We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

BOOK CITATION INDEX
CLARIVATE ANALYTICS
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Overview of Green Sample Preparation Techniques in Food Analysis

Burak Demirhan, Hayriye Eda Şatana Kara and
Buket Er Demirhan

Additional information is available at the end of the chapter

Abstract

Nowadays, the significance of food analysis could be emphasized in consequence of growing world population besides the increased consumer demands for the safe food. The reliability and accuracy of analysis are highly affected by sample preparation, extraction, enrichment, and isolation of the analytes. Traditional sample preparation techniques are not only costly but also time-consuming and generally labor-intensive, and furthermore, these techniques required high solvent content, which generates waste, pollutes sample, and enriches the analyte for the food analysis. In recent years, new extraction techniques have been discovered as an alternative to the conventional sampling procedure. Simple, fast, cost-effective and green (environmentally friendly) techniques can be preferred gradually instead of traditional methodologies in order to the extraction of the sample. The aim of the chapter will be to compile and discuss the advantages, pro and cons, and use of some sample preparation techniques that are relevant to the green chemistry.

Keywords: food, green chemistry, microextraction, microwave, ultrasound

1. Introduction

Analytical control analysis for food safety and quality is developing steadily. Sample preparation is one of the main steps of food analysis**.** Direct analysis of several compounds in foodstuff is very difficult without any sample preparation methods. Generally, a huge amount of toxic organic solvents is required in traditional techniques. Thus, these techniques are both costly and environmentally harmful, and produce waste [1]. The necessity of the novel analytical techniques in the food science is related to the demand of information about the process,

quality control, adulteration, contamination, and food regulations. For this purpose, chemists, regulatory agencies, and quality control laboratories request faster, more powerful, clean, and inexpensive analytical procedure to meet this demand. Improvement in the modern analytical techniques causes clear development in the quality of analysis [2].

Green chemistry could be applied to the chemistry to decrease or eliminate the harmful substances in the chemical products design and process [3]. Green analytical chemistry arose from green chemistry in 2000. The key goals of greening analytical methods should be ensured by reductions of sample number, reagents, energy, waste, risk, and hazard [4]. Green extraction techniques are the alternative to classical sample preparation techniques [5]. These techniques provide opportunities to reduce or eliminate the chemical solvent usage while improving the quality of extract, efficiency of the methods, and extraction of products [6].

2. Green analytical chemistry and food analysis

Chemistry has long been perceived as dangerous, and chemical and toxic words are often associated with chemistry by humans. Several security precautions such as protecting clothing could be taken to reduce the risk. Therefore, the purpose of the green chemistry is minimizing the risk occurred during the chemical life cycle. Also, risk should be defined as the ability to create an adverse effect on human and environment [7]. Green chemistry can be determined as a design of chemical products and process to reduce or eliminate the formation and use of the harmful substances. This definition and green chemistry concept were first introduced in the early 1990s [7, 8]. Green chemistry is the methodology and chemical techniques to eliminate or reduce the use of a solvent, reagent, products, and by-products that harmful to the human health and environment. In brief, green chemistry is the use of the chemistry in order to avoid pollution. Analytical laboratories previously developed the green chemistry ideas and same philosophy. Environmental side effects of analytical methods are reduced by three ways: (i) to reduce the amount of solvent in sample pretreatment; (ii) to reduce the amount and toxicity of solvent and reagents during the measurement; and (iii) to develop alternative analytical procedures that avoid the use of solvent and reagents [9]. For this purpose, green chemistry has a set of principles to reduce or prevent the harmful substances which are used in the design, production, and application process of the chemical products [10]. Twelve principles of green chemistry were introduced in 1998 by Anastas and Warner [11] and they were given in **Figure 1** [7, 8, 11, 12]. Principles of the green analytical chemistry for sample preparation and final analysis stage are given in **Figure 2** [13].

Chemical substance reduction or elimination, effective energy consumption and waste management, and enhancement of the safety are key goals of the green analytical methods [4]. Food analysis has been serious for the purpose of quality control of raw and processed foods, specifying of the nutritional value of foods, and monitoring the food additives and toxic contaminants [14]. Life quality should be improved in developing countries due to the application of cheap, fast and environmental safety procedures during the analysis of foods [5]. Application of these principles should be actualized whole analytical process steps: sampling,

1. **Prevention-** Prevention of waste.
2. **Atom economy-** Designing synthetic method.
3. **Less hazardouschemical synthesis-** Synthesis less harmful chemical.
4. **Desiginig safer chemical-** Design of safer chemicals.
5. **Safer solvents and auxiliaries-** Use of safer solvents and auxiliaries such as separating agents.
6. **Design for energy efficiency-** Minimizing the energy requirements of chemical process.
7. **Use of renewable feedstocks-** Use of renewable materials.
8. **Reduce derivatives-** Minimizing the derivatization process.
9. **Catalysis-** Use of catalytic reagents.
10. **Design for degradation-** Designing innocuous degradation products.
11. **Real-time analysis for pollution prevention-** Real time analysis for in-process monitoring.
12. **Inherently safer chemistry for accident prevention-** Safer chemistry to prevent accidents

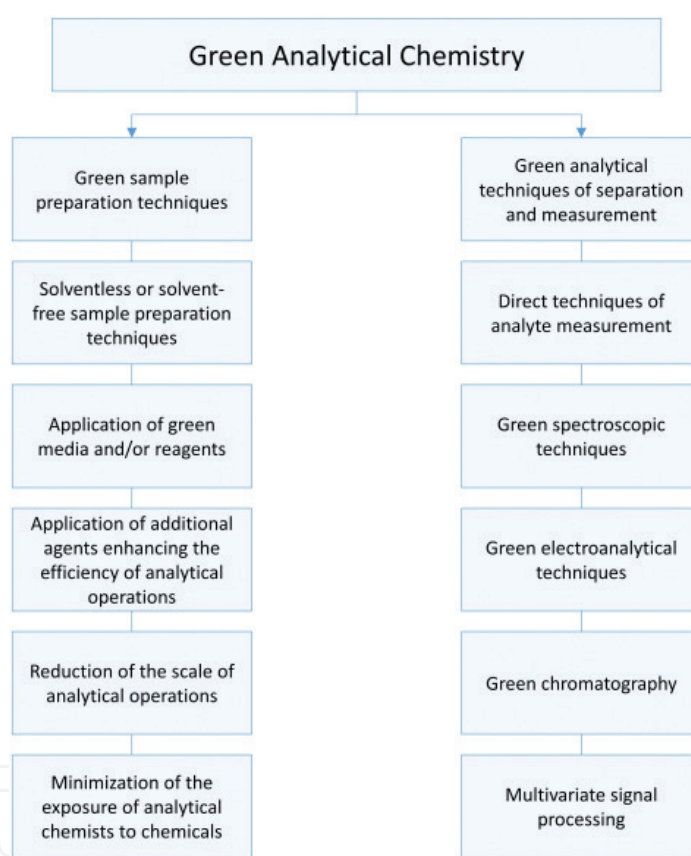**Figure 1.** Twelve principles of green chemistry [7, 8, 11, 12].

Figure 2. Principles of the green analytical chemistry for sample preparation and final analysis stage [13].

preparing samples, separation, detection, and data analysis [15]. The purpose of the sample preparation is to enable to the isolation of the target analytes, to minimize the complexity of the samples and to prevent most of the matrix interferents, before the analytical detection (e.g., chromatographic techniques) [16]. Sample preparation has been considered as a time-consuming process of the analytical procedures among these steps. Therefore, simple and environmentally friendly techniques can be preferred gradually instead of traditional methodologies in order to extraction and preconcentration of analytes [17]. Separation techniques

are applied for food analysis after sample preparation. Application of the principles of green chemistry into gas chromatography (GC) can be performed in many ways. Liquid chromatography (LC) is generally recognized less green than GC, due to the solvents requirement for the separation. On the other hand, LC offers more possibilities for "greening" [13]. Capillary zone electrophoresis (CZE) has also some advantages such as environmental friendliness, analysis time, and cost-effectiveness [18].

3. Sample preparation and greener approach

In general, foods cannot be analyzed without any presample preparation steps, because of diluted analytes and complex matrix structure of the foods [1]. Sample preparation is an extraction process, which extracts the chemical residues from the sample. Therefore, isolation of target residues and removal of interferents are ensured by sample preparation. Sample preparation has been the major part of the analytical procedures as well as separation and detection techniques, and effective sample preparation gives rise to reliable results and provides the instrumental performance [19]. The reliability and accuracy of analysis are highly affected by sample preparation, extraction, enrichment and isolation of the analytes [1]. Sample preparation should be recognized as possibly causative steps to problems and complications due to the time consumption, cost, contamination, and low extraction efficiency [16]. Several analytical steps such as purification, gel permeation chromatography (GPC), sulfuric acid treatment, and adsorption chromatography (alumina, silica gel, Florisil) should be applied as single or in combination with in order to avoid interferent compounds (e.g., lipids, carbohydrates, water, and chlorophyll), which can be extracted as well as the target analyte during the extraction of food samples. Acid digestion or saponification is a destructive method in order to remove the lipids [20].

Occasionally, transfer to the liquid phase should be necessary, by reason of difficult analysis of solid samples. Leaching the analyte (i.e., solid-liquid extraction or lixiviation) is one of the simpler, most widely applied sample treatments. Soxhlet extraction, which is basic reference against new leach methods, can be still employed in the routine analysis due to the lower costs and robustness. Soxhlet system is basic, easy to use and provides to use a large amount of sample. Unfortunately, there are several disadvantages such as long extraction periods and high solvent consumption [5]. Several extraction methods have been applied for the sample preparation in food analysis. Soxhlet and pressurized extraction techniques (e.g., supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE)) have been employed to sample analysis. Large bore open-tubular glass liquid chromatographic (LC) columns operating at gravity pressure and liquid-liquid extraction (LLE) techniques are used in the liquid samples [16]. Conventional LLE and solid phase extraction (SPE) have been used widely in food analysis in order to prepare food samples [21].

In food analysis, traditional sample preparation techniques are not only costly, but also time-consuming and generally labor intensive, and furthermore, these techniques required high solvent content, which generates waste, pollutes sample, and enriches the analyte. Additionally,

more than one clean-up steps are necessary before detection steps. Extraction of organic analytes from food samples generally begins with homogenization, and subsequently, exhaustive liquid extraction steps with one or more clean-up steps and purification of the extract before the detection of the analyte are required [20]. Consequently; several alternative techniques were developed to solve this trouble [2].

In recent years, some new extraction methods were discovered as an alternative to the conventional sampling procedure. Green extraction, which could be an alternative renewable sample preparation technique, improves the sensitivity and selectivity of analytical methods according to the classical sample preparation methods [5]. Current trends in the sample preparation have been focused on the low-cost operations owing to the miniaturization, automation, high efficiency performance, online analytical instruments, and extremely low- or nonsolvent consumption. Minimizing the sample preparation steps can be effective due to the reducing errors, time, and cost, and has some advantages in order to measure trace and ultratrace analytes in complex matrices. Due to the disadvantages such as time-consuming procedures and excess use of liquid organic solvents, new sample preparation methods allow using less organic solvents and can be alternative to the conventional methods [21]. Microextraction methods (e.g., solid phase microextraction (SPME), stir bar sorptive extraction (SBSE), and liquid phase microextraction (LPME)) have been becoming important in order to prepare samples in comparison with conventional techniques [1]. By definition microextraction means, all modes of these techniques require using small volumes of extraction medium during the extraction conditions. The large number of variable parameters such as extraction time, temperature, pH, salt concentration, stirring rate, sample volume, etc. and relationships between them often require the avoiding from the classical approach in order to optimization, which does not take into account the interactions between the variables [22]. These methods are carried out even though the complexity of the samples of food analysis [1].

4. Sample preparation techniques relevant to green chemistry

4.1. Solid phase microextraction

Most common techniques for purification have been adsorption chromatography that uses solid phase extraction (SPE) techniques [20]. SPME methods should be recognized as a green approach for the sample preparation due to the reduction of the solvent consumption and waste production. Additionally, SPME has some advantages such as time-saving and cost-effective against conventional methods [17]. SPME can allow to extraction and enrichment process in a single step that produces solvent-free sample preparation. SPME was first developed in 1990 by Arthur and Pawliszyn [23]. Appropriate adsorbent phase coated silica fiber has been used in this technique. The analyte is directly extracted from the sample and then concentrated to the fiber coating [1, 24]. The efficiency of the analyte preconcentration can be depended on the several parameters such as the type of fiber, sample stirring, extraction time etc. in the SPME technique [25]. SPME should be defined as a sample preparation technique that uses fused silica fiber coated with appropriate stable phase. Volatile and semivolatile

compounds in the food samples can be extracted by SPME in combination with GC and GC/ mass spectrometry (MS). SPME is also used in combination with high-performance liquid chromatography (HPLC) and LC-MS to extract weak volatile or thermally unstable compounds which are unsuitable to the GC or GC-MS. SPME-HPLC interface has special desorption chamber, and it is used in order to desorption of the solvent before the HPLC analysis instead of thermal desorption in the injection port of the GC. In-tube SPME, which is new SPME-HPLC systems and is appropriate to the automation, has been recently developed using an open tubular fused silica capillary column. Automatic sample processing procedure not only reduces the total analysis duration but also provides more accuracy and precision according to the manual techniques [24].

Simplicity, speed, solvent free, high sensitivity, and small sample volume are the main advantages of the SPME [1, 26]. SPME techniques have also been significant due to the reproducibility, repeatability, and possible quantitative determination. Polar and nonpolar compounds in gaseous, liquid, and solid samples can be analyzed by SPME which is successfully combined with various analytical instruments such as GC, HPLC, etc [1].

SPME should be applied for various food analyses. SPME has lowest detection limits when compared to several common sample preparation methods which are important to the analysis of the main flavor and odor compounds [27].

There are two available extraction types in the fiber SPME; headspace extraction SPME (HS-SPME) is the first, and direct extraction SPME (DI-SPME) is the second [14, 24]. Furthermore, HS-SPME exposes a lower background than DI-SPME and is appropriate to the molecular extraction of more volatile analytes in the gas, liquid, and solid food samples. DI-SPME should be used to the extraction of semi or less volatile analytes in the liquid samples [24].

4.1.1. Direct extraction SPME

Fiber should be placed directly to the liquid samples in the direct extraction (DI-SPME). Agitation can be necessary to accelerate the extraction in the sample matrix [1]. Additionally, the natural flow of air should be sufficient to ensure balance to the volatile compounds in gaseous samples [1, 24].

4.1.2. Headspace extraction SPME

Headspace extraction (HS-SPME) is comprised of two equilibriums; the first equilibrium is between sample matrix and gaseous phase (headspace) above it, and the second equilibrium is between headspace and coating on the extracting fiber [1]. HS-SPME methods, in which 100 μm polydimethylsiloxane (PDMS) fiber is used, can be used in combination with GC or GC-MS for the purpose of the analysis of various foods [14]. A lifetime of the fiber can be extended in the HS-SPME technique, in consequence of not contacting with the sample directly. Less volatile compounds are also extracted directly from the solution in DI-SPME [25]. SPME should be used almost completely as headspace extraction in the food matrices (the presence of sugars, proteins, colorants, and other nonvolatiles), because of the specificity of this food matrix [1].

4.1.3. In-tube SPME

This is the effective sample preparation technique that uses the open tubular fused-silica capillary column as an extraction device [28]. Although in-tube SPME can be appropriated to these compounds, particles must be removed from samples by filtration before the extraction in order to avoid plugging of the flow line and capillary column during the extraction so that in-tube SPME has preferred to the extraction of the clean samples [14]. Tube design of the SPME can be used with very similar arrangements of the SPE; however, the main difference is to add a volume of the extraction phase due to the fact that the purpose of the SPME is never detailed extraction [29]. In-tube SPME is an ideal sample preparation technique in food analysis due to the fast operation and easy automation of technique, and being solvent free and inexpensive [28]. In-tube SPME, which is an appropriate technique for automation, includes automated sample handling to ensure reduced total analysis time and better accuracy and precision compared to manual techniques [14]. This can be facilitated by the design of this system [29]. In-tube SPME has two extraction modes, which are static and dynamic modes. In the static mode, mere diffusion is responsible for the transfer of the analytes to the stationary phase. The dynamic mode includes repeated draw/eject cycles for the purpose of sample extraction [30].

4.2. Stir bar sorptive extraction

Stir bar sorptive extraction (SBSE), which is the microextraction methods introduced by Baltussen et al. [31], fulfills the requirements of the green chemistry by removing excessive solvent usage, and reducing labor-intensive and time-consuming sample preparation steps. PDMS coated 10–40-mm-long magnetic stirrers can be used as mobile sorptive elements in the original SBSE. Therefore, the total volume of the sorbent is used to the extraction of the analyte [31]. SBSE is very easy to handle samples and allows great selectivity and sensitivity for complex matrices [32].

This sorptive extraction technique has been basically the same principle with SPME, but extraction capacity of the SBSE is higher [1]. In contrast to the coated fiber SPME, magnetic stir bar should be used in order to capture the analytes during the stirring in SBSE. Coated phase is usually PDMS fiber which has 50–250 times higher extraction volume compared to the SPME fiber, resulting in higher recoveries and higher sample loading capacity. Normally, SBSE can be applied to the extraction of semi-volatile and volatile organic compounds in the aqueous matrix of the foods. Because of this goal, stir bar can be basically added and rotated for the sample extraction, after a while molecules captured by bars should be thermally desorbed in the GC or added to the solvent for the LC. Manually operation in most cases is the main disadvantage of the SBSE [33]. Coated stir bar should be added to the sample for the purpose of the stirring and extraction (Direct SBSE) or exposed to the sample headspace (HS-SBSE) in SBSE technique [1]. The efficiency of the SBSE compared to the other sorptive techniques was investigated. Different types of organic compounds in aqueous solutions can be extracted by SBSE technique. The detection limit of SBSE may be reduced by its use in combination with thermos desorption-GC-MS [25]. SBSE is not popular technique as well as SPME, but it has been recognized as a green alternative technique for the extraction of pesticide residue in the sugarcane [9].

4.3. Liquid phase microextraction techniques

Liquid phase microextraction (LPME) is the alternative extraction techniques to the SPME and should be classified as three types: single drop phase microextraction (SDME), hollow fiber liquid phase microextraction (HF-LPME), and dispersive liquid-liquid microextraction (DLLME) [1]. All of the types of LPME, especially SDME, use organic solvents as microliter volume, resulting in being environmentally friendly [21]. LPME which was developed in 1996, is an easy, fast, efficient, and cheap sample preparation technique. Extraction, concentration and sample input can be integrated into a single step [34]. LPME term should be used as a little solvent volume of LLE (acceptor phase-water immiscible) to the extraction of the analytes from liquid solution (donor phase) [1]. Extraction in the LPME normally consists of between small amount of water-immiscible solvent and an aqueous phase containing target analyte. The acceptor phase is not only immersed for the direct extraction but also suspended on the sample for the headspace extraction. Receiving phase volume is ranged microliter or below; considering this, higher enrichment factors should be obtained due to the ratio of the high volume of sample to the acceptor phase [21]. Since then, different LPME approaches have been developed to analysis various compounds in foods: SDME, HF-LPME, DLLME, with each group having a variety of modifications [1, 35].

LPME advantages can be summarized as simple and highly selective extraction method; it has been combined with HPLC, capillary gas chromatography (GC), and capillary electrophoresis (CE), environmentally friendly due to less solvent usage, in which μL solvent is used to extraction of an analyte from various samples [36].

4.3.1. Single-drop microextraction

Single-drop microextraction (SDME) technique was developed in 1996 by Liu and Dasgupta, and this technique uses suspension of a microdrop (~1.3 μL) of water-immiscible organic solvent in an aqueous solution [37]. SDME has been a first successful application in the LPME technique in order to concentrate and purified of the analytes during the liquid and gaseous samples analysis [38]. SDME is a new, simple, fast, and environmentally friendly method, and effects of nature of organic solvents, microdrop volume, microdrop depth in the samples, extraction time, and stirring speed on the extraction efficiency have been separately demonstrated by Li et al. [39]. This method is successfully applied to the GC-MS for the purpose of the determining the phthalate esters in food samples [39].

Fiber should be necessary to the extraction of the analytes in both SPME and HF-LPME techniques, but only single microdrop is used as solvent acceptor phase in SDME, which is more simple, practicable and almost costless in comparison with SPME and HF-LPME [1]. SDME uses organic solvent at the end of the microsyringe and is developed from LPME technique. SDME should be classified as direct immersion SDME (DI-SDME) and headspace SDME (HS-SDME). Water immiscible solvent drop can be suspended apex of the microsyringe needle which is immersed in the aqueous sample in DI-SDME. Sample headspace or flowing air sample stream involves a microdrop of an appropriate solvent to extract the volatile compounds in the HS-SDME. Advantages of the HS-SDME are to choose a wide variety of solvents. On the contrary, the necessity of the different apparatus to extraction and injection is the disadvantages of the HS-SDME techniques [36].

4.3.2. Dispersive liquid-liquid microextraction

Recent years, dispersive liquid-liquid microextraction (DLLME) is a new miniaturize extraction technique which has been introduced by Rezaee and co-workers in 2006 [40]. DLLME basically depends on the three-component solvent systems (aqueous sample, dispersive solvent, and extractive solvent). The appropriate mixture of the extraction solvent (organic) and dispersive solvent (water-organic miscible solvent) can be injected into the aqueous sample, and thus, cloudy solvent should be formed. Subsequently, via the centrifuge, analytes are separated from the organic phase. In the extractive solvent, concentrated analytes should be injected to the GC, LC or electromigration instruments for the purpose of separation and detection [21].

4.3.3. Hollow fiber liquid phase microextraction

Hollow fiber liquid phase microextraction (HF-LPME) was introduced by Bjergaard and Rasmussen in 1999 [41]. The main basis of the hollow fiber-based LPME is to fill the little sample vial with the targeted liquid sample, and porous hollow fiber is placed into the samples. The volume of liquid sample and length of fiber are varying between 0.1 and 4 mL and 1.5–10 cm, respectively. Before the extraction, immersed a part of the hollow fiber to the organic solvent immobilizes the solvent on the hollow fiber and then excess of the solvent is removed [42]. HF-LPME is a simple and cheap technique that ensures analyte extraction from complex samples. The analyte can be extracted by extractant from liquid samples in the two phase LPME sampling mode. This extractant is into the porous hollow fiber which is made from polypropylene material supported with microinjector. In this sampling mode, acceptor phase is organic, so that this system is compatible with GC and HPLC in order to total analysis [43]. HF-LPME can be done in two modes such as static or dynamic, and the second one gives less operating time, while it cannot be automated, and therefore, it is necessary to optimize and control [44]. This technique is successfully used in the complex matrix such as foodstuffs for the purpose of the cleaning and extracting of the samples [1].

4.4. Ultrasound-assisted extraction

Over the last decade, application of ultrasound for extraction has increased, due to a number of disadvantages associated with conventional or other newer techniques, such as high capital investment and energy consumption, and the use of toxic organic substances used for extraction. In the preapplication steps, ultrasound-assisted extraction (UAE) is a method that ultrasound technique is applied, and this technique can be preferred in terms of being environmentally friendly and clean extraction [45]. Consequently, use of UAE has been recognized as green and economically viable alternative to conventional techniques in food [46]. Therefore, ultrasound is an easy to use, the multi-directional, flexible and low investment required technique when compared to the other extraction techniques such as SFE, PLE or ASE. Ultrasonic area of the spectrum is important because of the conventional applications. Ultrasound generally should be classified as low intensity sonication (<1 W/cm^2) and high density sonication (10–100 W/cm^2). High intensity sonication is performed to the extraction and process applications, while low intensity sonication is used as a nondestructive analytic technique for the

quality assurance and process control. Ultrasound application enlarges the solvent selection range of generally recognized as safe (GRAS) instead of toxic organic solvents [45].

4.5. Microwave-assisted extraction

Microwave-assisted extraction (MAE) can be applied in order to the extraction of organic compounds from a different type of matrix. In this method, lower extraction time and the lower organic solvent are used compared to the conventional extraction [9]. Nowadays, MAE should be applied to solid samples as a versatile extraction technique and desorb analytes using electromagnetic radiation. While the microwave frequency varies between 300 MHz and 100 GHz that can be used the whole of the frequency, conventional ovens should only operate at 2.45 GHz. Very fast heating, high temperatures, and ease of operation are the main advantages of the MAE, and the only disadvantage of the MAE is the limited heating of the sample solvent due to the dielectric constant [47].

4.6. Supercritical fluid extraction

Supercritical fluid extraction (SFE) is green, easily and totally automatable analytical method [9]. Environmentally friendly sample preparation method (e.g., typically SFE) is a method that uses environmentally friendly solvents such as water. SFE can relatively eliminate the risk of activity loss using short extraction time, lower pressure and temperature, and it can protect the integrity of functional compounds of food [33]. SFE advantages are getting clean extract due to the reduced solvent usage and extraction time. There are no further clean-up steps in the extraction of the analytes. In this technique, nontoxic and nonpolluting extraction fluids such as carbon dioxide can be most widely used in the sample pretreatment [2, 20]. The main advantages of the SFE are quantitative, simple, fast, selective and environmentally friendly. SFE is used to the extraction of the pesticide residue from fruits [9].

4.7. Pressurized fluid extraction

Pressurized fluid extraction (PFE) is similar with soxhlet extraction except that the usage of the solvent is near the supercritical area. PFE could cause to higher extraction efficiency due to the lower solvent volume as 15–40 mL and short extraction time as 15–20 min. PFE is also known as ASE was first introduced in 1996. Additionally, ASE, known as pressurized solvent extraction (PSE), pressurized liquid extraction (PLE) and solvolytic extraction, is a solid-liquid extraction process which is operated at high temperatures (50–200°C) and pressure (10–15 MPa). While organic solvent is generally used in the ASE, pressurized hot water can be used in this technique. Main advantages of ASE technique are reducing the extraction time and solvent usage in comparison with the traditional extraction methods [9].

4.8. Cloud-point extraction

The cloud-point extraction (CPE) is other greener sample pretreatments, and it was first developed by Watanabe and Tanaka for the preconcentration of metal ions from aqueous samples [9].

CPE consists of three steps: (i) solubilize the analytes in the micelle aggregates; (ii) cloudiness; and (iii) phase separation for the analysis [48]. Nonionic surfactants can be able to form a micelle in aqueous solutions and become turbid at a specific temperature which is described as cloud point temperature. Over this point, micelle solution is divided into two phase: little volume phase that enriches in terms of surfactant and diluted aqueous phase. When metal ions react with an appropriate ligand, it can form aqueous low solubility complex, and there-fore, these ions should be extracted from aqueous solution in the little volume enriched phase in terms of surfactant. This method is simple experimental procedure due to the low cost, eco-friendly, high capacity to preconcentration of the several analytes and good recovery with high enrichment factor. CPE is also simple, sensitive and rapid methods for concentration and separation of the essential elements [49].

CPE uses water and prevents the use of expensive, toxic and flammable organic solvents in a large volume. In addition to this, CPE should introduce several significant advantages such as faster operating, easy manipulation, short time, lower cost, higher recovery and enrich-ment factor, and less stringent requirements for the separation [50]. Diluted solvents of the surfactant can be used as an extractor media in the CPE, resulting in lower laboratory waste and cost-effective likely being economical reagents. Also, surfactants are less flammable than organic solvents [48].

4.9. Novel approaches in the field of solid phase extraction

Over the years, many new extraction techniques have been improved in food analysis. Selected applications involving extraction methods in food analysis are presented in **Table 1**. Recently, SPE has been improved according to the development of a simple and original device, which also serves as a magnetic stirrer [22]. Adsorptive μ-extraction (AμE) known as innovative extraction technique and its two versions (bar adsorptive μ-extraction (BAμE) and multi-spheres adsorptive μ-extraction (MSAμE)) were detailed. This technique used for determi-nation of phenolic acid and triazines in some foods and beverages [81, 82]. Stir-rod-sorptive extraction (SRSE) device consists of a metallic wire with a magnet at one end which is the sorbent-coated glass [83]. SRSE allows extracting fluoroquinolones in honey [84]. Microsolid phase extraction (μ-SPE) was first developed in 2006. This new technique consists of positive features of SPE and capacity of membrane methods. A small bag (1–4 cm²) contains adsorbent in its inside, and this bag is made of a porous membrane, and then, this bag should move freely in the sample or should be mixed in the sample headspace [22]. The main advantages of μ-SPE procedure are good analytical performance, reduced matrix effects, analysis time and solvent usage [85]. When compared to classical solid phase extraction, μ-SPE is more basic, more economical, more sensitive and less time-consuming process. Analytes are dissolved in a little solvent especially hexane and methanol after the extraction and then can be determined by GC or HPLC [22]. The μ-spe technique should be applied for the detection of biogenic amines in orange juice [77], and of organophosphorus pesticides from wheat [85]. Stir cake sorptive extraction (SCSE) is also another solvent free extraction methods and first reported in 2011. Monolithic cake of sorbent knowing as microporous material can be used as an extrac-tion medium in SCSE, resulting in the high specific surface area. In the SCSE method, a special

Sample	Analyte	Selected sample preparation techniques	Ref
Madeira Wine	Aroma compounds	SPME/SBSE	[51]
Milk, egg, chicken and fish	Quinolone antibacterials	In-tube SPME	[52]
Water	Chlorophenols	HS-SPME	[53]
Tea infusions	Polycyclic aromatic hydrocarbons	HS-SPME	[54]
Wines, fruits, and vegetables	Famoxadone	DI-SPME	[55]
Food	Polycyclic aromatic hydrocarbons	SBSE	[56]
Juice	Pesticide residues and benzo[a]pyrene	SBSE	[57]
Vegetable	Organochlorine pesticides	SBSE	[58]
Bovine milk	Phenoxy herbicides	LLLME-hollow fiber membrane	[59]
Green tea leaves	Organochlorine pesticides	HF-LPME	[60]
Several foods	Nitrosamine	HF-LPME	[61]
Food	Phthalate esters	SDME	[39]
Orange juice	Organophosporus pesticide	SDME	[62]
Fruit juice and fruit extract	Organic acids	SDME	[63]
Water and wine	2, 4, 6-Tricholoroanisole	HS-IL-SDME	[64]
Egg yolks	Sudan dyes	MSPD–DLLME-	[65]
Grapes	Amino acids	UAE	[66]
Papaya seed oil	Physicochemical properties of papaya seed oil	UAE	[67]
Carrot	Carotenoids	UAE	[68]
Vegetables	Dichlorvos	MAE-HS-SPME	[69]
Meat products	Volatile nitrosamines	MAE-DLLME	[70]
Smoked fish	Polycyclic aromatic hydrocarbons	MAE-DLLME	[71]
Brazilian cherry seed	Phenolic compound	PFE	[72]
Scenedesmus obliquus	Carotenoids and chlorophylls a, b and c	SFE	[73]
Wine	Volatile components	SFE	[74]
Apple, green bean, carrot	Pesticide residue	SFE	[75]
Mineral water and drinkable water	Lead and cadmium	CPE	[76]
Orange juice	Biogenic amines	μ-SPE	[77]

Sample	Analyte	Selected sample preparation techniques	Ref
Water and food	Cobalt	Chelating agent free (CAF)-SPE	[78]
Food	Carotenoids	ASE	[79]
Bovine milk and dairy products	Nonsteroidal anti-inflammatory drugs	DLLME	[80]

Table 1. Selected applications of extraction techniques in food analysis.

holder consists of stationary phase and it has been developed to act as a magnetic stirrer; therefore, the holder has a significant role in both extractions of analytes and sample stirring [22]. SCSE method has some advantages such as basic operation, higher extraction capacity, cost-effectiveness, flexibility, and environmentally friendly. Monolith-based SCSE technique is applied to the juices such as soft drinks and milk, and honey to determine the sorbic acids, benzoic acid and cinnamic acid by Lin et al. [86] and to determine anthelmintics by Yulei et al. [87]. Polymeric ionic liquid-based SCSE is also used to determine organic preservatives in orange juice and tea drinks [88].

5. Conclusion

The preparation of food samples and preconcentration of analytes for the purpose of the analysis is necessary. Sample preparation is the main step in food analysis, greatly influencing the reliability and accuracy of results of analysis. Green chemistry approaches in the sample preparation techniques, as a sustainable and eco-friendly alternative to the classical techniques, are mandatory. At the same time, green sample preparation techniques are rapid, simple, generally solvent-free, sensitive, reliable and cost-effective. Different green microextraction techniques and its novel modifications have found an important role in sample preparation because of their inherent advantages over the conventional procedures. Modern trends in sample preparation techniques are toward the simplification and miniaturization of sample preparation, and the minimization of sample size and organic solvent used. In the forthcoming years, it is very probable that the greener techniques for sample preparation will be increasingly applied in food analysis, which is highly desirable.

Author details

Burak Demirhan[1], Hayriye Eda Şatana Kara[2] and Buket Er Demirhan[1]*

*Address all correspondence to: erbuket@gmail.com

1 Department of Food Analysis, Faculty of Pharmacy, Gazi University, Ankara, Turkey

2 Department of Analytical Chemistry, Faculty of Pharmacy, Gazi University, Ankara, Turkey

References

[1] Farajzadeh MA, Khoshmaram L, Sheykhizadeh S. A review on application of micro-extraction techniques for analysis of chemical. Analytical and Bioanalytical Chemistry Research. 2014;**1**(1):1-19

[2] Mendiola JA, Herrero M, Cifuentes A, Ibanez E. Use of compressed fluids for sample preparation: Food applications. Journal of Chromatography A. 2007;**1152**:234-246. DOI: 10.1016/j.chroma.2007.02.046

[3] Anastas PT, Kirchhoff MM, Williamson TC. Catalysis as a foundational pillar of green chemistry. Applied Catalysis A: General. 2001;**221**:3-13. PII: S0926-860X(01)00793-1

[4] Gałuszka A, Migaszewski Z, Namieśnik J. The 12 principles of green analytical chemistry and the significance mnemonic of green analytical practices. Trends in Analytical Chemistry. 2013;**50**:78-84. DOI:10.1016/j.trac.2013.04.010

[5] Armenta S, Garrigues S, Guardia M. The role of green extraction techniques in Green Analytical Chemistry. Trends in Analytical Chemistry. 2015;**71**:2-8. DOI: 10.1016/j.trac.2014.12.011

[6] Tiwari BK. Ultrasound: A clean, green extraction technology. Trends in Analytical Chemistry. 2015;**71**:100-109. DOI: 10.1016/j.trac.2015.04.013

[7] Anastas P, Eghbali N. Green chemistry: Principles and practice. Chemical Society Reviews. 2010;**39**:301-312. DOI: 10.1039/b918763b

[8] Warner JC. Cannon AS, Dye KM. Green chemistry. Environmental impact assessment: Review. 2004;**24**:775-799. DOI: 10.1016/j.eiar.2004.06.006

[9] Armenta S, Garrigues S, Guardia M. Green analytical chemistry. Trends in Analytical Chemistry. 2008;**27**(6):497-511. DOI:10.1016/j.trac.2008.05.003

[10] Anastas PT, Bartlett LB, Kirchhoff MM, Williamson TC. The role of catalysis in the design, development, and implementation of green chemistry. Catalysis Today. 2000;**55**:11-22. PII: S0920-5861(99)00222-9

[11] Anastas PT, Warner JC. In Green Chemistry: Theory and Practice. New York: Oxford University Press; 1998

[12] Horvath I and Anastas PT. Introduction: Green Chemistry. Chemical Reviews. 2007;**107**:2167-2168. DOI: 10.1021/cr0783784

[13] Płotka J, Tobiszewski M, Sulej AM, Kupska M, Górecki T, Namiesnik J. Green chromatography. Journal of Chromatography A. 2013;**1307**:1-20. DOI: 10.1016/j.chroma.2013.07.099

[14] Kataoka H, Lord HL, Pawliszyn J. Review: Applications of solid-phase microextraction in food analysis. Journal of Chromatography A. 2000;**880**:35-62. PII: S0021-9673(00)00309-5

[15] Hailemariam T, Bekele T. Recent advances in sample preparation techniques for environmental matrix. International Journal of Modern Chemistry and Applied Science. 2015;**2**(2):92-107

[16] Fumes BH, Silva MR, Andrade FN, Nazario CED, Lanças FM. Recent advances and future trends in new materials for sample preparation. Trends in Analytical Chemistry. 2015;**71**:9-25. DOI: 10.1016/j.trac.2015.04.011

[17] Moliner-Martinez Y, Herráez-Hernández R, Verdú-Andrés J, Molins-Legua C,Campíns-Falcó P. Recent advances of in-tube solid-phase microextraction. Trends in Analytical Chemistry. 2015;**71**:205-213. DOI: 10.1016/j.trac.2015.02.020

[18] Er Demirhan B, Demirhan B, Baş Yarımkaya S, Yentür G, Öktem AB. Investigation of melamine presence in canned tuna fish by capillary zone electrophoresis method. Journal of Agricultural Sciences. 2015;**21**:310-315

[19] Kinsella B, O'Mahony J, Malone E, Moloney M, Cantwell H, Furey A, Danaher M. Current trends in sample preparation for growth promoter and veterinary drug residue analysis. Journal of Chromatography A. 2009;**1216**(46):7977-8015. DOI: 10.1016/j.chroma.2009.09.005

[20] Beyer A, Biziuk M. Applications of sample preparation techniques in the analysis of pesticides and PCBs in food. Food Chemistry. 2008;**108**:669-680. DOI:10.1016/j.foodchem.2007.11.024

[21] Andrašcíková M, Matisová E, Hrouzková S. Liquid phase microextraction techniques as a sample preparation step for analysis of pesticide residues in food. Separation & Purification Reviews. 2015;**44**:1-18. DOI: 10.1080/15422119.2013.872125

[22] Spietelun A, Marcinkowski L, Guardia M, Namiesnik J. Review: Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry. Journal of Chromatography A. 2013;**1321**:1-13 DOI: 10.1016/j.chroma.2013.10.030

[23] Arthur CL, Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers. Analytical Chemistry. 1990;**62**(19):2145-2148. DOI: 10.1021/ac00218a019

[24] Vas G, V´ekey K. Solid-phase microextraction: A powerful sample preparation tool prior to mass spectrometric analysis. Journal of Mass Spectrometry. 2004;**39**:233-254. DOI: 10.1002/jms.606

[25] Curyło J, Wardencki W, Namieśnik J. Green aspects of sample preparation—a need for solvent reduction. Polish Journal of Environmental Studies. 2007;**16** 1:5-16

[26] Kumar A, Gaurav, Malik AK, Tewary DK, Singh B. A review on development of solid phase microextraction fibers by sol-gel methods and their applications. Analytica Chimica Acta. 2008;**610**:1-14. DOI: 10.1016/j.aca.2008.01.028

[27] Wilkes JG, Conte ED, Kim Y, Holcomb M, Sutherland JB, Miller DW. Review: Sample preparation for the analysis of flavors and off-flavors in foods. Journal of Chromatography A. 2000;**880**:3-33. PII: S0021-9673(00)00318-6

[28] Kataoka H. Automated sample preparation using in tube solid phase microextraction and its application—A review. Analytical and Bioanalytical Chemistry. 2002;**373**(1):31-45. DOI: 10.1007/s00216-002-1269-z

[29] Pawliszyn J. Theory of solid-phase microextraction. Journal of Chromatographic Science. 2000;**38**:270-278

[30] Merkle S, Kleeberg KK, Fritsche J. Recent developments and applications of solid phase microextraction (SPME) in food and environmental analysis—A review. Chromatography. 2015;**2**:293-381. DOI: 10.3390/chromatography2030293

[31] Baltussen E, Sandra P, David F, Cramers C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. Journal of Microcolumn Separations. 1999;**11**:737-747. DOI: 10.1002/(SICI)1520667X(1999)11:10<73 7::AIDMCS7>3.0.CO;24

[32] Nogueira JMF. Stir-bar sorptive extraction: 15 years making sample preparation more environment-friendly. Trends in Analytical Chemistry. 2015;**71**:214-223. DOI: 10.1016/j.trac.2015.05.002

[33] Chen Y, Guo Z, Wang X, Qiu C. Review: Sample preparation. Journal of Chromatography A. 2008;**1184**:191-219. DOI: 10.1016/j.chroma.2007.10.026

[34] Yu C, Liu Q, Lan L, Hu B. Comparison of dual solvent-stir bars microextraction and U-shaped hollow fiber-liquid phase microextraction for the analysis of Sudan dyes in food samples by high-performance liquid chromatography-ultraviolet/mass spectrometry. Journal of Chromatography A. 2008;**1188**:124-131. DOI: 10.1016/j.chroma.2008.02.065

[35] Alsharif AMA, Huat TG, Mun CY, Lawal A. Liquid phase microextraction for analysis of mycotoxins in food samples: Review. Research Journal of Chemical and Environmental Sciences. 2015;**l3**:05-21

[36] Sarafraz-Yazdi A, Amiri A. Liquid-phase microextraction. Trends in Analytical Chemistry. 2010;**29**(1):1-14. DOI: 10.1016/j.trac.2009.10.003

[37] Liu H, Dasgupta PK. Analytical chemistry in a drop. Solvent extraction in a microdrop. Analytical Chemistry. 1996;**1, 68**(11):1817-1821. DOI: 10.1021/ac960145h

[38] Kokosa JM. Recent trends in using single-drop microextraction and related techniques in green analytical methods. Trends in Analytical Chemistry. 2015;**71**:194-204. DOI: 10.1016/j.trac.2015.04.019

[39] Li M, Li Y, Mao L. Application of single drop microextraction in the determination of phthalate esters in food by gas chromatography mass spectrometry. Se Pu Chinese Journal of Chromatography. 2007;*25*(1):35-38

[40] Rezaeea M, Assadia Y, Hosseinia MRM, Aghaeea E, Ahmadia F, Berijani S. Determination of organic compounds in water using dispersive liquid–liquid microextraction. Journal of Chromatography A. 2006;**1116**(1-2):1-9. DOI: 10.1016/j.chroma.2006.03.007

[41] Bjergaard SP, Rasmussen KE. Liquid-Liquid-Liquid microextraction for sample preparation of biological fluids prior to capillary electrophoresis. Analytical Chemistry. 1999;**71**:2650-2656. DOI: 10.1021/ac990055n

[42] Rasmussen KE, Bjergaard SP. Developments in hollow fibrebased, liquid-phase microextraction. Trends in Analytical Chemistry. 2004;**23**(1):1-10. DOI: 10.1016/S0165-9936 (04)00105-0

[43] Pena-Pereira F, Lavilla I, Bendicho C. Miniaturized pre-concentration methods based on liquid–liquid extraction and their application in inorganic ultra-trace analysis and speciation: A review. Spectrochimica Acta Part B. 2009;**64**:1-15. DOI:10.1016/j.sab.2008.10.042

[44] Ridgway K, Lalljie SPD, Smith RM. Review: Sample preparation techniques for the determination of trace residues and contaminants in foods. Journal of Chromatography A. 2007;**1153**:36-53. DOI: 10.1016/j.chroma.2007.01.134

[45] Tiwari BK. Ultrasound: A clean, green extraction technology. Trends in Analytical Chemistry. 2015;**71**:100-109. DOI: 10.1016/j.trac.2015.04.013

[46] Chemat F, Rombaut N, Sicaire AG, Meullemiestre A, Tixier ASF, Vian MA. Ultrasound assisted extraction of food and natural products. Mechanisms, techniques, combinations, protocols and applications: A review. Ultrasonics Sonochemistry. 2017;540-560. DOI: 10.1016/j.ultsonch.2016.06.035

[47] Koning S, Janssen HG, Brinkman UAT. Modern methods of sample preparation for GC analysis. Chromatographia Supplement. 2009;**69**:s33-s78. DOI: 10.1365/s10337-008-0937-3

[48] Sahin CA, Efecınar M, Satıroglu N. Combination of cloud point extraction and flame atomic absorption spectrometry for pre-concentration and determination of nickel and manganese ions in water and food samples. Journal of Hazardous Materials. 2010;**176**:672-677. DOI: 10.1016/j.jhazmat.2009.11.084

[49] Wang S, Meng S, Guo Y. Cloud point extraction for the determination of trace amounts of cobalt in water and food samples by flame atomic absorption spectrometry. Journal of Spectroscopy. 2013;**735702**:1-7. DOI: 10.1155/2013/735702

[50] Citak D, Tuzen M. A novel pre-concentration procedure using cloud point extraction for determination of lead, cobalt and copper in water and food samples using flame atomic absorption spectrometry. Food and Chemical Toxicology. 2010;**48**:1399-1404. DOI: 10.1016/j.fct.2010.03.008

[51] Alves RF, Nascimento AMD, Nogueira JMF. Characterization of the aroma profile of Madeira wine by sorptive extraction techniques. Analytica Chimica Acta. 2005;**546**:11-21. DOI: 10.1016/j.aca.2005.05.012

[52] Zheng MM, Ruan GD, Feng YQ. Evaluating polymer monolith in-tube solid-phase microextraction coupled to liquid chromatography/quadrupole time-of-flight mass spectrometry for reliable quantification and confirmation of quinolone antibacterials in edible animal food. Journal of Chromatography A. 2009;**1216**:7510-7519. DOI: 10.1016/j. chroma.2009.03.054

[53] Holopainen S, Luukkonen V, Nousiainen M, Sillanpää M. Determination of chlorophenols in water by headspace solid phase microextraction ion mobility spectrometry (HS-SPME-IMS). Talanta. 2013;**114**:176-182. DOI: 10.1016/j.talanta.2013. 04.023

[54] Vinas P, Campillo N, Aguinaga N, Pérez-Cánovas E, Hernández-Córdoba M. Use of headspace solid-phase microextraction coupled to liquid chromatography for the analysis of polycyclic aromatic hydrocarbons in tea infusions. Journal of Chromatography A. 2007;**1164**:10-17. DOI: 10.1016/j.chroma.2007.06.056

[55] Aguinaga N, Campillo N, Viñas P, Hernández-Córdoba M. Solid phase microextraction coupled to gas chromatography–mass spectrometry for the analysis of famoxadone in wines, fruits, and vegetables. Spectroscopy Letters. 2009;**42**:320-326. DOI: 10.1080/003870 10903178723

[56] Zhang W, Zhang Z, Zhang J, Meng J, Bao T, Chen Z. Covalent immobilization of graphene onto stainless steel wire for jacket-free stir bar sorptive extraction. Journal of Chromatography A. 2014;**1351**:12-20. DOI: 10.1016/j.chroma.2014.05.038

[57] Zuin VG, Schellin M, Montero L, Yariwake JH, Augusto F, Popp P. Comparison of stir bar sorptive extraction and membrane-assisted solvent extraction as enrichment techniques for the determination of pesticide and benzo[a]pyrene residues in Brazilian sugarcane juice. Journal of Chromatography A. 2006;**1114**:180-187. DOI: 10.1016/j.chroma.2006.03.035

[58] Barriada-Pereira M, Serôdio P, González-Castro MJ, Nogueira JMF. Determination of organochlorine pesticides in vegetable matrices by stir bar sorptive extraction with liquid desorption and large volume injection-gas chromatography-mass spectrometry towards compliance with European Union directives. Journal of Chromatography A. 2010;**1217**:119-126. DOI: 10.1016/j.chroma.2009.10.076

[59] Zhu L, Ee KH, ZhaoL, Lee HK. Analysis of phenoxy herbicides in bovine milk by means of liquid-liquid-liquid microextraction with a hollow-fiber membrane. Journal of Chromatography A. 2002;**963**:335-343. PII: S0021-9673(02)00138-3

[60] Huang SP, Huang SD. Dynamic hollow fiber protected liquid phase microextraction and quantification using gas chromatography combined with electron capture detection of organochlorine pesticides in green tea leaves and ready-to-drink tea. Journal of Chromatography A. 2006;**1135**:6-11. DOI: 10.1016/j.chroma.2006.09.027

[61] Raharjo Y, Handajani US, Khasanah M. The application of hollow fiber-liquid phase microextraction based on green chemistry to analyze carcinogenic nitrosamines in food samples. Journal of Chemical and Pharmaceutical Research. 2014;**6**(5):1274-1280

[62] Zhao E, Han L, Jiang S, Wang Q, Zhou Z. Application of a single-drop microextraction for the analysis of organophosphorus pesticides in juice. Journal of Chromatography A. 2006;**1114**:269-273. DOI: 10.1016/j.chroma.2006.03.011

[63] Saraji M, Mousavinia F. Singledrop microextraction followed by in syringe derivatization and gas chromatography mass spectrometric detection for determination of organic acids in fruits and fruit juices. Journal of Separation Science. 2006;**29**(9):1223-1229

[64] Márquez-Sillero I, Aguilera-Herrador E, Cárdenas S, Valcárcel M. Determination of 2, 4, 6-tricholoroanisole in water and wine samples by ionic liquid-based single-drop microextraction and ion mobility spectrometry. Analytica Chimica Acta. 2011;**702**:199-204. DOI: 10.1016/j.aca.2011.06.046

[65] Yan H, Wang H, Qiao J, Yang G. Molecularly imprinted matrix solid-phase dispersion combined with dispersive liquid–liquid microextraction for the determination of four Sudan dyes in egg yolk. Journal of Chromatography A. 2011;**1218**:2182-2188. DOI: 10.1016/j.chroma.2011.02.042

[66] Carrera C, Ruiz-Rodríguez A, Palma M, Barroso CG. Ultrasound-assisted extraction of amino acids from grapes. Ultrasonics Sonochemistry. 2015;**22**:499-505. DOI: 10.1016/j.ultsonch.2014.05.021

[67] Samaram S, Mirhosseini H, Tan CP, Ghazali HM. Ultrasound-assisted extraction and solvent extraction of papaya seed oil: Crystallization and thermal behavior, saturation degree, color and oxidative stability. Industrial Crops and Products. 2014;**52**:702-708. DOI: 10.1016/j.indcrop.2013.11.047

[68] Li Y, Fabiano-Tixier AS, Tomao V, Cravotto G, Chemat F. Short Communication: Green ultrasound-assisted extraction of carotenoids based on the bio-refinery concept using sunflower oil as an alternative solvent. Ultrasonics Sonochemistry. 2013;**20**:12-18. DOI: 10.1016/j.ultsonch.2012.07.005

[69] Chen YI, Su YS, Jen JF. Determination of dichlorvos by on-line microwave-assisted extraction coupled to headspace solid-phase microextraction and gas chromatography–electron-capture detection. Journal of Chromatography A. 2002;**976**:349-355. P II: S0021-9673(02)01144-5

[70] Campillo N, Vinas P, Martínez-Castillo N, Hernández-Córdoba M. Determination of volatile nitrosamines in meat products by microwave-assisted extraction and dispersive liquid–liquid microextraction coupled to gas chromatography–mass spectrometry. Journal of Chromatography A. 2011;**1218**:1815-1821. DOI: 10.1016/j.chroma.2011.02.010

[71] Ghasemzadeh-Mohammadi V, Mohammadi A, Hashemi M, Khaksar R, Haratian P. Microwave-assisted extraction and dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry for isolation and determination of polycyclic aromatic hydrocarbons in smoked fish. Journal of Chromatography A. 2012;**1237**:30-36. DOI: 10.1016/j.chroma.2012.02.078

[72] Oliveira AL, Destandau E, Fougère L, Lafosse M. Isolation by pressurised fluid extraction (PFE) and identification using CPC and HPLC/ESI/MS of phenolic compounds from Brazilian cherry seeds (*Eugenia uniflora* L.). Food Chemistry. 2014;**145**:522-529. DOI: 10.1016/j.foodchem.2013.08.065

[73] Guedes AC, Gião MS, Matias AA, Nunes AVM, Pintado ME, Duarte CMM, Malcata FX. Research note: Supercritical fluid extraction of carotenoids and chlorophylls a, b and c, from a wild strain of *Scenedesmus obliquus* for use in food processing. Journal of Food Engineering. 2013;**116**:478-482. DOI: 10.1016/j.jfoodeng.2012.12.015

[74] Karasek P, Planeta J, Ostra EV, Mikesova M, Golias J, Roth M, Vejrosta J. Direct continuous supercritical fluid extraction as a novel method of wine analysis Comparison with conventional indirect extraction and implications for wine variety identification. Journal of Chromatography A. 2003;**1002**:13-23. DOI: 10.1016/S0021-9673(03)00561-2

[75] Lehotay SJ. Determination of pesticide residues in nonfatty foods by supercritical fluid extraction and gas chromatography/mass spectrometry: Collaborative study. Journal of AOAC International. 2002;**85**(5):1148-1166

[76] Silva EL, Roldan PS. Simultaneous flow injection pre-concentration of lead and cadmium using cloud point extraction and determination by atomic absorption spectrometry. Journal of Hazardous Materials. 2009;**161**:142-147. DOI: 10.1016/j.jhazmat.2008.03.100

[77] Basheer C, Wong W, Makahleh A, Tameem AA, Salhin A, Saad B, Lee HK. Hydrazone-based ligands for micro-solid phase extraction-high performance liquid chromatographic determination of biogenic amines in orange juice. Journal of Chromatography A. 2011;**1218**:4332-4339. DOI: 10.1016/j.chroma.2011.04.073

[78] Diniz KM, Gorla FA, Ribeiro ES, Nascimento MBO, Corrêa RJ, Tarley CRT, Segatelli MG. Preparation of $SiO_2/Nb_2O_5/ZnO$ mixed oxide by sol–gel method and its application for adsorption studies and on-line pre-concentration of cobalt ions from aqueous medium. Chemical Engineering Journal. 2014;**239**:233-241. DOI: 10.1016/j.cej.2013.11.027

[79] Breithaupt DE. Analytical, nutritional and clinical methods simultaneous HPLC determination of carotenoids used as food coloring additives: Applicability of accelerated solvent extraction. Food Chemistry. 2004;**86**:449-456.DOI: 10.1016/j.foodchem.2003.10.027

[80] Alshana U, Göğer NG, Ertaş N. Dispersive liquid–liquid microextraction combined with fieldamplified sample stacking in capillary electrophoresis for the determination of nonsteroidal anti-inflammatory drugs in milk and dairy products. Food Chemistry. 2013;**38**(2-3):890-897. DOI: 10.1016/j.foodchem.2012.11.121

[81] Neng NR, Sequeiros RCP. Combining bar adsorptive microextraction with capillary electrophoresis—Application for the determination of phenolic acids in food matrices. Electrophoresis. 2014;**35**(17):2488-2494. DOI: 10.1002/elps.201400101

[82] Andrade FN, Ide AH, Neng Nda R, Lanças FM, Nogueira JM. Determination of trace levels of triazines in corn matrices by bar adsorptive microextraction with a molecularly imprinted polymer. Journal of Separation Science. 2016;**39**(4):756-761. DOI: 10.1002/jssc.201501101

[83] Namieśnik J, Spietelun A, Marcinkowski L. Green sample preparation techniques for chromatographic determination of small organic compounds. International Journal of Chemical Engineering and Applications. 2015;**6**(3):215-219. DOI: 10.7763/IJCEA.2015.V6.484

[84] Luo YB, Ma Q, Feng YQ. Stir rod sorptive extraction with monolithic polymer as coating and its application to the analysis of fluoroquinolones in honey sample. Journal of Chromatography A. 2010;**1217**:3583-3589. DOI: 10.1016/j.chroma.2010.03.036

[85] Pelle FD, Di Crescenzo MC, Sergi M, Montesano C, Di Ottavio F, Scarpone R. Micro-solid-phase extraction (μ-SPE) of organophosphorous pesticides from wheat followed by LCMS/MS determination. Food Additives and Contaminants: Part A. 2016;**33**:291-299. DOI: 10.1080/19440049.2015.1123818

[86] Lin F, Nong S, Huang X, Yuan D. Sensitive determination of organic acid preservatives in juices and soft drinks treated by monolith-based stir cake sorptive extraction and liquid chromatography analysis. Analytical and Bioanalytical Chemistry. 2013;**405**:2077-2081. DOI: 10.1007/s00216-012-6646-7

[87] Yulei W, Jie Z, Xiaojia H, Dongxing Y. Preparation of stir cake sorptive extraction based on polymeric ionic liquid for the enrichment of benzimidazole anthelmintics in water, honey and milk samples. Analytica Chimica Acta. 2014;**46**:33-41. DOI: 10.1016/j.aca.2014.06.039

[88] Chen L, Huang X. Preparation of a polymeric ionic liquid-based adsorbent for stir cake sorptive extraction of preservatives in orange juices and tea drinks. Analytica Chimica Acta. 2016;**916**:33-41. DOI: 10.1016/j.aca.2016.02.030