry, *Trends Anal. Chem.* 71 (2015) 2–8.
- [23] S. Armenta, S. Garrigues, F.A. Steve-Turrilas, M. de la Guardia, Green extraction techniques in green analytical chemistry, *Trends Anal. Chem.* 116 (2019) 248–253.
- [24] M.E.S. Padrón, C. Afonso-Olivares, Z. Sosa-Ferrera, J.J. Santana-Rodríguez, Microextraction techniques coupled to liquid chromatography with mass spectrometry for the determination of organic micropollutants in environmental water samples, *Molecules* 19 (2014) 10320–10349.
- [25] D.B. Giulia, Development of advanced analytical methods for the determination of emerging pollutants in environmental waters, *J. Sep. Sci.* 32 (2009) 1249–1261.
- [26] S. Risticvic, V.H. Niri, D. Vuckovic, J. Pawliszyn, Recent developments in solid phase microextraction, *Anal. Bioanal. Chem.* 393 (2009) 781–795.
- [27] S. Wang, K.D. Oakes, L.M. Bragg, J. Pawliszyn, G. Dixon, M.R. Servos, Validation and use of in vivo solid phase micro-extraction (SPME) for the detection of emerging contaminants in fish, *Chemosphere* 85 (2011) 1472–1480.
- [28] L. Vallecillos, E. Pocurull, F. Borrull, A simple and automated method to determine macrocyclic musk fragrances in sewage sludge samples by headspace solid-phase

microextraction and gas chromatography–mass spectrometry, *J. Chromatogr. A* 1314 (2013) 38–43.

[29] L.M. Madikizela, S. Ncube, L. Chimuka, Recent developments in selective materials for solid phase extraction, *Chromatographia* (2018) 1-19. <https://doi.org/10.1007/s10337-018-3644-8>.

[30] S. Seidi, Y. Yamini, M. Rezazadeh, Electrochemically assisted solid based extraction techniques: A review, *Talanta* 132 (2015) 339-353.

[31] R. Esfandiarnjad, H. Sereshti, Designing an absolutely solvent-free binary extraction system as a green strategy for ultra-trace analysis of chlorophenols, *Microchem. J.* 146 (2019) 701-707.

[32] D. Wianowska, M. Gil, New insights into the application of MSPD in various fields of analytical chemistry, *Trends Anal. Chem.* 112 (2019) 29-51.

[33] H. Matusiewicz, Sample decomposition techniques in inorganic trace elemental analysis, in *Handbook of Trace Analysis: Fundamentals and Applications*, Springer International Publishing, 2016, pp. 75-122.

[34] P.H. Pacheco, R.A. Gil, L.D. Martínez, P. Smichowski, Preconcentration, speciation, and determination of key elements in biological samples in Latin America, *Anal. Bioanal. Chem.* 405 (2013) 7563-7571.

[35] M. Tobiszewski, A. Mechlińska, B. Zygmunt, J. Namieśnik, Green analytical chemistry in sample preparation for determination of trace organic pollutants, *Trends Anal. Chem.* 28 (2009) 943-951.

[36] B. Welz, D.L.G. Borges, F.G. Lepri, M.G.R. Vale, U. Heitmann, High-resolution continuum source electrothermal atomic absorption spectrometry - An analytical and

diagnostic tool for trace analysis, *Spectrochim. Acta Part B At. Spectrosc.* 62 (2007) 873-883.

[37] C. Bendicho, I. Lavilla, F. Pena-Pereira, V. Romero, Green chemistry in analytical atomic spectrometry: A review, *J. Anal. Atom. Spectrom.* 27 (2012) 1831-1857.

[38] L.D. Martínez, R.A. Gil, P.H. Pacheco, S. Cerutti, Elemental composition analysis of food by FAES and ICP-OES in *Handbook of Mineral Elements in Food*, Wiley, 2015, pp. 219-238.

[39] S. Cerutti, R.A. Gil, P.H. Pacheco, D. Gómez, P. Smichowski, L.D. Martínez, *Sample Preservation and Measurement Techniques for the Determination of Air Quality in Comprehensive Analytical Chemistry*, Elsevier, 2016, pp. 233-265.

[40] M. Savio, S. Cerutti, L.D. Martinez, P. Smichowski, R.A. Gil, Study of matrix effects and spectral interferences in the determination of lead in sediments, sludges and soils by SR-ETAAS using slurry sampling, *Talanta* 82 (2010) 523-527.

[41] M. Savio, R.A. Olsina, L.D. Martinez, P. Smichowski, R.A. Gil, Determination of Pb in airborne particulate matter with a heavy matrix of silicon by SR-ETAAS, *Microchem. J.* 96 (2010) 243-246.

[42] F. Moyano, E. Verni, H. Tamashiro, S. Digenaro, L.D. Martinez, R.A. Gil, Single-step procedure for trace element determination in synovial fluid by dynamic reaction cell-inductively coupled plasma mass spectrometry, *Microchem. J.* 112 (2014) 17-24.

[43] E.R. Verni, A. Londonio, C. Bazán, E. Strasser, E. Perino, R.A. Gil, REE profiling in basic volcanic rocks after ultrasonic sample treatment and ICPMS analysis with oxide ion formation in ICP enriched with O₂, *Microchem. J.* 130 (2017) 14-20.

- [44] C. Ruberto, A. Mazzinghi, M. Massi, L. Castelli, C. Czelusniak, L. Palla, N. Gelli, M. Betuzzi, A. Impallaria, R. Brancaccio, E. Peccenini, M. Raffaelli, Imaging study of Raffaello's "La Muta" by a portable XRF spectrometer, *Microchem. J.* 126 (2016) 63-69.
- [45] N. Antonopoulou-Athera, E. Chatzitheodoridis, A. Terlix, M. Doulgerides, A.A. Serafetinides, Reconstructing the colour palette of the Konstantinos Parthenis' burnt paintings, *Spectrochim. Acta Part A* 201 (2018) 315-327.
- [46] A. Botto, B. Campanella, S. Legnaioli, M. Lezzerini, G. Lorenzetti, S. Pagnotta, F. Poggialini, V. Palleschi, Applications of laser-induced breakdown spectroscopy in cultural heritage and archaeology: A critical review, *J. Anal. Atom. Spectrom.* 34 (2019) 81-103.
- [47] J. Colwell, P. Hsiao, W. Zhang, X. Wang, R. Akter, A. Lennon, Laser ablation ICP-MS for detection of substrate contamination from plated metal contacts in silicon solar cells, *J. Anal. Atom. Spectrom.* 33 (2018) 422-430.
- [48] N. Ahmed, Z.A. Umar, R. Ahmed, M. Aslam Baig, On the elemental analysis of different cigarette brands using laser induced breakdown spectroscopy and laser-ablation time of flight mass spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 136 (2017) 39-44.
- [49] H. Ahmad, A. Ahmad, S.S. Islam, Magnetic Fe₃O₄@poly(methacrylic acid) particles for selective preconcentration of trace arsenic species, *Microchim. Acta* 184 (2017) 2007-2014.
- *[50] K. Huang, K. Xu, J. Tang, L. Yang, J. Zhou, X. Hou, C. Zheng, Room Temperature Cation Exchange Reaction in Nanocrystals for Ultrasensitive Speciation Analysis of Silver Ions and Silver Nanoparticles, *Anal. Chem.* 87 (2015) 6584-6591.

Cd-Te ionic nanocrystals (NCs) were “bombarded-and-exploded” (exchanged) with Ag⁺ for speciation analysis of Ag⁺ and Ag-nanoparticles. Signal amplification sampling via chemical vapor generation allowed the obtention of outstanding detection limits.

[51] A. Baranik, A. Gagor, I. Queralt, E. Marguí, R. Sitko, B. Zawisza, Determination and speciation of ultratrace arsenic and chromium species using aluminium oxide supported on graphene oxide, *Talanta* 185 (2018) 264-274.

[52] Naeemullah, M. Tuzen, T.G. Kazi, A new portable micropipette tip-syringe based solid phase microextraction for the determination of vanadium species in water and food samples, *J. Ind. Eng. Chem.* 57 (2018) 188-192.

[53] D. Deng, S. Zhang, H. Chen, L. Yang, H. Yin, X. Hou, C. Zheng, Online solid sampling platform using multi-wall carbon nanotube assisted matrix solid phase dispersion for mercury speciation in fish by HPLC-ICP-MS, *J. Anal. Atom. Spectrom.* 30 (2015) 882-887.

[54] E. Lukojko, E. Talik, A. Gagor, R. Sitko, Highly selective determination of ultratrace inorganic arsenic species using novel functionalized miniaturized membranes, *Anal. Chim. Acta* 1008 (2018) 57-65.

[55] C. Wang, M. He, B. Chen, B. Hu, Polymer monolithic capillary microextraction on-line coupled with ICP-MS for determination of inorganic selenium species in natural waters, *Talanta* 188 (2018) 736-743.

[56] R. Sitko, P. Janik, B. Zawisza, E. Talik, E. Margui, I. Queralt, Green approach for ultratrace determination of divalent metal ions and arsenic species using total-reflection x-ray fluorescence spectrometry and mercapto-modified graphene oxide nanosheets as a novel adsorbent, *Anal. Chem.* 87 (2015) 3535-3542.

- [57] L. Li, Z. Wang, S. Zhang, M. Wang, Directly-thiolated graphene based organic solvent-free cloud point extraction-like method for enrichment and speciation of mercury by HPLC-ICP-MS, *Microchem. J.* 132 (2017) 299-307.
- [58] P. Janik, B. Zawisza, E. Talik, R. Sitko, Selective adsorption and determination of hexavalent chromium ions using graphene oxide modified with amino silanes, *Mikrochim. Acta* 185 (2018) 117-124.
- [59] R.A. Campos, P.R. Patricio, S.J.R. Vargas, L.H.M. Da Silva, M.C. Hespanhol, Green speciation of iron using aqueous two-phase system, *An. Acad. Bras. Ciênc.* 90 (2018) 1929-1944.
- [60] E. Covaci, S.B. Angyus, M. Senila, M. Ponta, E. Darvasi, M. Frentiu, T. Frentiu, Eco-scale non-chromatographic method for mercury speciation in fish using formic acid extraction and UV-Vis photochemical vapor generation capacitively coupled plasma microtorch optical emission spectrometry, *Microchem. Journal* 141 (2018) 155-162.
- [61] D.S. Porto, N. Akiba, M.A.L. De Oliveira, I. Gaubeur, Speciation of chromium in water samples after dispersive liquid-liquid microextraction, and detection by means of high-resolution continuum source atomic absorption spectrometry, *J. Braz. Chem. Soc.* 28 (2017) 266-276.
- [62] Z. Bahadir, V.N. Bulut, M. Hidalgo, M. Soylak, E. Marguá, Cr speciation in water samples by dispersive liquid-liquid microextraction combined with total reflection X-ray fluorescence spectrometry, *Spectrochim. Acta Part B At. Spectrosc.* 115 (2016) 46-51.
- [63] S. Sadeghi, A.Z. Moghaddam, Chromium speciation using task specific ionic liquid/aqueous phase biphasic system combined with flame atomic absorption spectrometry, *J. Mol. Liq.* 221 (2016) 798-804.

[64] X. Wang, G. Xu, X. Guo, X. Chen, J. Duan, Z. Gao, B. Zheng, Q. Shen, Effervescent tablets containing magnetic ionic liquids as a non-conventional extraction and dispersive agent for speciation of arsenite and arsenate in vegetable samples, *J. Mol. Liq.* 272 (2018) 871-877.

*[65] R.A. Zounr, M. Tuzen, M.Y. Khuhawar, Ultrasound assisted deep eutectic solvent based on dispersive liquid liquid microextraction of arsenic speciation in water and environmental samples by electrothermal atomic absorption spectrometry, *J. Mol. Liq.* 242 (2017) 441-446.

A deep eutectic solvent was used in combination with sodium diethyldithiocarbamate (DDTC) for the green extraction and speciation of As (III) and As (V) in water samples.

[66] A.H. Panhwar, M. Tuzen, T.G. Kazi, Ultrasonic assisted dispersive liquid-liquid microextraction method based on deep eutectic solvent for speciation, preconcentration and determination of selenium species (IV) and (VI) in water and food samples, *Talanta* 175 (2017) 352-358.

[67] R. Akramipour, M.R. Golpayegani, S. Gheini, N. Fattahi, Speciation of organic/inorganic mercury and total mercury in blood samples using vortex assisted dispersive liquid-liquid microextraction based on the freezing of deep eutectic solvent followed by GFAAS, *Talanta* 186 (2018) 17-23.

[68] A. Thongsaw, Y. Udnan, G.M. Ross, W.C. Chaiyasith, Speciation of mercury in water and biological samples by eco-friendly ultrasound-assisted deep eutectic solvent based on liquid phase microextraction with electrothermal atomic absorption spectrometry, *Talanta* 197 (2019) 310-318.

[69] Y. Lin, Y. Yang, Y. Li, L. Yang, X. Hou, X. Feng, C. Zheng, Ultrasensitive Speciation Analysis of Mercury in Rice by Headspace Solid Phase Microextraction Using Porous

Carbons and Gas Chromatography-Dielectric Barrier Discharge Optical Emission Spectrometry, *Environ. Sci. Technol.* 50 (2016) 2468-2476.

*[70] A. Maratta, B. Carrizo, V.L. Bazán, G. Villafañe, L.D. Martínez, P. Pacheco, Antimony speciation analysis by hydride trapping on hybrid nanoparticles packed in a needle trap device with electro-thermal atomic absorption spectrometry determination, *J Anal At Spectrom.* 33 (2018) 2195-2202.

Novel hybrid nanoparticles (oxidized multiwall carbon nanotubes-TiO₂) were packed in a needle trap device to retain volatile Sb specie.

[71] A. Gałuszka, Z.M. Migaszewski, P. Konieczka, J. Namieśnik, Analytical eco-scale for assessing the greenness of analytical procedures, *Trends Anal. Chem.* 37 (2012) 61–72.

[72] M. Tobiszewski, M. Marć, A. Gałuszka, J. Namieśnik, Green chemistry metrics with special reference to green analytical chemistry, *Molecules* 20 (2015) 10928-10946.

[73] M. Tobiszewski, Metrics for green analytical chemistry, *Analytical Methods* 8 (2016) 2993-2999.

[74] A. Kurowska-Susdorf, M. Zwierdzynski, A. Martinovi Bevanda, S. Talic, A. Ivankovi, J. Płotka-Wasyłka, Green analytical chemistry: Social dimension and teaching, *Trends Anal. Chem.* 111 (2019) 185-196.

Figure captions

Figure 1. Milestones in the green sample preparation field.

Figure 2. General classification of sample treatment strategies for organic and elemental compounds in environmental samples.

Figure 3. Comparison of regular strategies and green strategies for sample preparation and determination for speciation analysis. A: Free of organic solvent, low reagent consumption; B, Miniaturization; C, low power, no carrier gas. M: minicolumn; NTD: Needle Trap Device; FAAS, Flame Atomic Absorption Spectroscopy; EDXRF: Energy dispersive X-ray fluorescence spectrometry.

Table 1. Comparison of green and classic sample treatment strategies.

Green sample treatment strategies	Classic sample treatment strategies
Elemental analysis	
Solid sampling <ul style="list-style-type: none"> - Free of acid consumption - Free of heating programs - No waste generation In situ analysis <ul style="list-style-type: none"> - No sample preparation 	Wet acid digestion <ul style="list-style-type: none"> - Acid consumption. - High energy consumption for heating. - Emission of vapors and gases to the air. - Elevated waste generation
Speciation analysis	
Green Extraction <ul style="list-style-type: none"> - Free or reduced organic solvents - Miniaturization - No carrier gas - No elution step 	Classic extraction <ul style="list-style-type: none"> - High organic solvents consumption - Emission of vapors and gases to the air. - Elevated waste generation
Organic analysis	
Advantages when compared with traditional alternatives.	
<ul style="list-style-type: none"> • Reduction <ul style="list-style-type: none"> - Amount of sample - Volume of reagents - Chemicals (and they are obtained from renewable sources) - Time of analysis and complexity - Energy saving - Waste generation (on-line waste treatment) • Minimization <ul style="list-style-type: none"> - Risks of contamination, analytes losses and operator exposition • Procedures <ul style="list-style-type: none"> - Simplification, automation • Equipment <ul style="list-style-type: none"> - On-line procedures and on-field analysis. - Portable equipment and integrated systems. 	

Table 2. Green sample preparation techniques for speciation analysis.

Sorbent / extractant	Determination technique	Elemental specie	Green characteristic	PPs*	Reference
SOLID-LIQUID EXTRACTION					
Fe ₃ O ₄ @Poly-Methacrylic acid	HG-MP AES ¹	As III, As V	Reduced organic solvent	12	32
Cd-Te nanocrystals	ICP MS ²	Ag ⁺	Free of organic solvent	19	33
(Al ₂ O ₃ /Graphene oxide)	EDXRF ³	As V, Cr III	Free of organic solvent	20	34
Tetra ethylene pentamine functionalized multiwalled carbon nanotubes	ETAAS ⁴	V V	Miniaturization	18	35
Multiwalled carbon nanotubes	LC ⁵ -ICP MS ²	Hg ²⁺ , CH ₃ Hg ⁺	Reduced organic solvent	16	36
Amorphous silica coating on cellulose fibers modification with (3-mercaptopropyl)-trimethoxysilane	EDXRF ³	As III	No elution step, Miniaturization, Free of organic solvent, low power, no carrier gas	16	37
Ethylenediamine modified poly(glycidyl methacrylate-ethylene dimethacrylate)	ICP MS ²	Se VI	Free of organic solvent, low reagent consumption	10	38
3- mercaptopropyl trimethoxysilane on a graphene oxide	TRXRF ⁶	Arsenite	No elution step Free of organic solvent	18	39
Thiolated graphene oxide	LC ⁵ -ICP MS ²	Hg ²⁺ , CH ₃ Hg ⁺	Free of organic solvent	14	40
Graphene oxide-amino silanes	EDXRF ³	Cr VI	Free of organic solvent	20	41
LIQUID-LIQUID EXTRACTION					
1,10-phenanthroline in polymer rich phase	FAAS ⁷	Fe II	Free of organic solvent	6	42
Formic acid	HG-MP AES ¹	Hg ²⁺ , CH ₃ Hg ⁺	Miniaturization	16	43
Ammonium pyrrolidine dithiocarbamate 1-undecanol and ethanol	HR CS AAS ⁸	Cr VI	Non chloride solvents, Miniaturization	19	44
Ammonium pyrrolidine dithiocarbamate in methanol and CCl ₄	TRXRF ⁶	Cr VI Cr III	Miniaturization, Free of organic solvent, No carrier gas	16	45
1-octyl-3-methylimidazoliumsalicylate	FAAS ⁷	Cr III	Free of organic solvent	14	46
[(C ₄ mim)(FeCl ₄)]-Ammonium molybdate	ETAAS ⁴	As V	Free of organic solvent, low reagent consumption	15	47
Sodium diethyldithiocarbamate-Phenol/choline chloride	ETAAS ⁴	As III	Free of organic solvent	20	48
3,3'-diaminobenzidine- different deep eutectic solvents	ETAAS ⁴	Se IV	Free of organic solvent	20	49
1-octyl-3-methylimidazolium chloride / 1-undecanol	ETAAS ⁴	Hg ²⁺ , RHg ⁺	Free of organic solvent	8	50
SOLID-GAS EXTRACTION					

Porous carbon	GC ⁹	Hg ²⁺ , RHg ⁺	Miniaturization, low power, no carrier gas	12	51
Multiwalled carbon nanotubes – TiO ₂	ETAAS ⁴	Sb III	Miniaturization, no carrier gas	14	52

*Penalty Points [71].

¹ HG-MP AES: Hydride generation - Microwave Plasma Atomic Emission Spectrometry

² ICP MS: Inductively Coupled Plasma Mass Spectrometry

³ EDXRF: Energy dispersive X-ray fluorescence spectrometry

⁴ ETAAS: Electrothermal Atomic Absorption Spectrometry

⁵ LC: Liquid Chromatography

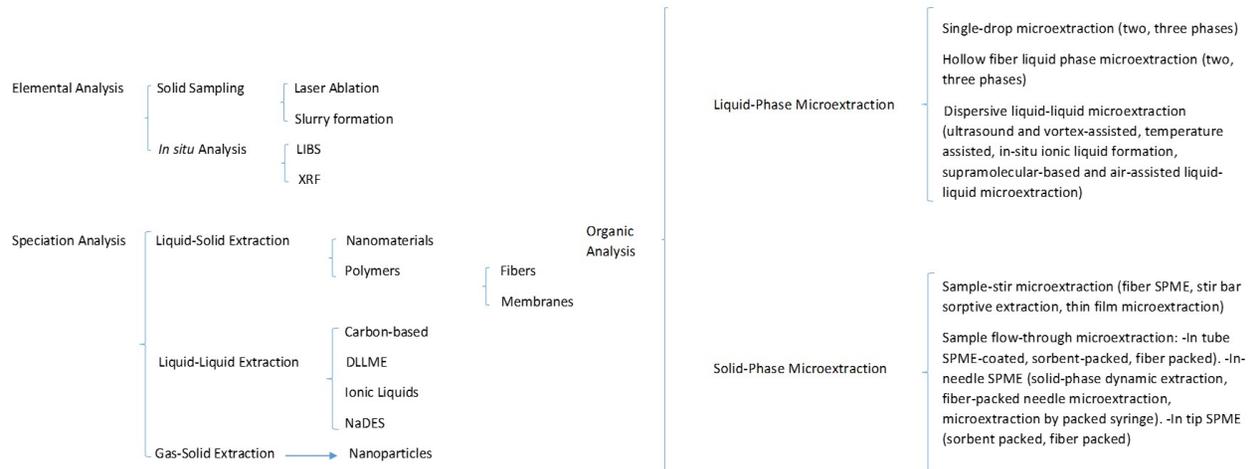
⁶ TRXRF: Total reflection X-ray fluorescence spectrometry

⁷ FAAS: Flame Atomic Absorption Spectrometry

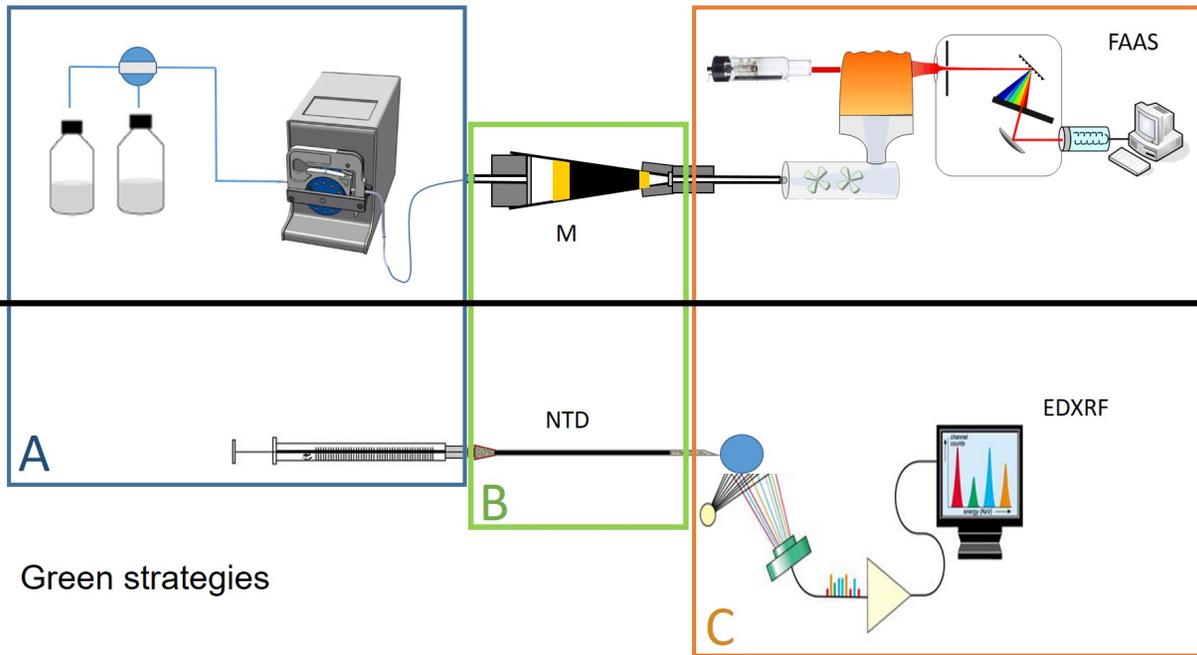
⁸ HR CS AAS: High Resolution Continuum Source Spectroscopy

⁹ GC: Gas Chromatography

1971	<ul style="list-style-type: none">• Polymer fibers sorbents
1972	<ul style="list-style-type: none">• Polymer membranes sorbents• Nanomaterials sorbents
1985	<ul style="list-style-type: none">• Microwave-assisted extraction• Supercritical fluid extraction
1987	<ul style="list-style-type: none">• Carbon-based sorbents
1988	<ul style="list-style-type: none">• Ionic liquids
1990	<ul style="list-style-type: none">• Solid phase extraction
1991	<ul style="list-style-type: none">• Cloud point extraction• Slurry digestion
1993	<ul style="list-style-type: none">• Head-space SPME• Molecularly imprinted solid-phase extraction
1994	<ul style="list-style-type: none">• Pressurized assisted-solvent extraction
1995	<ul style="list-style-type: none">• Laser ablation
1996	<ul style="list-style-type: none">• Lab-on-a-chip
1998	<ul style="list-style-type: none">• Ultrasound-assisted extraction
1999	<ul style="list-style-type: none">• Magnetic solid-phase extraction
2000	<ul style="list-style-type: none">• Lab-on-valve
2001	<ul style="list-style-type: none">• Single drop microextraction
2003	<ul style="list-style-type: none">• Hollow-fiber liquid-phase microextraction
2006	<ul style="list-style-type: none">• Dispersive liquid-liquid microextraction• Polymer-functionalized magnetic materials
2007	<ul style="list-style-type: none">• Multi-walled carbon nanotubes magnetic particles
2011	<ul style="list-style-type: none">• Natural deep eutectic solvents
2013	<ul style="list-style-type: none">• Nanoparticles for gas sorption• Parallel artificial liquid membrane extraction
2014	<ul style="list-style-type: none">• Lab-on-skin
2018	<ul style="list-style-type: none">• Ultrasound-assisted solvent extraction of porous membrane packed solid



Regular strategies



Declarations of interest: none

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