

# Accepted Manuscript

Title: The role of green extraction techniques in green analytical chemistry

Author: Sergio Armenta, Salvador Garrigues, Miguel de la Guardia

PII: S0165-9936(15)00131-4

DOI: <http://dx.doi.org/doi:10.1016/j.trac.2014.12.011>

Reference: TRAC 14444

To appear in: *Trends in Analytical Chemistry*



Please cite this article as: Sergio Armenta, Salvador Garrigues, Miguel de la Guardia, The role of green extraction techniques in green analytical chemistry, *Trends in Analytical Chemistry* (2015), <http://dx.doi.org/doi:10.1016/j.trac.2014.12.011>.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# The role of green extraction techniques in Green Analytical Chemistry

Sergio Armenta, Salvador Garrigues, Miguel de la Guardia

*Department of Analytical Chemistry, University of Valencia, Research Building "Jeroni Muñoz", Dr. Moliner str., 46100 – Burjassot (Valencia), Spain*

## HIGHLIGHTS

- Green extraction methods are evaluated on the frame of Green Analytical Chemistry
- Analyte extraction is identified as a critical step
- Microextraction techniques are basic tools to greening sample treatment

## ABSTRACT

Greening extraction techniques to improve the sensitivity and the selectivity of analytical methods is the sustainable alternative to classical sample-preparation procedures used in the past. In this update, we review the main strategies employed in the scientific literature to reduce deleterious side-effects of extraction techniques. We demonstrate that the evolution of sample-treatment procedures is focused on the simultaneous improvement of the main analytical features of the method and its practical aspects, including the economic case.

### *Keywords:*

Green Analytical Chemistry  
Extraction  
Liquid-liquid extraction  
Microextraction  
Sample preparation  
Selectivity  
Sensitivity  
Side-effect  
Solid-phase extraction  
Sustainability

Corresponding author. Tel.: +34 96 354 4838; Fax: +34 96 354 4845.

*E-mail address:* miguel.delaguardia@uv.es (M. de la Guardia)

## 1. The Green Wave

In a changing world, with the tremendous impact of human presence, the urgent need for sustainability of all of our activities has accelerated the evolution from the chemurgical paradigm to the ecological paradigm in which the environmental side effects of our chemical activities must be seriously taken into consideration [1]. Green Chemistry [2–4] and Green Analytical Chemistry (GAC) [5–9] evolved from the academic sphere to the real world, so there is a tremendous research activity on greening all aspects concerning the analysis of any kinds of sample, not only those for environmental studies. We are absolutely convinced that GAC will be really useful in the years ahead. The application of cheap, fast and environmentally safe procedures in environmental, clinical and food analysis will improve the quality of life in developing countries [10]. So, it can be seen that GAC has been the key tool to move from the chemurgical paradigm to the ecological paradigm in analytical chemistry and to create

sustainable tools for challenges in the increasing demand in analysis for a clever combination of environment-friendly and cheap methodologies (see Fig. 1).

Based on the 12 principles of GAC [11], many green methods were proposed in recent years, and scientific journals have published special issues regarding GAC practice in research and applied laboratories, as can be observed in Table 1, so creating a wave that modified the concepts and the practice of analysis.

In summary, GAC has been well accepted by the scientific community. However, the change from qualitative to quantitative observation of the green character of analytical methodologies has evolved much more slowly than the scientific production in the field. In this sense, Life Cycle Assessment (LCA), a holistic tool encompassing all environmental exchanges (i.e., resources, energy, emissions, and waste) occurring during all stages of the life cycle of activities, is a useful tool, especially when applied to products or services for which the life-cycle concept and its stages are clearly defined [12]. An additional semi-quantitative criterion was developed by the Green Chemistry Institute (GCI) of the American Chemical Society (ACS). The criterion was applied to the National Environmental Methods Index (NEMI), a free Internet-searchable database of environmental methods [13]. The profile criterion was based on four key terms concerning reagents employed as:

- (1) persistent, bioaccumulative and toxic (PBT);
- (2) hazardous;
- (3) corrosive; and,
- (4) the amount and the nature of waste.

A similar criterion includes energy as a key point to be considered [14]. The addition of energy as a criterion is important due to the high reliance on non-renewable resources for production of electrical energy.

In recent years, an ecological scale was developed for the evaluation of analytical methods based on the introduction of penalty points [15]. According to it, a 100 score corresponds to a completely eco-friendly methodology, but subtracting penalty points of the method due to the volume and the toxicity of reagents consumed, energy consumed, emissions, operator hazard and waste generation. Methods are classified according to the eco-scale as:

- excellent green analysis (> 75 points);
- acceptable green analysis (> 50 points); and,
- inadequate green analysis (<50 points).

More recently, a new criterion was proposed to relate the penalty-point values to the volumes of reagents consumed and wastes generated using mathematical expressions and to associate the eco-scale value to a category class (A–G) in a so-called Green Certificate [16].

## 2. Greening analytical procedures

Remote sensing and direct measurements on untreated samples are the green dream of analysts and many strategies have been developed for the analysis of target compounds based on the use of spectroscopy and electroanalytical signals [17] and image processing [18]. However, in most analytical methodologies, sample treatment is an unavoidable step and the use of a classical methodology, similar to that in Fig. 2 (sampling, sample transport and sample preparation before the acquisition of analytical measurements) is absolutely necessary. Typical sample-treatment methods include homogenization, filtration, centrifugation, clean-up, analyte extraction, preconcentration and/or derivatization. On evaluating the environmental impact of methods, sample preparation is, by far, the most challenging step regarding both the main features and the green parameters of the methods. Sample dissolution and analyte extraction involve the use of reagents and energy, and special care must be taken to select the procedure as

simple as possible at room temperature, and the least hazardous reagents. In this context, options for greening methods must be based on avoidance of the use of toxic reagents and a strong reductions in consumption of energy and reagents, waste generation, time taken and operator effort. As a result, minimization and automation have been the basic tools for greening the analytical methods.

### 3. Facing the problem of sample treatment

Sample treatment has been the focus of intensive research from the GAC perspective in the past 20 years, since it is the bottleneck of analytical procedures.

It is worth stressing that the 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. The sample-treatment step must guarantee a quantitative recovery of target analytes, avoiding contamination and providing matrix isolation as far as possible, in order to reduce potential interferences and matrix effects during the measurement step.

We should notice that there is no universal sample-preparation technique suitable for all types of sample, and that sample preparation depends on the matrix, the nature of analytes and the final measurement mode. Moreover, an appropriate method for a target analyte may not be good for comprehensive screening of compounds.

In recent years, sample-preparation methodologies evolved from hard strategies to soft methods based on room-temperature, ultrasound-assisted leaching [19–21] or microwave-assisted digestion using closed systems [22–24], so providing a fast, safe methodology, especially for sample digestion and sample dissolution.

Analyte extraction has the double purpose of matrix isolation and analyte preconcentration, and the appropriate selection of solvents and reagents and the control of the preconcentration process are absolutely necessary in order to:

- separate quantitatively the target analyte from the matrix; and,
- increase the concentration level of the target analyte in the final solution to be measured.

Sometimes, solid samples are difficult to analyze due to the need to transfer the target analytes to a liquid phase. Leaching the analyte (i.e., solid–liquid extraction or lixiviation) is one of the easiest, most widely used sample treatments. Classically, leaching has been widely carried out by maceration, based on the correct choice of solvents and the use of room temperature or controlled temperature and/or agitation to increase the solubility of compounds and the rate of mass transfer. In general, heating the system increases the solubilization power of the reagents or solvents used, but involves environmental side-effects (i.e., energy consumption). Despite the extensive use of leaching, it is characterized by long extraction protocols with low efficiency.

In 1879, Franz von Soxhlet developed Soxhlet extraction, which is the most widely used leaching technique [25]. Soxhlet extraction is a primary reference against which performance in new leaching methods is measured. It is still an attractive option for routine analysis because of its general robustness and relatively low cost. The Soxhlet system is simple and easy to use, and it enables the use of a large amount of sample (i.e., 1–100 g). However, the main drawbacks are long extraction times and large amounts of solvent required, which also mean that the solvent must be evaporated to concentrate the analytes before their determination [26].

However, when samples are water or aqueous solutions with a complex matrix (e.g., wastewater or seawater, body fluids or juices) it can be necessary to move from the original solution to a new phase using immiscible solvents or solid phases, suitable to extract the analytes selectively.

In short, there are several strategies proposed in the literature for analyte extraction [27,28], involving liquid-liquid extraction (LLE) [29-31] and solid-phase extraction

(SPE) [32,33]. LLE and SPE are the most widely used techniques for the extraction of liquid samples. In the first type, an appropriate selection of the extraction solvent permits removal of the analyte from the original solution to the new phase, directly or after a previous derivatization.

From our point of view, SPE is probably the best option to improve analyte concentration and to separate it from a complex matrix. Generally, SPE consists of four steps:

- 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.

The most common design applied in SPE is the polypropylene cartridge with placed sorption phase, which vary in size from micro-sized disks in 1 mL syringes to 6 mL syringes. SPE can manage relatively high volumes of samples for analyte preconcentration being suitable to be eluted on-line with microliters of an appropriate solvent to do their determination.

The sample preparation step can be performed off-line, at-line or on-line. At-line procedures are performed with a robotic system or autosampler and no manual preparation is required, which is the case of off-line systems. On the other hand, on-line procedures combine directly the sample preparation step with the measurement mode, usually via a multiport valve.

#### 4. Green extraction solutions

Fig. 3 shows, as a scheme, the different variables to be considered on greening the extraction steps which, in short, involve the nature and amount of used reagents and the reduction of the energy employed for extraction.

As it has been aforementioned, leaching of the analyte from a solid sample is one of the easiest and most widely used sample treatments. As a consequence, a variety of sample preparation methods have been developed over the past decades with the objective to improve the extraction performance as well as to reduce overall analysis time and cost. Recent developments based on ultrasound assisted treatments [34,35] enhance the solid-liquid equilibrium, reducing the extraction time. Ultrasonic energy causes an effect known as cavitation, which generates numerous tiny bubbles in liquid media and mechanical erosion of solids, including particle rupture. Sonication provides an efficient contact between the solid and the extractant, usually resulting in a good recovery of the analyte [36].

On the other hand, there are no doubts on the need of a quantitative evaluation of the energy requirements of extraction steps and it is one reason to look for greener alternatives to traditional Soxhlet [37]. Pressurized liquid extraction (PLE), also named accelerated solvent extraction (ASE) [38-40] and microwave-assisted extraction (MAE) are techniques that can be used instead of Soxhlet for the extraction of organic compounds, providing a clear improvement of the extraction processes based on a drastic reduction of time and temperature and solvent requirements.

Moreover, different alternatives combining the different strategies previously commented have been developed to overcome the main drawbacks of the Soxhlet extraction. For instance, high-pressure Soxhlet extraction in which the extractants do not reach supercritical conditions and the time required and the solvents consumed are drastically reduced [41]. The combination of Soxhlet and ultrasound assisted extraction has been developed to take advantage of both methodologies and reduce the number of Soxhlet cycles, greening the methodology [41].

Between the attempts to improve Soxhlet performance, the most successful has been the use of microwaves, being the microwave-assisted Soxhlet extraction the most interesting improvement of conventional Soxhlet extraction [41]. The main limitations overcome by this approach is the long extraction time periods, the possibility to automate the procedure and the ability to quantitatively extract strongly retained analytes.

On the other hand, the LLE procedure is suitable to be miniaturized as for example based on the single drop extraction strategies [42-45], dispersive liquid-liquid microextraction (DLLME) [46] and hollow fiber liquid-phase microextraction (HF-LPME) [47]. These methods differ in design, but they all have one common feature: namely, they use only microvolumes of organic solvent and thus comply with the requirements of GAC. Other reported a LLME technique, is the continuous flow microextraction (CFME). In this method, the extraction solvent drop is injected into a glass chamber by a conventional microsyringe and held at the outlet tip of a PTFE connecting tube, the sample solution flows right through the tube and the extraction glass unit to waste, the solvent drop interacts continuously with the sample solution and extraction proceeds simultaneously [48]. In recent years, it has been developed the directly-suspended droplet microextraction technique (DSDME) [49] in which a small volume of an immiscible organic solvent is added to the surface of the aqueous solution gently stirred. The vortex results in the formation of a single droplet at or near the center of rotation.

Additionally, the use of membrane-mediated [50] extraction techniques can favor analyte extraction processes and move it from the original sample to an accepting solution ready to be employed for analyte measurement. As indicated in Table 2, it involves a simultaneous two-step process and a medium preconcentration, when used on a closed circuit of the accepting phase which can be relatively easy automatized based on flow-injection analysis (FIA) [51], sequential injection analysis (SIA) [52] or the use of automated syringe systems [53].

Interesting alternatives to the use of classical organic solvents as extraction media have been provided based on ionic liquids [54-57], agro-solvents, like alcohols or terpenes [58] or the use of surfactant solutions [59,60]. The aforementioned procedures provides specific solutions for greening classical extraction methods based on the use of alkanes, aromatic hydrocarbons or chlorinated solvents. However, the deleterious effects of those alternative solvents are not well known or understood, especially in the case of ionic liquids, and it must be taken into account in order to clearly identify the strengths, weakness, opportunities and threats of the alternative extraction process.

Recent advances in SPE extraction involve the evolution of formats, sorbent types and modes of interaction [61]. Typically, a commonly utilized format is a polypropylene cartridges consisting of a 20  $\mu\text{m}$  frit, made of polyethylene or polytetrafluoroethylene, at the bottom of the syringe with the relevant sorbent with an additional frit at the top. Alternatives to SPE cartridges include disks, the SPE pipette tip, 96-well SPE microtiter plates and also small columns, which can be on-line connected to a liquid chromatography (LC) system. From a green perspective, the on-line SPE is preferred. Usually, when it is coupled to a liquid chromatograph, it consists of a small pre-column placed in a six-port high-pressure switching valve. During injection, the sample is pre-concentrated on a pre-column and later the analytes are eluted onto the analytical column by valve switches. The main advantages are higher throughput and limited manual processing, as well as low cost.

An alternative to SPE is the quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction method [62], 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. This QuEChERS approach offers a user-friendly alternative to traditional LLE and SPE.

The idea of scaling down SPE has led to the development of analytical microextraction procedures. Those methods can be defined as non-exhaustive sample-preparation steps using a very small volume (microliter range or smaller) of extracting phase (solid, semi-solid polymeric or liquid material), relative to the sample volume.

The field of microextraction gained in significance with the invention of solid-phase microextraction (SPME) in 1990 [63], which later, in 1993, became commercially available. In this technique, a small amount of extracting phase dispersed on a solid support, normally, a fused-silica fiber or a metal core, is exposed to the sample, or its headspace, for a well-defined period of time.

The several implementations of SPME include mainly open-bed extraction concepts, such as agitation mechanism [i.e., stir-bar sorptive extraction (SBSE), stir-rod sorptive extraction (SRSE), stir-cake sorptive extraction (SCSE), rotating-disk sorptive extraction (RDSE)], dispersed particles into the solution, also called dispersive SPME (DSPME) and needles. In the last case, in-needle SPME, solid-phase dynamic extraction (SPDE), microextraction by packed sorbent (MEPS), microextraction in a packed syringe, fiber-packed-needle microextraction (FNME) have been proposed [64].

Novel designs for the SPME include membrane SPME (M-SPME) [65], which involved physical separation between the polar extraction medium and the analyzed sample by means of a membrane. Another membrane-based procedure is polymer-coated hollow-fiber membrane (PC-HFM), a simple and inexpensive extraction technique that involves coupling HFM with SPME and SBSE technology [66]. Another extraction method, membrane extraction with sorbent interface (MESI) [67], consists of a permeable silicone membrane coupled with an adsorbent trap for sampling and concentration of organic compounds.

The use of electrochemically-aided SPME in analytical practice has also been reported [68]. However, this particular technique has very low extraction efficiency and cannot be coupled to a chromatographic system, so a new variant, electrosorption-enhanced SPME (EE-SPME) [69], was proposed in 2007. Advances in electrochemically-assisted solid-based extraction techniques were recently reviewed [70].

Special attention must be paid to developments in solvent-free extraction methods for sample preparation and analyte separation [71,72]. The use of thermal desorption systems is a good option for the elution of analytes retained on solid phases and, because of that, headspace-based methodologies have been developed for SPME analysis of volatile and semi-volatile compounds by gas chromatography (GC) [73–75]. Those procedures can be considered a serious alternative to the use of solvents in extraction processes and they should be seriously evaluated in order to quantify the amount of energy consumed and, thus, their environment-friendly character.

In any case, it is clear that the replacement of classical extraction procedures with microextraction techniques does not imply only a change of scale. It is a new concept in which the amount of sample and reagents used substantially decreases and the speed and sustainability of methods are improved. The main trouble is that reduction in the sample size can affect the representativeness of analytical data, especially in the case of the analysis of highly heterogeneous samples.

## 5. Future trends in green extraction

Pioneering efforts in the automation of extraction procedures through FIA have been demonstrated to be one of the best ways to reduce operator risks and to avoid environmental side-effects by reducing consumption of reagents and generation of waste. However, the microscale of FIA procedures was not enough to assure their sustainability. Additional efforts in recent years on miniaturization of extraction also offered an interesting way to improve the greenness of analytical procedures. Recent

developments on microfluidic systems [76] and on-chip  $\mu$ SPE include the use of disposable sorbents using mesofluidic platforms [77], which open new possibilities to green analytical methodologies. So, it is clear that in the years ahead much more effort will be made to link these approaches, which can also be improved by clever selection of the phases, solvents and solid, employed in the preconcentration steps to guarantee the inert character of residues and to consume as little energy as possible.

One of the key factors in evaluating the sustainability of the different methodologies proposed concerns the correct evaluation of environmental risks regarding reagents, wastes and the energy employed. Those factors must be balanced in order to provide simultaneously the best analytical features and the smallest environmental side-effects. As indicated previously [78], the greenest methodology is that suitable to solve an analytical problem with the minimum environmental impact, but stress must be placed on the first part of this sentence – finding the solution to the problem.

Concerning the reagents used in the extraction steps, efforts should also be made in evaluating new solvents (e.g., agro-solvents, ionic liquids or surfactant solutions), other organized media {e.g., crown [79] and crypta ethers, and calixarenes) and lipidic structures (e.g., liposomes and vesicles). The development of new solid phases suitable for use in the selective extraction of target analytes {e.g., imprinting solid phases [80] and nano-materials [81–83]} will contribute to improving the analytical features of the methods and to reducing dramatically the amounts of reagents and energy used. So, we must be optimistic about the future, and, once again, it will be demonstrated that GAC can be a driving force to expand basic research in analytical chemistry, to make an ethical commitment to the environment and to reduce the cost of the analytical methods, thereby contributing to the sustainability of laboratories and enterprises.

## Acknowledgements

Authors acknowledge the financial support the *Ministerio de Economía y Competitividad-Feder* (Project CTQ2011-25743 and Project CTQ2012-38635) and *Generalitat Valenciana* (Project PROMETEO-II 2014-077).

## References

- [1] H. Malissa, Changes of paradigms in Analytical Chemistry, in *Reviews on Analytical Chemistry, Euroanalysis VI* (ed. E. Roth), Les Editions de Physique, Paris, 1988.
- [2] P.T. Anastas, Green chemistry and the role of analytical methodology development, *Crit. Rev. Anal. Chem.* 29 (1999) 167-175.
- [3] P.T. Anastas, J.C. Warner, *Green Chemistry: theory and practice*, Oxford University Press, Oxford (1998).
- [4] P.T. Anastas, T.C. Williamson, *Green Chemistry: frontiers in benign chemical syntheses and processes*, Oxford University Press, Oxford (1998).
- [5] M. de la Guardia, S. Armenta, *Green Analytical Chemistry: Theory and Practice*, Elsevier, Amsterdam, 2011.
- [6] M. de la Guardia, S. Garrigues (Ed.), *Challenges in Green Analytical Chemistry*, RSC Publishing, Cambridge, 2011.
- [7] M. de la Guardia, S. Garrigues (ed.), *Handbook of Green Analytical Chemistry*, John Wiley & Sons, Ltd., Chichester, 2012.
- [8] S. Armenta, S. Garrigues, M. de la Guardia, *Green Analytical Chemistry*, *TrAC-Trend. Anal. Chem.* 27 (2008) 497-511.
- [9] M. Koel, M. Kaljurand, *Green Analytical Chemistry*, RSC Publishing, Cambridge (2010).
- [10] M. de la Guardia, S. Garrigues, The social responsibility of environmental analysis, *Trends in Environmental Analytical Chemistry*, 3-4 (2014) 7-13.
- [11] A. Galuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices, *TrAC-Trends Anal. Chem.* 50 (2013) 78–84.



- [12] Eionet, European Topic Centre on Sustainable Consumption and Production, <http://scp.eionet.europa.eu/themes/lca>
- [13] National Environmental Methods Index (NEMI) 2002. <https://www.nemi.gov/home/> Accessed December 2014.
- [14] D. Raynie, J.L. Driver, Green assessment of chemical methods, Presented at 13th Green Chemistry and Engineering Conference, Washington, DC, 2009.
- [15] A. Gałuszka, P. Konieczka, Z.M. Migaszewski, J. Namiesnik, Analytical Eco-Scale for assessing the greenness of analytical procedures, *TrAC-Trends Anal. Chem.* 37 (2012) 61-72.
- [16] S. Armenta, M. de la Guardia, J. Namiesnik, Green Microextraction, in *Analytical Microextraction Techniques*, Valcarcel, M. (ed.) Bentham Science, ebook, 2015.
- [17] S. Garrigues, M. de la Guardia, Non-invasive analysis of solid samples, *TrAC-Trends Anal. Chem.* 43 (2013) 161-173.
- [18] M. Dowlati, M. de la Guardia, M. Dowlati, S. Saeid Mohtasebi, Application of machine-vision techniques to fish-quality assessment, *TrAC-Trends Anal. Chem.* 40 (2012) 168-179.
- [19] Y. Picó, Ultrasound-assisted extraction for food and environmental samples, *TrAC-Trends Anal. Chem.* 43 (2013) 84-99.
- [20] M.M. Delgado-Povedano, M.D. Luque de Castro, Ultrasound-assisted analytical emulsification-extraction, *TrAC-Trends Anal. Chem.* 45 (2013) 1-13.
- [21] C. Bendicho, I. De La Calle, F. Pena, M. Costas, N. Cabaleiro, I. Lavilla, Ultrasound-assisted pretreatment of solid samples in the context of green analytical chemistry, *TrAC-Trends Anal. Chem.* 31 (2012) 50-60.
- [22] K. Srogi, A review: Application of microwave techniques for environmental analytical chemistry, *Anal. Lett.* 39 (2006) 1261-1288.
- [23] K.J. Lamble, S.J. Hill, Microwave digestion procedures for environmental matrices, *Analyst* 123 (1998) 103R-133R.
- [24] F.E. Smith, E.A. Arsenault, Microwave-assisted sample preparation in analytical chemistry, *Talanta* 43 (1996) 1207-1268.
- [25] F. Soxhlet, Die gewichtsanalytische Bestimmung des Milchfettes, *Dinglers' Polytechnisches Journal* 232 (1879) 461-465.
- [26] T. Hyötyläinen, Critical evaluation of sample pretreatment techniques, *Anal. Bioanal. Chem.* 394 (2009) 743-758.
- [27] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namieśnik, Green aspects, developments and perspectives of liquid phase microextraction techniques, *Talanta*, 119 (2014) 34-45.
- [28] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namieśnik, Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry, *J. Chromatogr. A* 1321 (2013) 1-13.
- [29] C. Mahugo-Santana, Z. Sosa-Ferrera, M.E. Torres-Padrón, J.J. Santana-Rodríguez, Application of new approaches to liquid-phase microextraction for the determination of emerging pollutants, *TrAC-Trends Anal. Chem.* 30 (2011) 731-748.
- [30] F. Pena-Pereira, I. Lavilla, C. Bendicho, Liquid-phase microextraction techniques within the framework of green chemistry, *TrAC-Trends Anal. Chem.* 29 (2010) 617-628.
- [31] J.M. Kokosa, Advances in solvent-microextraction techniques, *TrAC-Trends Anal. Chem.* 43 (2013) 2-13.
- [32] A. Mehdinia, M.O. Aziz-Zanjani, Advances for sensitive, rapid and selective extraction in different configurations of solid-phase microextraction, *TrAC-Trends Anal. Chem.* 51 (2013) 13-22.
- [33] S. Risticovic, V.H. Niri, D. Vadoud, D. Vuckovic, J. Pawliszyn, Recent developments in solid-phase microextraction, *Anal. Bioanal. Chem.* 393 (2009) 781-795.
- [34] V. Andruch, M. Burdel, L. Kocúrová, J. Šandrejová, I.S. Balogh, Application of ultrasonic irradiation and vortex agitation in solvent microextraction, *TrAC-Trends Anal. Chem.* 49 (2013) 1-19.
- [35] A. Szreniawa-Sztajnert, B. Zabiegała, J. Namieśnik, Developments in ultrasound-assisted microextraction techniques for isolation and preconcentration of organic analytes from aqueous samples, *TrAC-Trends Anal. Chem.* 49 (2013) 45-54.

- [36] J.L. Capelo, A.M. Mota, Ultrasonication for analytical chemistry, *Curr. Anal. Chem.*, 1 (2005) 193-201.
- [37] A. Pastor, E. Vazquez, R. Ciscar, M. de la Guardia, Efficiency of the microwave-assisted extraction of hydrocarbons and pesticides from sediments, *Anal. Chim. Acta* 344 (1997) 241-249.
- [38] A. Nieto, F. Borrull, E. Pocurull, R.M. Marcé, Pressurized liquid extraction: A useful technique to extract pharmaceuticals and personal-care products from sewage sludge, *TrAC-Trends Anal. Chem.* 29 (2010) 752-764.
- [39] H.W. Sun, X.S. Ge, Y.K. Lu, A.B. Wang, Application of accelerated solvent extraction in the analysis of organic contaminants, bioactive and nutritional compounds in food and feed, *J. Chromatogr. A* 1237 (2012) 1-23.
- [40] A. Mustafa, C. Turner, Pressurized liquid extraction as a green approach in food and herbal plants extraction: A review, *Anal. Chim. Acta* 703 (2011) 8-18.
- [41] M.D. Luque de Castro, F. Priego-Capote, Soxhlet extraction: Past and present panacea, *J. Chromatogr. A*, 1217 (2010) 2383-2389.
- [42] E Psillakis, N Kalogerakis, Developments in single-drop microextraction, *TrAC-Trends Anal. Chem.* 21 (2002) 54-64.
- [43] A. Jain, K.K. Verma, Recent advances in applications of single-drop microextraction: A review, *Anal. Chim. Acta* 706 (2011) 37-65.
- [44] M.A. Jeannot, A. Przyjazny, J.M. Kokosa, Single drop microextraction-Development, applications and future trends, *J. Chromatogr. A* 1217 (2010) 2326-2336.
- [45] L. Kocurova, I.S. Balogh, V. Andruch, A glance at achievements in the coupling of headspace and direct immersion single-drop microextraction with chromatographic techniques, *J. Sep. Sci.* 36 (2013) 3758-3768.
- [46] M. Rezaee, Y. Assadi, M.R. Millani, E. Aghaee, F. Ahmadi, S. Berijani, Determination of organic compounds in water using dispersive liquid-liquid microextraction, *J. Chromatogr., A* 1116 (2006) 1-9.
- [47] S. Pedersen-Bjergaard, K.E. Rasmussen, Liquid-liquid-liquid microextraction for sample preparation of biological fluids prior to capillary electrophoresis, *Anal. Chem.* 71 (1999) 2650-2656.
- [48] W. Liu, H.K. Lee, Continuous-flow microextraction exceeding 1000-Fold concentration of dilute analytes, *Anal. Chem.* 72 (2000) 4462-4467.
- [49] Y. Lu, Q. Lin, G. Luo, Y. Dai, Directly suspended droplet microextraction, *Anal. Chim. Acta* 566 (2006) 259-264.
- [50] L. Chimuka, E. Cukrowska, M. Michel, B. Buszewski, Advances in sample preparation using membrane-based liquid-phase microextraction techniques, *TrAC- Trends Anal. Chem.* 30 (2011) 1781-1792.
- [51] M. Miró, W. Frenzel, Automated membrane-based sampling and sample preparation exploiting flow-injection analysis, *TrAC-Trends Anal. Chem.* 23 (2004) 624-636.
- [52] P. Kuban, B. Karlberg, Flow/sequential injection sample treatment coupled to capillary electrophoresis. A review, *Anal. Chim. Acta* 648 (2009) 129-145.
- [53] F. Maya, B. Horstkotte, J.M. Estela, V. Cerdà, Automated in-syringe dispersive liquid-liquid microextraction, *TrAC-Trends Anal. Chem.* 59 (2014) 1-8.
- [54] E.M. Martinis, P. Berton, R.G. Wuilloud, Ionic liquid-based microextraction techniques for trace-element analysis, *TrAC-Trends Anal. Chem.* 60 (2014) 54-70.
- [55] M.J. Trujillo-Rodríguez, P. Rocío-Bautista, V. Pino, A.M. Afonso, Ionic liquids in dispersive liquid-liquid microextraction, *TrAC-Trends Anal. Chem.* 51 (2013) 87-106.
- [56] E. Aguilera-Herrador, R. Lucena, S. Cárdenas, M. Valcárcel, The roles of ionic liquids in sorptive microextraction techniques, *TrAC-Trends Anal. Chem.* 29 (2010) 602-616.
- [57] P.J. Zhang, L. Hu, R.H. Lu, W.F. Zhou, H.X. Gao, Application of ionic liquids for liquid-liquid microextraction, *Anal. Methods-UK* 5 (2013) 5376-5385.
- [58] F. Chemat, M.A. Vian, G. Cravotto, Green Extraction of Natural Products: Concept and Principles, *Int. J. Mol. Sci.* 13 (2012) 8615-8627.
- [59] A. Sarafraz Yazdi, Surfactant-based extraction methods, *TrAC-Trends Anal. Chem.* 30 (2011) 918-929.
- [60] L. Alexandru, A. Binello, S. Mantegna, L. Boffa, F. Chemat, G. Cravotto, Efficient green extraction of polyphenols from post-harvested agro-industry vegetal sources in Piedmont, *C.R. Chim.* 17 (2014) 212-217.

- [61] B. Buszewski, M. Szultka, Past, Present, and Future of Solid Phase Extraction: A Review, *Crit. Rev. Anal. Chem.* 42 (2012) 198–213.
- [62] M. Anastassiades, S.J. Lehotay, D. Stajnbaher, F.J. Schenck. Fast and Easy Multiresidue Method Employing Acetonitrile Extraction/Partitioning and “Dispersive Solid-Phase Extraction” for the Determination of Pesticide Residues in Produce, *J. AOAC International*, 86 (2003) 412-431.
- [63] C.L. Arthur, J. Pawliszyn, Solid phase microextraction with thermal desorption using fused silica optical fibers, *Anal. Chem.* 62 (1990) 2145-2148.
- [64] A. Spietelun, A. Kloskowski, W. Chrzanowski, J. Namiesnik, Understanding Solid-Phase Microextraction: Key Factors Influencing the Extraction Process and Trends in Improving the Technique, *Chem. Rev.* 113 (2013) 1667-1685.
- [65] A. Kloskowski, M. Pilarczyk, J. Namieśnik, Membrane solid-phase microextraction - A new concept of sorbent preparation, *Anal. Chem.* 81 (2009) 7363-7367.
- [66] C. Basheer, V. Suresh, R. Renu, H.K. Lee, Development and application of polymer-coated hollow fiber membrane microextraction to the determination of organochlorine pesticides in water, *J. Chromatogr. A* 1033 (2004) 213–220.
- [67] Y.Z. Luo, J. Pawliszyn, Calibration of membrane extraction for air analysis, *Anal. Chem.* 72 (2000) 1064-1071.
- [68] M.O. Aziz-Zanjani, A. Mehdinia, Electrochemically prepared solid-phase microextraction coatings-a review, *Anal. Chim. Acta* 781 (2013) 1-13.
- [69] X. Chai, Y. He, D. Ying, J. Jia, T. Sun, Electrosorption-enhanced solid-phase microextraction using activated carbon fiber for determination of aniline in water. *J. Chromatogr. A* 1165 (2007) 26-31.
- [70] S. Seidi, Y. Yamini, M. Rezazadeh, Electrochemically assisted solid based extraction techniques: A review, *Talanta* 132 (2015) 339-353.
- [71] Y. Li, A.S. Fabiano-Tixier, M.A. Vian, F. Chemat, Solvent-free microwave extraction of bioactive compounds provides a tool for green analytical chemistry, *TrAC-Trends Anal. Chem.* 47 (2013) 1-11.
- [72] A. Kabir, K.G. Furton, A. Malik, Innovations in sol-gel microextraction phases for solvent-free sample preparation in analytical chemistry, *TrAC-Trends Anal. Chem.* 45 (2013) 197-218.
- [73] P.K. Rout, Y.R. Rao, S. Naik, Analysis of Floral Volatiles by Using Headspace-Solid Phase Microextraction: A Review, *Asian J. Chem.* 24 (2012) 945-956.
- [74] E.E. Stashenko, J.R. Martinez, Sampling volatile compounds from natural products with headspace/solid-phase micro-extraction, *J. Biochem. Biophys. Meth.* 70 (2007) 235-242.
- [75] A. Valenzuela, G. Lespes, W. Quiroz, L.F. Aguilar, M.A. Bravo, Speciation analysis of organotin compounds in human urine by headspace solid-phase micro-extraction and gas chromatography with pulsed flame photometric detection, *Talanta* 125 (2014) 196-203.
- [76] A. J. de Mello, N. Beard, Dealing with 'real' samples: sample pre-treatment in microfluidic systems, *Lab. Chip* 3 (2003) 11N–19N.
- [77] M. Miró, On-chip microsolid-phase extraction in a disposable sorbent format using mesofluidic platforms, *TrAC-Trends Anal. Chem.* 62 (2014) 154-161.
- [78] M. de la Guardia, S. Garrigues, Partial least squares attenuated total reflectance IR spectroscopy versus chromatography: the greener method, *Bioanalysis* 4 (2012) 1267-1269.
- [79] R.M. Kakhki, Recent developments in microextraction techniques based on crown ethers, *J. Incl. Phenom. Macrocycl. Chem.* 76 (2013) 253-261.
- [80] A. Beltran, F. Borrull, R.M. Marcé, P.A.G. Cormack, Molecularly-imprinted polymers: useful sorbents for selective extractions, *TrAC-Trends Anal. Chem.* 29 (2010) 1363-1375.
- [81] K. Farhadi, A.A. Matin, H. Amanzadeh, P. Biparva, H. Tajik, A.A. Farshid, H. Pirkharrati, A novel dispersive micro solid phase extraction using zein nanoparticles as the sorbent combined with headspace solid phase micro-extraction to determine chlorophenols in water and honey samples by GC-ECD, *Talanta* 128 (2014) 493-499.
- [82] C.C. Acebal, B.M. Simonet, M. Valcárcel, Nanoparticles and continuous-flow systems combine synergistically for preconcentration, *TrAC-Trends Anal. Chem.* 43 (2013) 109-120.
- [83] G. Lasarte-Aragones, R. Lucena, S. Cardenas, M. Valcarcel, Nanoparticle-based microextraction techniques in bioanalysis, *Bioanalysis* 3 (2011) 2533-2548.

## Captions

**Fig. 1.** Green Analytical Chemistry: shift from chemurgical paradigm to ecological paradigm.

**Fig. 2.** Strategies for greening an analytical method.

**Fig. 3.** Aspects to be considered on greening extraction procedures.

**Table 1.**

Special issues of journals on Green Analytical Chemistry

Journal	Special issue (no. of papers)	Year, vol. (no.)
<i>The Analyst</i> (RSC)	Environmentally Conscientious Analytical Chemistry (5)	1995, 120 (2)
<i>Spectroscopy Letters</i>	Green Spectroscopy and Analytical Techniques (18)	2009, 42 (6–7)
<i>Trends in Analytical Chemistry</i>	Green Analytical Chemistry (10)	2010, 29 (7)
<i>Analytical and Bioanalytical Chemistry</i>	Green Analytical Methods (7)	2012, 404 (3)

**Table 2.**

Comparison of analyte-extraction strategies

Liquid-liquid	Membrane mediated	Solid
Low preconcentration level	Medium preconcentration	High preconcentration
Single step	Simultaneously two steps	Two separate steps
Easy automation	Relatively easy automation	Very easy automation

Accepted Manuscript