VERSITA

Cent. Eur. J. Chem. • 10(4) • 2012 • 938-976
DOI: 10.2478/s11532-011-0160-1

Central European Journal of **Chemistry**

Analytical sonochemistry; developments, applications, and hyphenations of ultrasound in sample preparation and analytical techniques

Review Paper

Shahram Seidi, Yadollah Yamini*

Department of Chemistry, Tarbiat Modares University,
P.O. Box 14115-175, Tehran, Iran

Received 21 August 2011; Accepted 12 December 2011

Abstract: Ultrasonic assistance is one of the great successes of modern analytical chemistry, which uses this energy for a variety of purposes in relation to sample preparation and development of methods for the analysis of numerous contaminants including organic and inorganic compounds. This review will attempt to provide an overview of more recent applications of ultrasound in different environmental and biological samples such as food, soil and water as well as a brief description of the theoretical understanding of this method. Also, the possibility of coupling ultrasound with other analytical techniques will be discussed.

Keywords: *Sonochemistry • Ultrasound • Extraction • Sample preparation*

1. Introduction

Ultrasound (US) is an energy source pitched above human hearing that has potential for enhancing a variety of purposes in diverse areas [1]. When an US is exposed to a liquid or solution, fine bubbles are generated, called cavitation bubbles. Inside the bubbles, there is an instant when the conditions rise to about 5000 K and 2000 atm [2]. The research and application utilizing the reaction field of localized high temperature and high pressure thus obtained by US is called sonochemistry.

According to Luche, sonochemistry applications could be subdivided into ‘‘true’’ sonochemistry which refer to real chemical effects induced by cavitation and ‘‘false’’ sonochemistry that could be mainly ascribed to the mechanical impact of bubble collapse [3]. These mechanical effects have not held the interest of synthetic chemists as much as the so-called true ones, but nevertheless, they are certainly important in areas such as processing.

Specialists in US such as Mason [3] have identified three main “strands” in ultrasonics research. He has shown there are mutual links between these strands that can serve to strengthen research in the general area of power US [3].

US has been used in many areas of chemistry. The pioneering work on the chemical applications of US was conducted in the 1920s by Richards and Loomis in their classic survey of the effects of high-frequency sound waves on a variety of solutions, solids and liquids [4].

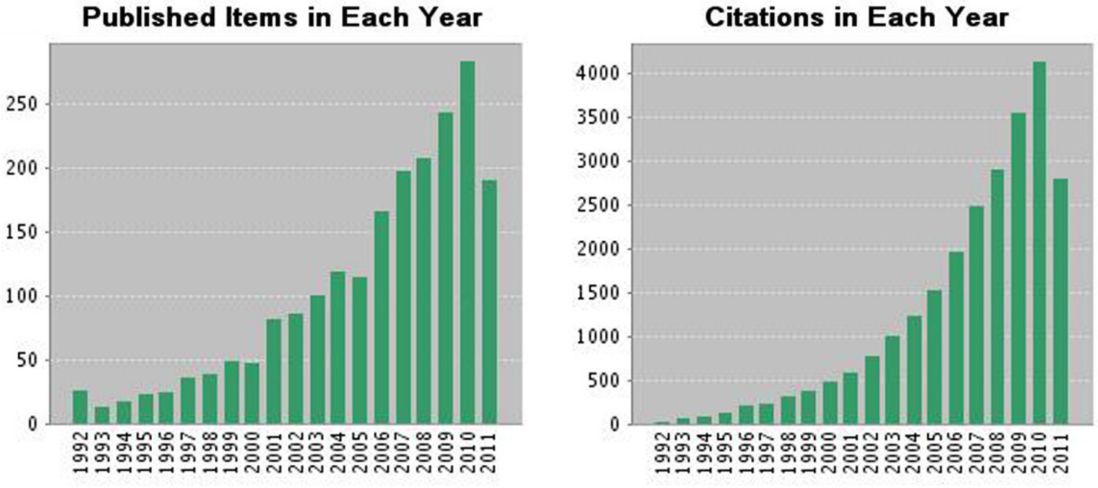
In organic and inorganic chemistry, US is used widely particularly to improve and accelerate synthetic reactions [5]. The parallels between the aims of the two areas of green chemistry and sonochemistry are striking. In 2007, Mason has reviewed some applications of US for treatment of sewage sludge and the control of crystallization [6].

Ultrasonic assistance is gradually becoming quite common place in analytical chemistry, so that sonochemistry is widely used in sample preparation procedures such as digestion, leaching, liquid-liquid extraction and derivatization. In fact, the number of publications in the last eight years that include the words “ultrasound extraction” has noticeably increased (Fig. 1). Also, the number of citations each year (Fig. 1) indicates popularity and the place of importane which ultrasound has found in analytical chemistry.

This review deals with the use of US in sample preparation including solids, liquids and heterogeneous samples with special emphasis on ultrasound assisted

---

* *E-mail: yyamini@modares.ac.ir*


Published Items in Each Year

Citations in Each Year

Figure 1. Evolution of the number of publications and citations in each year based on “ultrasound extraction” (source ISI Web of Science database).

liquid phase microextraction (USA-LPME) methods as one of the recent applications of US in analytical sonochemistry and demonstrates how this energy can enhance various steps of analyses. The advantages and disadvantages of US in sample preparation techniquels as well as the possibility of coupling US with other analytical techniques will be also discussed.

2. Type of ultrasounds and their comparison

Among the various types of laboratory instrumentation currently available for sonochemistry namely, whistle reactors, ultrasonic cleaning baths, probes and cup-horn devices, the ultrasonic bath and the probe system also called a “sonotrode” are the most commonly available to the chemist. Both of them are usually operated at a fixed frequency dependent on the particular type of transducer, which are usually 20 kHz for common probe systems and 40 kHz for baths [1,2]. Cavitation efficiency in a probe is higher than an ultrasound bath because the probe system can introduce a much greater intensity to a specific zone.

Also, the number of variables that must be taken into account with the ultrasonic bath is greater thanfor the probe and includes water volume inside the bath, sample position and the water bath temperature. Therefore, ultrasonication with a probe can be done in less time and it is not necessary to carefully control variables as with the ultrasonic bath. Therefore, the choice between baths and probes depends on the requirements of a particular analysis [2,7].

3. Physical principals of ultrasound

Ultrasound can transmit through any elastic media and cause an oscillation of particles. When particle oscillation takes place in a medium, a disturbance is caused. If the disturbance is periodically repeated, expansion and compression cycles travelling through a medium will occur [2]. Compression cycles push molecules together, whereas expansion cycles pull them apart. In a liquid, the expansion cycle produces negative pressure that pulls molecules away from one another [8]. If the US intensity is high enough, the expansion cycle can create bubbles or cavities in the liquid which varies depending on nature and purity of liquid [8]. Fig. 2A shows a state of the generation of bubbles when an ultrasound is emitted into water. Within several seconds, bubbles grow, get unstable mechanically when they reach a particular size and go into rapid contraction [9]. The process by which bubbles form, grow and undergo implosive collapse is known as “cavitation”. The size of a bubble, depends remarkably on ultrasonic frequency and intensity, has a radius of usually several dozen μm when it contracts [2]. Different factors influence cavitation threshold including gas and particulate matter, external pressure, solvent viscosity, solvent surface tension, solvent vapor pressure, applied frequency, temperature, intensity, field type, attenuation and types of ultrasound cavitation [2,5].

If the compression process can be assumed to progress adiabatically, at the moment when a bubble becomes smallest, a high temperature and high pressure field are throught to be generated, about 5000 K and 2000 atm [10], as shown in Fig. 2A.

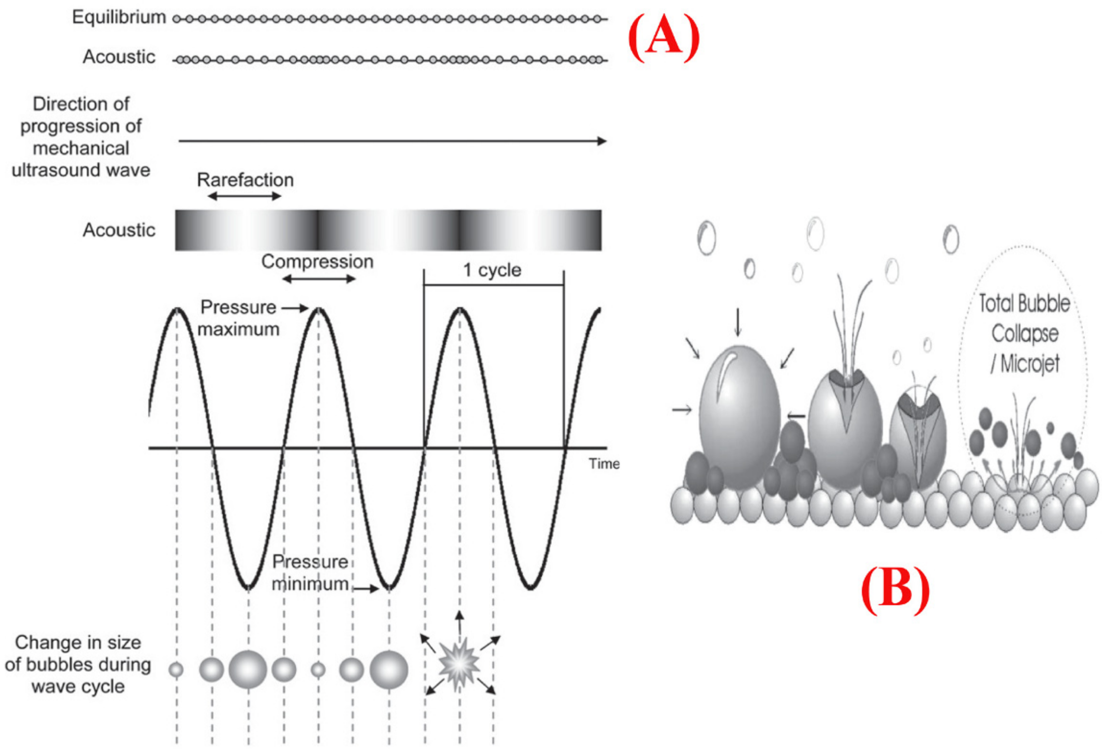


Figure 2. (A) Development and collapse of cavitation bubbles, and (B) schematic depicting classically thought bubble collapse at the solid surface (reproduced with permission of Elsevier and RSC-modified [9,13]).

This field with a high temperature and a high pressure is called a hot spot [10]. The position several hundred nm away from the bubble has a normal conditions of temperature and pressure, and thus the space inside a bubble becomes a field repeating a high speed heating and a rapid cooling at a cycle of approximately 10^{10} K s^{-1}. This is why cavitation is also known as “cold boiling” [10].

When cavitation occurs in a liquid close to a solid surface, the dynamics of cavity collapse change dramatically (Fig. 2B). In pure liquids, the cavity retains its spherical shape during collapse as its surroundings are uniform. Close to a solid boundary, however, cavity collapse is rather asymmetric and produces high-speed jets of liquid [2]. Liquid jets driving into the surface at speeds close to 400 km h^{-1} have been observed [2]. The impact of the jets on the solid surface is very strong. This can result in serious damage to impact zones and produce newly exposed, highly reactive surfaces. Distortions of bubble collapse depend on surfaces several times larger than the resonant size of the bubble [2]. Recently, Kim *et al*. used the acoustic and heat transfer modes in COMSOL Multiphysics™ to predict the pressure and heat transfer profile in four different solvents [11].

4. Overview of analytical applications of US

Ultrasonic assistance is gradually becoming quite common place in analytical chemistry, which uses this energy for a variety of purposes but with very disparate frequency [12]. The different steps of the analytical process which can be expedited and/or improved by use of ultrasound energy, including those less known by analytical chemists, are revised in Fig. 3.

A distinction is made between application of ultrasound before the analysis, during it (for sample preparation), and for assisting or as detection technique in this figure. This classification has been done according to recent publications, especially the reviews, about different aspects of US [1,2,5,12]. Professor Luque de Castro and Dr. Priego Capote have assembled a vast amount of information in a book with the title of “*Analytical Applications of Ultrasound*” [2]. Also, professor Capelo-Martinez has assembled another book with the title of “*Ultrasound in Chemistry*” [5]. These books provide a wealth of information for those interested in exploiting ultrasound to enhance different steps in an analysis and are recommended readings. This paper focuses on the ways analytical chemists can use ultrasound energy properly for sample preparation in both micro and macro-scale.

4.1. US assisted sample preparation techniques

One of the most common applications of US is sample preparation which can be used in micro or macro-scale modes as well as different states of samples including solid, liquid and heterogeneous. The most application of US in sample preparation has been focused on macro-scale mode so far, but its application for sample preparation in micro-scale is progressing which will be discussed in detail in the following sections.

4.1.1. Solid samples

In the case of solid samples, ultrasound can be used for preparation of these samples in variety ways including digestion, leaching, slurry formation and physical removing (see Fig. 3) [2,13]. Preparations of solid samples are almost unavoidable due to incompatibility of these samples with the most of analytical instruments.

IUPAC defines digestion as “a chemical process for softening or solubilizing a material with heat, chemical reagents, and moisture”. Sample matrix is decomposed and loses most of its initial structure. Thermal energy can be replaced by or supplemented with auxiliary energy, for example ultrasound, to accelerate sample digestion. In ultrasound assisted digestion (USAD), both the mechanical and chemical effects are simultaneous but their impact differs [2].

Another way of converting the target analytes to a liquid phase is solid–liquid extraction [14,15], which is also known as leaching or lixiviation [2]. Leaching separates the soluble components from some material by percolation. However, leaching is not a specific step, but only more selective than digestion because it maintains most matrix interferences in the solid [2].

Another choice for solid sample preparation is the use of slurries. Slurries are prepared by adding a liquid to a previously ground, sieved, and weighed solid sample; this ensures the stability of the slurry during the time required to withdraw a sample for transfer to the measuring instrument, whether by hand or automatically [2,13]. Ultrasound assisted slurry formation is superior to digestion for preparation of solid samples. It circumvents problems associated with digestion of samples with

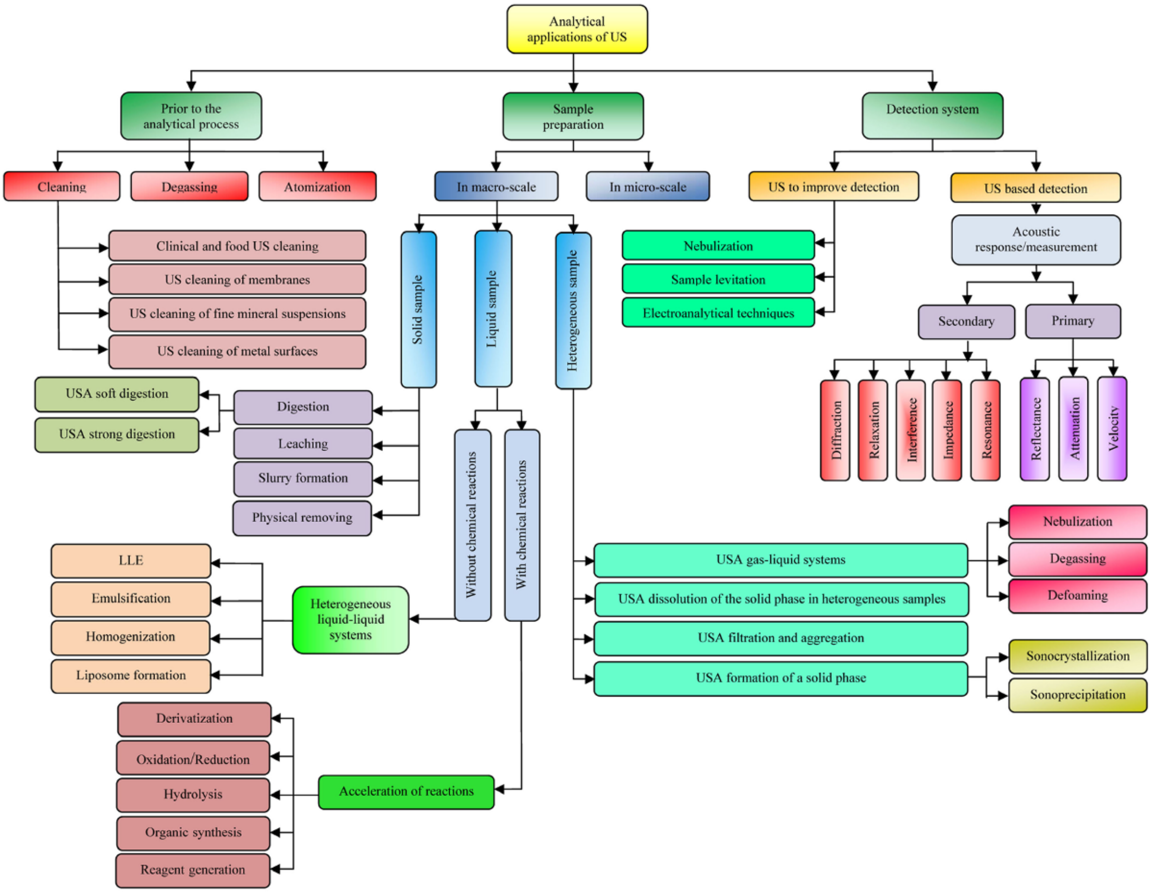


Figure 3. The different steps of the analytical process which can be expedited and/or improved by use of ultrasound energy.

complex matrices, because of the hazardous conditions required [2]. It is also an alternative to leaching when efficiencies are not quantitative [13].

4.1.2. Heterogeneous samples

The main purpose of US in handling heterogeneous media is for separating a solid from a liquid phase, dissolving it, or enhancing or accelerating the formation of a solid phase. The most applications of ultrasound are in gas-liquid heterogeneous systems include nebulization, degassing and defoaming [2,13].

Filtration is one of the usual ways to separate phases which is dramatically facilitated by US. Aggregation, which also known as agglomeration, is the formation of large particles from small ones which agglomerate rapidly and efficiently when subjected to ultrasound [2,13].

Sonocrystallization and sonoprecipitation are the applications of ultrasound in order to form solid phases [2]. Sonocrystallization is the currently accepted name for the use of power ultrasound to control and accelerate the course of a crystallization process [2,13]. Like crystallization, US also successfully assists the formation of extremely finely divided and uniform particles, which can be termed sonoprecipitation [2,13]. This effect, which has been exploited in analytical chemistry, can facilitate sample preparation in nephelometric and turbidimetric methods [2,13].

4.1.3. Liquid samples

Application of ultrasound in preparation of liquid samples can be divided in two general groups. The first group, is one in which ultrasound only accelerates physical operations. Although any chemical reaction may occur but if the outcome is unclear, it suggests the absence of chemical changes. This group includes liquid-liquid extraction (LLE), emulsification, homogenization and liposome formation [1,2]. The second group contains those that are accomplished with chemical reactions. The latter group can be classified as derivatization, oxidation/reduction, hydrolysis, organic synthesis and reagent generation chemical reactions which ultrasound accelerates [1,2]. In 2007, Castro and Capote have published two reviews [1,13], which in one of them, the influence of ultrasound on the development of chemical reactions has been described in detail [13]. Most of the chemical reactions exist in non-analytical areas whereas the first group has received more attention in analytical chemistry. Recently, Castro *et al.* have published a review about the role of ultrasound in analytical derivatization [16]. Both groups can be done in discrete (batch) or continuous ways which will be discussed for the first group in the following.

Emulsion is greatly promoted by US. This is the phenomenon occurring between two liquid immiscible phases by which one (dispersed) phase distributes in the other phase in the form of small droplets with diameters in general exceeding 0.1 μm [2,13]. The effect of US is based on droplet disruption in sonicated liquid–liquid systems as a result of cavitation.

Liposomes are spherical vesicles formed by aggregation of amphiphilic phospholipids molecules in a bilayer structure [1,2,13]. Liposomes have aroused interest in a great variety of areas from biochemistry and molecular biology to cosmetics and food technology. Nguyen *et al*. showed that ultrasound plays a prominent role in the preparation of sensors [17].

The present review focuses on the updated developments and applications of ultrasound in sample preparation for both macro and micro-scales. The micro-scale developments will be discussed separately in section 8. This section covers almost all the recent publications related to the procedure for different organic and inorganic compounds in different samples as well as different matrices including water, soil and food. The recent reports since 2008 are tabulated in Table 1 to Table 4.

5. Different modes of ultrasound assisted sample preparation techniques

This section intends to show analytical chemists different modes of ultrasound utilization for sample preparation that deals with a variety of samples including solid, liquid and heterogeneous samples. Extensive descriptions about these systems have been previously published by Luque de Castro and Priego Capote [1,2,12].

A schematic presentation for different instrumental modes of various sample preparation techniques are revised in Fig. 4.

As can be seen from this figure, the steps involved in sample preparation can be performed (a) in a discrete or batch manner or (b) in a continuous fashion. The most apparent differences between the two modes are as follows: In a discrete approach, the analytical system is confined in a vessel or container through the walls of which US energy is transmitted if an ultrasonic bath is used. The use of a US probe in this case can involve either to dip it into the vessel or into the transmitting liquid where the vessel is located. Recently, some efforts have been done for miniaturization of discrete USAE techniques. For example, a miniaturized extraction technique based on ultrasound radiation, named sonication assisted extraction in small columns (SAESC),

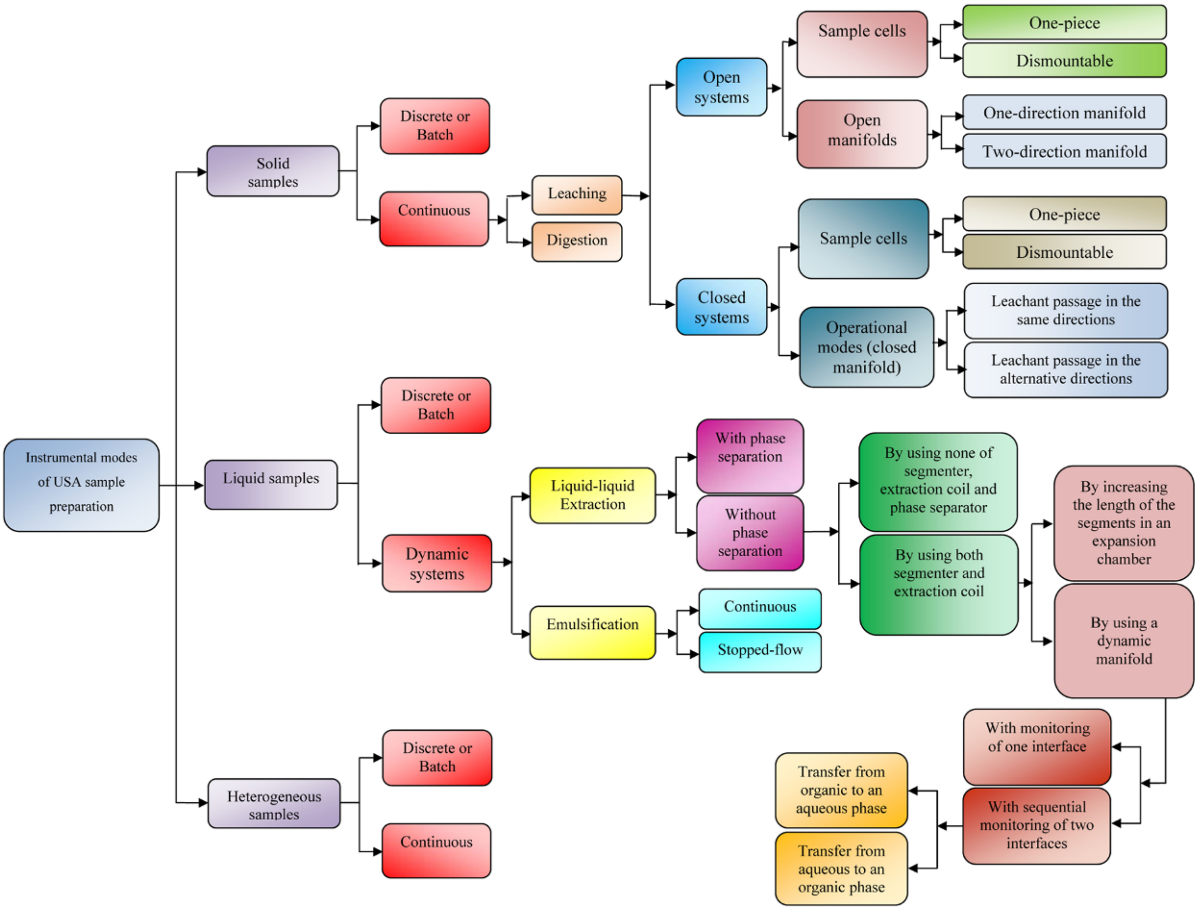


Figure 4. A schematic presentation for different instrumental modes of various sample preparation techniques.

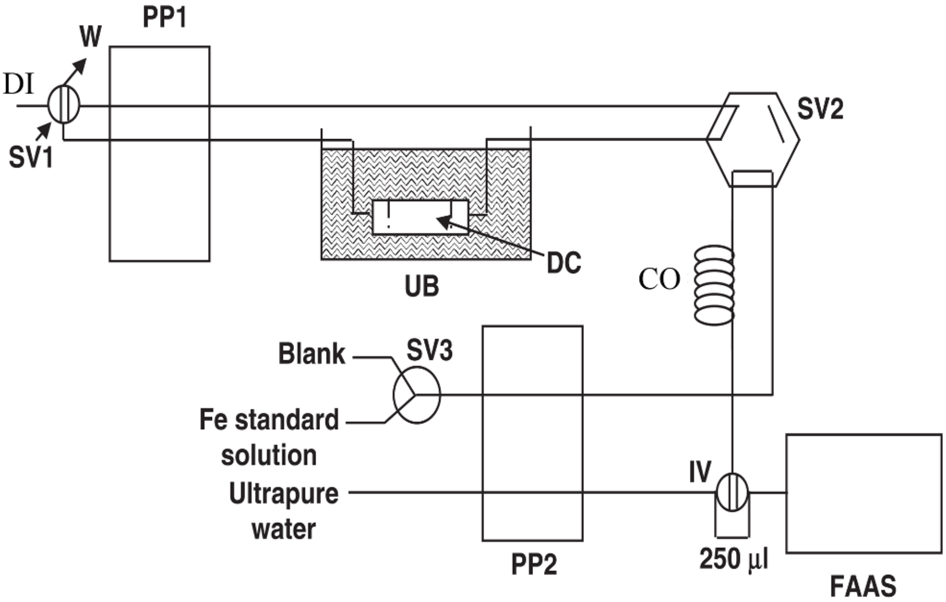


Figure 5. Schematic presentations for (A) continuous USAD coupled with FAAS; CO: coil, DI: digestant, DC: digestion chamber, IV: injection valve, PP: peristaltic pump, SV: switching valve, UB: ultrasonic bath and W: waste (reproduced with permission of Elsevier-modified [2]).

Table 1. Different ultrasound assisted extraction techniques for determination of organic compounds from food samples.

Matrix	Analyte	Determination technique	Sonication conditions							Recovery%	Ref.
			Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode^a	Extraction solvent			
								Composition	Volume (mL)		
Lonicera japonica Thunb	Chlorogenic acid	HPLC-DAD	40	60	UB	-	D	0.75 M [BMIM][BF4] (pH = 1.2)	20	94.6-103.2	[18]
Saffron	Volatile compounds	GC-MS GC-FID	30	25	UB	35	D	Diethyl ether	100	-	[19]
Honey	Linalool	GC-MS	10	-	UB	-	D	n-Pentane : diethylether (1:2)	15	-	[20]
Almond dregs	Protein	CBBM	30	37	UB	40	D	NaOH (pH = 10.1)	295	69.76	[21]
Fruits	Alkaloid	HPLC-UV	30	51	UB	40	D	Acidified MeOH (pH = 2)	33	96.6-104.9	[22]
Camptotheca acuminata seeds	Camptothecin	HPLC-UV	60	50	UB	40	D	0.5% Na_2CO_3 in water	20	-	[23]
Jellyfish	Glycoprotein	HPLC-UV	15	-	UP	-	D	Water	20	97.84	[24]
Mackerel	Amino acid composition	AAA	10	RT		40	D	Isopropanol	-	88.6	[25]
Leafy vegetables	Pesticide multi-residues	LC–MS/MS	35	25–45	UB	28	D	Ethyl acetate	45	83-98	[26]
Honey	Antibiotics	LC–MS/MS	8	RT	UB	-	D	ACN	4	68-98	[27]
Pork chicken	Sulfonamides	LC–UV	10	RT	UB	-	D	ACN	5	67-83	[28]
Pears	Amitraz and metabolites	LC–MS/MS	15	RT	UB	-	D	Ethyl acetate	25	70-106	[29]
Fish	PFOA, PFOS	LC–MS/MS	45	RT	UB	-	D	MTBE	12	90-113	[30]
Dairy products Fish	Melamine	CZE-DAD	10	RT	UB	-	D	Liquid samples: 1 mL 10% TCA+7 mL deionized water + 1 mL chloroform Solid samples: 1mL 10% TCA+ 9mL deionized water + 1 mL chloroform	9 11	93-104	[31]
Grape seeds	Phenolic compounds Antioxidants Anthocyanins	UV-Vis spectrophoto-meter	29.03 30.58 29.49	56.03 60.65 55.13	UB	40	D	53.15% (v/v) EtOH:water 53.06% (v/v) EtOH:water 52.35% (v/v) EtOH:water	100	-	[32]
Caraway seeds	Carvone Limonene	GC-FID GC-MS	60	69	CHSR	20	D	n-hexane	100	-	[33]
Hydrolysed rice bran wax	Policosanols	GC-FID	50	RT	A special type	20	D	4% (w/v) sodium hydroxide	1:2 (g mL^{-1})	-	[34]
Fish Mussel	Antibiotics	HPLC-DAD HPLC-FLD	5	RT	UP	-	D	Water and 50 μL of Proteinase-K solution	5.05	37.5-93.1	[35]
Spice	Fat-soluble colorants	HPLC-UV	15	-	UB	-	D	Acetone : CAN, 50:50 (v/v)	10	92-109	[36]
Soybean crops	BBI Lectin	LC–ESI-MS HPLC-UV	5	-	UP	-	D	Petroleum ether	10	92.2-106	[37]
Olive fruit	Phenolic compounds	HPLC-DAD HPLC-FLD HPLC-MS/MS	20	45	UB	30	D	MeOH	25	94.1–98.7	[38]
Brazilian seafood samples	Methyl mercury Ethyl mercury Inorganic mercury	LC–ICP-MS	15	-	UB	-	D	0.1% v/v HCl + 0.05% m/v L-cysteine + 0.1% v/v 2-mercaptoethanol	10	>90	[39]
Saffron spice	Safranal	UV–Vis spectrophoto-meter	15	25	UB	35	D	Chloroform or n-hexane	4	83-93	[40]
Milk, milk products, bakery goods and flour	Melamine	UPLC-MS/MS	25	RT	UB	-	D	ACN:water, 1:1 (v/v)	10	97-99	[41]
Orange peel	Polyphenols	HPLC-DAD	30	40	UB	25	D	EyOH:water 4:1 (v/v)	0.25 g mL^{-1}	-	[42]
Pomegranate peel	Antioxidants	UV–Vis spectrophotometer	6 -8 min with 59.2 Wcm^{-2} intensity level	25 ± 2	UP	20	D	Water	0.02, w/w (peel to water)	-	[43]
Tomatoe	Lycopene	HPLC-UV UV–Vis spectrophoto-meter	45.6	47.6±1	UB	37	D	n-hexane : acetone : EtOH (2:1:1)	74.4:1 (v/w)	-	[44]
Chickpea	Oil	GC-FID	20	50	UB	40	C	n-hexane : isopropanol, 3:1 (v/v)	8.5 mL, During extraction the direction of the leaching carrier (at a flow rate of 5 mL min^{-1}) was changed each 120 s	-	[45]
Auricularia auricula fruit bodies	Melanin	DAD spectrophoto-meter	36	63	UB	40	D	Water (initial pH was adjusted to 12 with 1 M NaOH)	43 mL g^{-1}	-	[46]

Continued **Table 1.** Different ultrasound assisted extraction techniques for determination of organic compounds from food samples.

Matrix	Analyte	Determination technique	Sonication conditions							Recovery%	Ref.
			Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode^a	Extraction solvent			
								Composition	Volume (mL)		
A single Zebrafish egg	Bonded long chain fatty acids	GC-MS	1	-	UB	40	D	100 μL of 0.5 M NaOH and then 200 μL of n-hexane	0.3	-	[47]
Vegetable foods	Haloacetic acids	GC-ECD (off line)	10	35	UP	20	C	10% sulphuric acid in MeOH	During extraction the direction of the leaching carrier (at a flow rate of 2 mL min^{-1}) was changed each 2 min	80-115	[48]
Wheat bran	Phenolic compounds	UV-Vis spectrophoto-meter	25	60	UB	40	D	EtOH : water, 60% (v/v)	100	-	[49]
Dietary supplements	Lecithin and soybean oil	GPC-ATR-FTIR	5	-	UB	-	D	DCM	10	-	[50]
Hazelnuts	Aflatoxins	LC-MS/MS	10	RT	UB		D	ACN: water, 80:20 (v/v)	20	93-101	[51]
Wheat germ	Defatted wheat germ proteins	(micro-Kjeldahl method)	24	-	UB	24	D	Reverse micellar solution (The reverse micellar systems were formed by AOT, isooctane and KCl solution)	50	45.6	[52]
Wine	Volatile compounds	GC-FID GC-MS	30 min (system 1) 15 min (system 2)	25	UB	-	D	System 1; diethyl ether : n-pentane (2:1) System 2; DCM	50 mL (system 1) 25 mL (system 2)	2.9-109.6 (system 1) 2.1-98.8 (system 2)	[53]
Vanilla planifolia	Vanillin	HPLC-DAD	6	RT	-	20	D	EtOH : water, 40:60 (v/v)	45	98.5-99.6	[54]

[a] Soncation modes: D; discrete, C; continuous or dynamic

Abbreviations: AAA: amino acid analyzer, ACN: acetonitrile, AOT: Sulphosuccinic acid bis (2-ethylhexyl) ester sodium salt, ATR: attenuated total reflectance, BBI: Bowman-Birk inhibitor, CBBM: Coomassie brilliant blue method, CHSR cup-horn sonoreactor, CZE: capillary zone electrophoresis, DAD: diode array detection, DCM: dichloromethane, ECD: electron-capture detector, ESI: electrospray ionization, EtOH: ethanol, FID: Flame ionization detector, FLD: fluorescence detector, FTIR: fourier transform infrared spectrometry, GC: gas chromatography, GPC: gel permeation chromatography, HPLC: high performance liquid chromatography, ICP: inductively coupled plasma, LC: liquid chromatography, LOD: limit of detection, LOQ: limit of quantification, MeOH: methanol, MS: mass spectrometry, PFOA: perfluorooctanoic acid, PFOS: perfluorooctane sulphonate, TCA: trichloroacetic acid, UB: ultrasonic bath, UP: ultrasonic probe.

was developed for the determination of pesticides in soil samples by Sánchez-Brunete *et al*. [156]. Also, Ozcan *et al*. developed a miniaturized USAE for determination of PAHs in soil samples [157].

In a continuous approach, the analytical system rarely comes into contact with the US source, which is accommodated in the transmitting liquid surrounding the dynamic system [2]. Whether or not the sample is placed in a fixed position in the dynamic system depends on its particular state [2]. Thus, if the sample is a solid, it is held in a chamber furnished with filters at its ends through which a leaching or digesting solution is circulated. Obviously, the chamber is the zone subjected to US. When the sample is a liquid, it can either be circulated through the dynamic system or stopped for a preset time so it can be subjected to ultrasonic radiation in order to facilitate a chemical reaction, a liquid–liquid extraction, emulsification, homogenization, crystallization, precipitation, *etc*. The design of the dynamic system depends on the particular process and the working conditions under which it is developed. The most applications of US are discrete in nature. This can be ascribed to the fact that few research groups have so far worked on continuous approaches despite such major advantages as automation and reduced chemical consumption. Fig. 5 shows a typical manifold used to implement the continuous ultrasound assisted digestion (USAD) [158].

6. Discrete versus continuous ultrasound assisted sample preparation techniques and comparison with other well-established extraction procedures

One of the greatest advantages of continuous ultrasound assisted operations is their ease of on-line connection to other operations in order to facilitate automation of the overall analytical process. In this way, the solutions obtained after each step need not be handled by the operator or come in contact with the atmosphere, which can be of enormous interest for some analytical systems. Fig. 5 shows one of the devices for assisting dynamic systems by US.

A number of alternatives to classical leaching methods since US was first used as auxiliary energy to assist a leaching process have been in use. The advantages of USAL over the classical leaching methods are obvious: frequently, the latter involve longer time preparation procedures under drastic conditions, the use of hazardous reagents and intensive intervention of the analyst, all with little room for automation. Similar to US, other auxiliary energies such as MWs or the use of high pressures and temperatures have proved effective with a view to accelerate and automate leaching. The advantages and disadvantages of USAL as compared to three widely used leaching alternatives

Table 2. Application of hyphenated techniques with ultrasound assisted extraction for determination of organic and inorganic compounds from different matrices.

Matrix	Analyte	Hyphenated[a] technique	Determination technique	Sonication conditions							Recovery%	Ref.
				Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode[b]	Extraction solvent			
									Composition	Volume (mL)		
Baby food	QU FQ	SPE MIP	LC–UV	15	RT	UB	-	D	MeOH	8	87-100	[55]
Agricultural soils	Sulfathiazole	SPE	LC-MS	5	-	UP	-	D	ACN:buffer pH 9 (20:80)	6	15–25	[56]
Agricultural soils	Sulfadimethoxie	SPE	LC-MS	5	-	UP	-	D	ACN:buffer pH 9 (20:80)	6	42–64	[56]
Sewage sludge	EDCs	SPE	GC-MS	30	55	UB	-	D	MeOH: water (5: 3)	8	74-92	[57]
Sewage sludge	PhACs	SPE	GC-MS	30	55	UB	-	D	MeOH: water (5: 3)	8	86-88	[57]
Fruits	Phenolic acids	SPE	HPLC-DAD	30	60	UB	-	D	MeOH	100	95.3-104.3	[58]
Mussel shells	PCBs	SPE	GC-ECD	10	-	UB	-	D	n-Hexane: acetone (50:50)	10	88-108	[59]
Fly ash	PCBs	SPE	GC-ECD	10	-	UB	-	D	n-Hexane: acetone (50:50)	10	70-105	[59]
Sewage sludge	PCBs	SPE	GC-ECD	10	-	UB	-	D	n-Hexane: acetone (50:50)	10	70-93	[59]
Shellfish	PCBs	SPE	GC-MS	60	45	UB	40	D	n-Hexane	40	80.92-93.89	[60]
Soils	Petroleum hydrocarbons	SPE	GD	40-60	-	UB	-	D	n-Hexane	35	80-95	[61]
Pollen	Fipronil	MSPD	GC-ECD	20	RT	UB	-	D	ACN	10	98-103	[62]
Fruits	OPPs Triazines	MSPD	GC–MS	1	32	CHSR	35	D	Ethyl acetate	-	73-118	[63]
Seafood; cereal; meat; legume; dried fruit and cheese	Ni	Chelating resin	FAAS (on line)	0.5-3 (depends on matrix)	RT	UB	40	C	HNO$_3$ 3 M (for legume) and 1.5 M (for the other)	2 mL (Flow of 3.5 mL min^{-1}, Direction changed each 20 s)	105-100	[64]
Soil	TBBPA, TCBPA, BPA	SPE	GC–MS	30	RT	UB	-	D	Ethyl acetate	10	88-108	[65]
Fruits, vegetables, juices, baby food, bread, mushrooms, beer, coffee powder	Chlormequat and mepiquat	SPE	LC–MS/MS	10	RT	UB	-	D	MeOH:ammonium formate buffer solution (100 mM; pH 3.5), 1:4 (v/v)	25	>78	[66]
Potato	Triazines	SPE	Non-aqueous CE	20	RT	UB	-	D	15 mL of water, 10 mL of DCM : acetone : n-hexane (1:1:1)	25	93-116	[67]
Infant food	PAHs and hydroxylated PAHs metabolites	SPE	LC-FLD	30	RT	UB	-	D	Native PAH : n-hexane	30	92-103	[68]
Propolis	Tetracyclines	SPE	LC–UV	60	50	UB	40	D	Na$_2$EDTA:McIlvaine buffer; 0.1 M	40	86-99	[69]
Bovine milk	FQ	SPE	LC–MS/MS	15	RT	UB	-	D	EDTA:McIlvaine buffer; pH = 4	10	63-94	[70]
Royal jelly	FQ	SPE	LC–FLD	60	25	UB	40	D	K$_2$HPO$_4$ (0.1 M) + Na$_2$EDTA (3%; w/v) pH = 2.5	30	62-89	[71]
Dairy products	Melamine	SPE	GC–MS	15	RT	UB	-	D	1% TCA	17	93-102	[72]
Fish	Alkylphenols β-estradiol	SPE GPC	GC-MS	2	-	UP	20	D	Acetone	5	79-126	[73]
Algae	Isoflavones	SFE	Fast-LC-MS/MS LC-DAD	30	-	UB UP	-	D	MeOH:H$_2$O 1:9 (v/v)	0.3	93.13- 100.42	[74]
Fish, egg, chicken	PBDEs	DSPE	GC-MS/MS	30	-	UB	40	D	n-hexane : DCM (8:2)	15	75-114	[75]
Olive leaves and drupes	Fatty alcohols Sterols	SPE	GC-MS/MS	10	-	UP	20	D	KOH 2 M	2	-	[76]
Edible food	Sodium nifurstyrenate and nitrovin	SPE	LC-MS/MS	15	50	UB	40	D	ACN	15	71-110	[77]
Soil	Pesticides	SPE	GC-NPD	15	-	UB	-	D	MeOH : ACN, 1:1(v/v)	10	12-91	[78]
Tobacco	Polyphenols	SPE	HPLC-DAD	10	35	UB	35	C	6 mL, Anhydrous MeOH (involving 0.5% ascorbic acid (w/v) at a flow rate of 0.5 mL min^{-1})	6	98-108	[14]
Trifolium L. (Clover) species	Isoflavone phytoestrogens	SPE	HPLC-DAD HPLC-FLD	30	75	UB	35	D	50 mL of MeOH 75% (v/v) and 5 mL of 35–38% HCl	55	>96	[79]
Milk	Cephalosporin	MSPD	HPLC-DAD	10	35	UB	35	D	MeOH:Water, 50:50 (v/v)	4	>93.4	[80]

[a] There are other hyphenated techniques including microextraction methods. These methods have been investigated in Table 5 and 6.

[b] Soncation modes: D; discrete, C; continuous or dynamic

Abbreviations: ACN: acetonitrile, BPA: bisphenol-A, CE: capillary electrophoresis, CHSR cup-horn sonoreactor, DAD: diode array detection, DCM: dichloromethane, DSPE: dispersive solid-phase extraction, ECD: electron-capture detector, EDCs: endocrine disrupting compounds, EDTA: ethylenediaminetetracetic acid, EtOH: ethanol, FAAS: flame atomic emission spectroscopy, FLD: fluorescence detector, FQ: fluoroquinolones, GC: gas chromatography, GD: gravimetric detection, GPC: gel permeation chromatography, HPLC: high performance liquid chromatography, LC: liquid chromatography, MeOH: methanol, MIP: molecularly imprinted polymer, MS: mass spectrometry, MSPD: matrix solid-phase dispersion, NPD: nitrogen-phosphor detector, NCI: negative chemical ionization, OPPs: organophosphates pesticides, PAHs: polycyclic aromatic hydrocarbons, PBDEs: polybrominated diphenyl ethers, PCBs: polychlorinated biphenyls, PhACs: pharmaceuticals, QU: quinolones, RT: room temperature, SFE: supercritical fluid extraction, SPE: solid phase extraction,TBBPA: tetrabromobisphenol-A, TCA: trichloroacetic acid, TCBPA: tetrachlorobisphenol-A, UB: ultrasonic bath, UP: ultrasonic probe.

Table 3. Different ultrasound assisted extraction techniques for determination of metal elements from different matrices.

Matrix	Analyte	Determination technique	Sonication conditions							Recovery%	Ref.
			Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode[a]	Extraction solvent			
								Composition	Volume (mL)		
Fish	Hg^{2+}; $MeHg^+$	LC–ICP-MS	90	70	UB	-	D	KOH 25% (w/v) in MeOH	9mL (3 times, 3 mL in each step)	99	[81]
Plants	Cd	FAAS	2	RT	UP	60	D	0.29 M nitric acid	6	23-105	[82]
Plants	Cu	FAAS	2	RT	UP	60	D	0.29 M nitric acid	6	48-86	[82]
Citric acid fermentation mediums	Fe	ETAAS	20-30	RT	UB	47	D	A mixture of HNO_3-H_2O_2	25	97.4-99.5	[83]
Citric acid fermentation mediums	Mn	ETAAS	20-30	RT	UB	47	D	A mixture of HNO_3-H_2O_2	25	96.7-100.3	[83]
Nile tilapia	Se	ETAAS	200 s	50	UB	-	D	0.10 M HCl	10	-	[84]
Soil	Cations	IC	10-50	17	UB	40	D	Deionized water	20	-	[85]
Soil	Elements	ICP-MS	3	20	UB	35	D	0.5 M $MgCl_2$ (pH= 7)	8	59.7-104.8	[86]
Rocks	Se	ETAAS	90	24	UP	-	D	Nanopure water	10	-	[87]
Rocks	As	ETAAS	90	24	UP	-	D	Nanopure water	10	-	[87]
Gravitation dust sediment	Cu	FAAS	5	RT	UP	-	D	2 M HNO_3	100	93.7-98.6	[88]
Gravitation dust sediment	Pb	FAAS	5	RT	UP	-	D	2 M HNO_3	100	80.4-87.0	[88]
Gravitation dust sediment	Zn	FAAS	5	RT	UP	-	D	2 M HNO_3	100	73.1-94.9	[88]
Fish and shellfish	As, Se, Ni, V	ETAAS	3	-	UP	20	D	HNO3 (3% or 0.5% for Se)	1.5	93–106	[89]
Palm oil	Cu Pb	SCP	60	25	UB	25	D	HCl conc:H_2O_2 (1:1)	2	98-105	[90]
Vegetables	As(III); As(V); DMA; MMA	HG-AFS	10	RT	UB	-	D	H_3PO_4 (1M) + Triton XT-114 (0.1%)	10	91-100	[91]
Infant formula	Ca; P; Mg; Zn; Fe; Cu; Mn	ICP-OES FAAS	2–5	-	UB	-	D	10 mL of aqueous solution with 250 μL of TMAH (10%) or 250 μL NH_4OH (25%) min	10.25	97-103	[92]
Fish feed	Ca; Mg; Mn; Zn	FAAS	30 s	-	UP	-	D	HCl 0.1 M	10	98-100	[93]
Mushroom	As(III); As(V)	HG-AFS	10	RT	UB	-	D	10 mL H_3PO_4 (1M) + Triton X-100 (0.1%) + 0.5 mL antifoam	10.5	91-108	[94]
Mussel **Fish**	Hg	LC–ICP-MS	5	-	Microtip UP	20	D	HCl 7 M (acidic leaching, method 1) Enzymatic solutions (method 2)	2 mL	81-90	[95]
Marine biological tissues	Pb	Multicollector ICP-MS	3	-	UR	24	D	HCl 2 M	1	-	[96]
Marine biological tissues	Rare earth elements	ICP_MS	3	-	UP	20	D	3% (v/v) HNO3 + 2% (v/v) HCl	5	63-85	[97]
Baby foods	Cd, Al, Ni, Pb	ETAAS	10	60	UB	35	D	HNO_3 10% (v/v)	10	96-98.8	[98]
Electro-plating sludge waste	Cu, Ni, Zn, Cr, Fe	XRF spectrometry	100	25	UP	20	D	H_2SO_4 Conc.:20 mL of H_2O_2 (step 1) Water: 20 mL of H_2O_2 (step 2)	-	97.42-100	[99]
Wastewater	Cu(II)	FAAS	3	25 ± 1	UP	22.5	D	D_2EHPA and surfactant (Span 80) in n-hexane	25	-	[100]
Soil and sediment	Ag Au	ETAAS	20	-	UP	24±1	D	25% v/v HNO3 + 25% v/v HF for Ag 25% v/v HNO3 + 25% v/v HCl for Au	1	81-107 91-105	[101]
Airborne	Sb(III) Sb(V)	HPLC-HG-AFS	3	-	UP	-	D	$NH_2OH \cdot HCl$ 100 mmol L^{-1}	10	97-99	[102]
Hair	Trace elements	ICP-MS	2	-	UP	-	D	First 2 mL of HNO_3 20% and then 8 mL of ultra pure water	10	-	[103]
Sediment	Heavy metals	FAAS	15-30	30–35	UB	35	D	Step 1: 20 mL of 0.11 M CH_3COOH Step 2: 20 mL of NH_2-HCl 0.5 M with pH 15 Step 3: 5 mL of H_2O_2 (8.8 M) and 25 mL of CH_3COONH_4 (1 M, pH = 2)	70	For all heavy metals, it was in the range of 75.1-114 (except Cr, 125.4)	[104]
Liver of diabetic rats	Zn, Cu, Fe, Mg, Mn	FAAS	8	-	UP	19	D	10% HNO_3	10	98-112	[105]
Bean seeds	Ba, Ca, Cu, Fe, K, Mg, Mn, Sr , Zn	ICP-OES	15	-	UB	-	D	HCl : CH_3COOH, 1:1 (v/v)	10	-	[106]

Continued **Table 3.** Different ultrasound assisted extraction techniques for determination of metal elements from different matrices.

Matrix	Analyte	Determination technique	Sonication conditions							Recovery%	Ref.
			Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode[a]	Extraction solvent			
								Composition	Volume (mL)		
Animal tissues, plant tissues, soil, sediment, fly ash, sewage sludge	Cd, Pb, Mn, Ni, Cr	ETAAS	3-40 Depends on matrix	-	CHSR	24	D	Diluted acids (HNO_3, HCl and HF) and oxidants (H_2O_2), the mixture of these solutions and their concentration depend on matrix.	1	>80	[107]
Fish tissues	Hg^{2+}, CH_3Hg^+	LC-ICP-MS	60	RT	-	-	D	Perchloric acid (1.5 mL, 0.6 mol L^{-1}), L-cysteine (500 μl, 0.75 mol L^{-1}) and 500 μl toluene:MeOH (1:1)	2.5	98.9-100.6	[108]
Sediments	Trace elements	ICP-MS	6	-	Glass UP	-	D	HNO_3 6.8 M (45%)	10-20	18.0-146.8	[109]

[a] *Soncation modes: D; discrete, C; continuous or dynamic*

Abbreviations: AFS: atomic fluorescence spectrometry, CHSR cup-horn sonoreactor, D_2EHPA: bis(2-ethylhexyl)phosphoric acid, DMA: dimethylarsinic acid, ETAAS: electrothermal atomic absorption spectrometry, FAAS: flame atomic emission spectroscopy, HG: hydride generation, IC: Ion chromatography, ICP: inductively coupled plasma, LC: liquid chromatography, $MeHg^+$: methyl mercury, MeOH: methanol, MMA: monomethylarsonic acid, MS: mass spectrometry, OES: optical emission spectroscopy, RT: room temperature, SCP: Stripping chronopotentiometry, TMAH: tetramethylammonium hydroxide, UB: ultrasonic bath, UP: ultrasonic probe, UR: ultrasonic reactor, XRF: X-ray fluorescence.

are discussed in many papers for extraction of different compounds from various matrices [159-165]. The three alternatives are classical Soxhlet leaching and two more recent techniques (namely, MAE and SFE), which are increasingly competing with ultrasound based methods in improved official methods of analysis. In fact, it is difficult to say exact superiority for USAL in comparison with other auxiliary techniques. However, the salient advantage of US is that it enables operation at ambient temperature; by contrast, the previous choices involve high temperatures. This results in improved safety as compared with conventional procedures of SFE and MAE digestion. Also, analyte losses by vaporization are generally eliminated, although losses can also be produced by alterations caused by the radicals generated by sonolysis of the liquid phase. Additional benefits include ease of use, availability of the experimental set-up, no special vessels required, relatively low costs and suitability for in-field digestion [166].

With respect to Soxhlet leaching, USAL has the disadvantages like inability of solvent renewing during the discrete USAL process, so the leaching efficiency is dictated by the solid–liquid partitioning equilibrium [2]. The need for filtering and rinsing after leaching lengthens the duration of this step, increases solvent consumption and also the risk of losses and/or contamination of the leachate [2]. Also, ultrasound radiation produces free radicals in the solvent which can alter the chemical composition of analytes and, hence, the analytical results. In comparison with MAE, USAL is subject to some shortcomings such as the influence of particle size on the USAL efficiency and being less robust than MAE [2].

Moreover, the general advantages mentioned for US-based technique, it surpasses SFE due to allowing leaching of a wide variety of compounds, whatever their polarity, so it can be used with any solvent. Also, supercritical fluid leaching uses almost exclusively CO_2 as leachant (with or without a co-leachant as a modifier), which restricts its scope to non-polar or low-polar analytes. On the other hand, USAL falls short of supercritical fluid leaching because, unlike the hazardous organic solvents used for sonication in some applications like dichloromethane and acetone, supercritical CO_2 is not environmentally hazardous, the precision of SFE methods is similar to or slightly better than that of their ultrasound assisted counterparts, especially when US baths are used and leachant removal after depressurization in supercritical CO_2 leaching allows the leached species to be dissolved in a fairly low volume of appropriate solvent [2].

In the case of liquid samples, regarding many advantages due to application of US for extraction of different compounds from various matrices rather than conventional liquid-liquid extraction methods, reported evidences show that US does not always favor mass transfer between two immiscible phases [2]. Also, emulsification is another problem which exists in this system and, it should be avoided [2].

Finally, careful selection of the type and characteristics of the US device will always be required as it can be the key to successful development of ultrasound assisted methods, particularly those involving organic reagents [7].

7. Coupling of ultrasound with other analytical techniques

7.1. Coupling with microwave (MW)

MWs are oscillating electromagnetic energy with frequencies in the 100 MHz to 3 GHz range with the

Table 4. Different ultrasound assisted extraction techniques for determination of organic and inorganic compounds from water, soil and plant samples.

Matrix	Analyte	Determination technique	Sonication conditions							Recovery%	Ref.
			Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode^{a}	Extraction solvent			
								Composition	Volume (mL)		
Cosmetics	Glycolic acid	HPLC-FTIR	20	-	UB	-	D	ACN: phosphate buffer (25 mM, pH 2.7) (3:97 v/v)	10	82.8-94.7	[110]
Desiccant and antimould sachets	Dimethyl fumarate	GC-MS	5	25	UB	40	D	Ethyl acetate	1	89-108	[111]
Desiccant and antimould sachets	Benzothiazole	GC-MS	5	25	UB	40	D	Ethyl acetate	1	89-103	[111]
Desiccant and antimould sachets	tert-Butylphenol	GC-MS	5	25	UB	40	D	Ethyl acetate	1	87-99	[111]
Chinese star anise	(-)-Shikimic acid	GC-MS	5	-	UB	-	D	MeOH: water (90 : 10)	15	73.1-90.5	[112]
Aloe	Aloe-emodin	HPLC-UV	30	-	UB	-	D	EtOH	40	-	[113]
Fish feed	Fe	FAAS	200 s	66	UP	-	D	0.50 M HCl	20	-	[114]
Sediment and soil	Chlorothalonil	GC-MS	60	RT	UB	-	D	Acetone	50	80-91	[115]
Sediment	OCPs	GC–ECD GC–MS	40	RT	UB	-	D	n-Hexane:acetone (5:2, v/v)	60	79-106	[116]
Soil	Acidic herbicides	FPIA	20	RT	UB	-	D	40% EtOH:20% MeOH in buffered water pH 12	20	80-132	[117]
Soil	PAHs	GC–MS	20	55	UB	-	D	Isopropanol:water (8:2, v/v)	30	46-110	[118]
Soil	PAHs	GC–MS	30	RT	UB	-	D	Ethyl acetate	10	90-102	[119]
Soil	Pharmaceuticals EDCs Hormones	GC–MS	20	RT	UB	42	D	Acetone:ethyl acetate, 10% acetic acid	20	81-118	[120]
Soil	PCBs	GC-ECD GC-MS	30	RT	UP	-	D	Acetone:n-hexane (0.75:1, v/v)	100	46-97	[121]
Soil	Parabens	LC–MS/MS	30	RT	UB	-	D	ACN	9	83-110	[122]
Sewage sludge	Insoluble soap	HPLC-FLD	25	-	UB	-	D	50 mL of Petroleum ether (step 1) 50 mL of MeOH (step 2)	100	-	[123]
Plant	Glyoxylate	Diode array spectrophotometer 3D-CE-DAD	10	20	UB	-	D	Water	1	-	[124]
Textile products	Allergenic disperse dyes	HPLC-DAD LC–MS–MS	15	70	UB	-	D	MeOH	20	-	[125]
Geological chert samples	Hydrocarbons	GC-MS	30	-	UP	20	D	60:40 DCM:Hexane	15	-	[126]
Indoor air	Fragrance allergens	GC-MS	5	45±3	UB	40	D	Ethyl acetate	2	>80	[127]
Water	Pyrethroids	GC-NCI-MS	5	35	UB	-	D	Chloroform	1	45–106	[128]
Hypericum polyanthemum	Benzopyrans Phloroglucinol derivative	HPLC-UV	20	-	UB	-	D	n-hexane	5	-	[129]
Greek marine species	Tributyltin	ETAAS	-	-	-	-	D	-	-	-	[130]
Mulberry leaves	Polysaccharides	Phenol–sulfuric acid colorimetric method, GC-FID	20	60	UB	-	D	Water	15	-	[131]
Stevia rebaudiana Bertoni	Carbohydrates	HPLC-UV Phenol–sulfuric acid colorimetric method	32	68	UP	20	D	Water (pH value was controlled with 0.01M pH 7 sodium phosphate)	1000	-	[132]
Citrus peel	Antioxidant flavonoids	LC-MS	30	40	UB	60	D	Water [Ca(OH)2 as basifying agent]	0.1 g mL^{-1}	-	[133]
Salvia miltiorrhiza root	Salvianolic acid B	HPLC-UV	25	30	UB	45	D	60% aqueous EtOH	0.05 g mL^{-1}	-	[134]
Forsythia suspensa	Phillyrin	HPLC-DAD	60	60	UB	40	D	20% MeOH	10	-	[135]
Rhizomes of Podophyllum peltatum	Podophyllotoxin	HPLC-DAD	10	0	UP	24	D	Water	100	-	[136]
Iris tectorum Maxim	Isoflavones	HPLC-DAD	45	45	UB	40	D	70% (v/v) MeOH solution	15 (mL g^{-1})	-	[137]
Jabuticaba skins	Antioxidant	TLC	120	RT	UB	40	D	EtOH 99.5%	1:10 (g mL^{-1})	-	[138]
River water Sediment	Pyrethroid	GC–NCI–MS	1	35	UB	-	D	Chloroform	1	47-105 51-105	[139]
Indoor emission from decorative candles	PAHs	GC-MS	20	35±1	UB	-	D	DCM	8	>78	[140]

Continued **Table 4.** Different ultrasound assisted extraction techniques for determination of organic and inorganic compounds from water, soil and plant samples.

Matrix	Analyte	Determination technique	Sonication conditions							Recovery%	Ref.
			Total Time (min)	Temp. (˚C)	Type	Freq. kHz	Mode^a	Extraction solvent			
								Composition	Volume (mL)		
Tobacco	Solanesol	HPLC-UV	240	60	UB	47±3	D	85 mL of n-hexane and 75 mL of EtOH for three repeated ultrasonic cycles	150	-	[141]
Portuguese red grape skins	Flavonoids	HPLC with electrochemical detection HPLC-DAD	15	25	UB	35	D	MeOH:HCl Conc., 99:1 (v/v)	3	-	[142]
Peats	PAHs	HPLC-FLD	10	-	UB	-	D	n-hexane : DCM (80:20)	10	67-89	[143]
Papaver plants	Opium alkaloids	CE-UV	60	40	UB	60	D	Water : MeOH, 4:1 (v/v)	10	100.4-100.9	[144]
Textiles	Formaldehyde	HPLC-UV (on line)	5	50	UB	40	C	Water	5 mL at a flow rate of 1.0 mL min^{-1}	933.5-99.5	[145]
Desiccant and mouldproof agents	Dimethyl fumarate	GC-μECD	5	25	UB	40	D	Ethyl acetate	1	>90	[146]
Serum	Fatty acids	GC-MS	No sonication for first step and 30 min for second step. Also, 20 min for derivatization	RT for first step, 70 ˚C for second step	UP	20	D	In a first step, 0.5 mL 0f 0.4 M KOH–MeOH, then 0.5 mL n-hexane was twice added twice. In the second step, 0.5 mL 1M H_2SO_4–MeOH, then 1 mL of n-hexane was added twice.	2	-	[147]
Hair	Risperidone 9-hydroxy-risperidone	LC-MS/MS	120	-	UB	-	D	Phosphate buffer pH = 9.5	2	86.9 86.7	[148]
Tablet formulations	Tris-(8-quinolinolato) gallium (III)	CE-DAD GC-MS	10	25	UB	-	D	Acetone : water (1:1)	3	96.7-101.8	[149]
Aromatic plants and flowers	Valuable compounds	GC-FID GC-MS	10	25	UB	20	C	EtOH	8.5 mL, During extraction the direction of the leaching carrier (at a flow-rate of 4 mL min^{-1}) was changed each 120 s,	-	[150]
Soil	butyl-, phenyl- and octyltin speciation	GC-PFPD	5-30	-	UB	40	D	Ethanoic acid	10	90-120 (for 5 min of sonication) 40-223 (for 30 min of sonication)	[151]
White birch bark	Betuli	HPLC-DAD	180	50	UP	5	D	EtOH 98%	1:42 (sample : solvent)	-	[153]
Sawdust	Pentachloro-phenol Tribromophenol	CE-UV GC-MS	30 s	-	Ultraso-nic bar	-	D	n-hexane	50	>99±2	[153]
Stephaniae tetrandrae	Fangchinoline Tetrandrine	HPLC-UV	40	-	UB	-	D	EtOH solution of [BMIM] [BF_4]	20	85.5–101.1	[154]
Cortex of Magnoliae officinalis	Magnolol Honokiol	HPLC-DAD	30	-	UB	-	D	EtOH solution of [BMIM] [PF_6]	20	90.8–102.6	[155]

^{a} Soncation modes: D; discrete, C; continuous or dynamic

Abbreviations: ACN: acetonitrile, CE: capillary electrophoresis, 3D: three dimentional, DAD: diode array detection, DCM: dichloromethane, ECD: electron-capture detector, EDCs: endocrine disrupting compounds, ETAAS: electrothermal atomic absorption spectrometry, EtOH: ethanol, FID: Flame ionization detector, FLD: fluorescence detector, FPIA: fluorescence polarization immunoassay, FTIR: fourier transform infrared spectrometry, HPLC: high performance liquid chromatography, MS: mass spectrometry, NCI: negative chemical ionization, OCP: organochlorine, PAHs: polycyclic aromatic hydrocarbons, PCBs: polychlorinated biphenyls, PFPD: pulsed flame photometric detector, RT: room temperature, TLC: thin layer chromatography, UB: ultrasonic bath, UP: ultrasonic probe.

most effective range for dielectric heating between 0.915 and 2.45 GHz [167]. This energy can act as a non-ionising radiation that causes molecular motion of ions and rotation of the dipoles but does not affect molecular structure [167]. The use of MW dielectric heating in analytical laboratories began in the late 1970s and was first seized upon by the food industry [168].

Microwave assisted extraction (MAE) was introduced in 1986 [169]. Two types of MAE have been developed, namely focused MAE (FMAE) and pressurized MAE (PMAE), corresponding to an open-style system under atmospheric pressure and a closed-style system under a certain pressure, respectively [170]. The PMAE method has been extensively used whereas FMAE has been less studied [171-173]. MAE as well as USAE is now recognized as efficient extraction technique in analytical chemistry because of dramatically cutting down working times, simplified manipulation and work-up, increasing yields and often higher purity of final product [168]. The combination of these two types of irradiation and their application to physical processes like digestion, dissolution and extraction appears interesting. Simultaneous ultrasonic/microwave assisted extraction (UMAE), an extraction technique utilizing microwave dielectric heating and sonochemistry, could drastically improve the speed and efficiency of extraction. Various developments of UMAE designs have been introduced by different research groups [167,174-179]. A typical UMAE instruments are shown in Fig. 6A. Ultrasound and microwave energy was provided simultaneously to the sample in the extraction flask to initiate the solvent extraction. The extractions are conducted under atmospheric pressure, and a condenser is used to minimize the loss of analytes by solvent evaporation. Now a question is created; how does simultaneous MW/US irradiation bring about a physical effect?

Chemat *et al*. [167] put forward a mechanism to account for the effects of US and MW on digestion. The mechanism assumes particle fragmentation and molecule excitation induced by the high energy level of bubble cavitation under US, and, also, microwave polarization to induce dielectric volumetric heating and selective heating of solid particles. A comparison between cavitation phenomena (US) and dielectric heating (MW) is illustrated in Fig. 6B.

Up to now, a few studies have combined these two techniques as an extraction tool [167,174-179]. Chemat *et al.* used UMAE for comparative study of digestion of edible oils for copper analysis and food products (powdered milk, rice, corn, flour, beef, corned beef and chick pea); for total *Kjeldahl* nitrogen analysis [167]. The digestion time, 10 min, was obtained which is much shorter than in the classical *Kjeldahl*, 180 min, and microwave digestion, 30 min, respectively. The device was also used to digest edible oils for the determination of metals, which took 30 min as compared to 40 and 60 min, with the classical and the microwave methods, respectively.

Lianfu *et al.* optimized and compared UMAE and USAE for extraction of *lycopene* from tomato paste [174]. A central composite design (CCD) was employed for optimization of process. The results showed that the optimal conditions for UMAE were 98W microwave power together with 40 KHz ultrasonic processing, the ratio of solvents to tomato paste 10.6:1 (v/w) and the extracting time 367 s; as for USAE, the extracting temperature was 86.4°C, the ratio of the solvents to tomato paste 8.0:1 (v/w) and the extracting time 29.1 min, while the percentage of *lycopene* yield was 97.4% and 89.4% for UMAE and USAE, respectively. These results implied that UMAE was far more efficient extracting method than USAE.

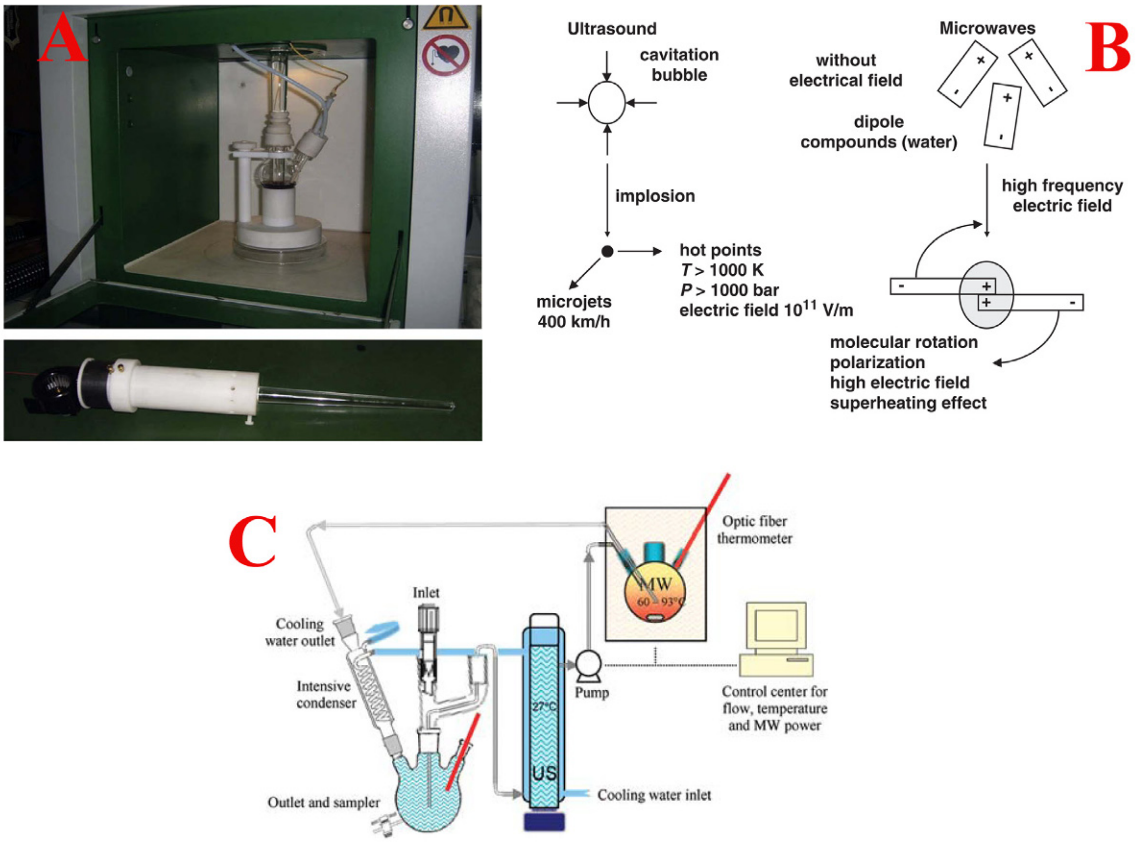


Figure 6. (A) A typical simultaneous and direct MW/US irradiation instrument (top) and US horn made of pyrex (bottom), (B) analogy between ultrasound cavitation and microwave heating and (C) circulating set-up using combined microwaves and ultrasound (reproduced with permission of Elsevier and ACS [167,177,181]).

Cravotto *et al.* evaluated ultrasound extraction of *soybean-germ* oil using several types of US apparatuses (cup horn, immersion horn, cavitating tube) working at different frequencies (19, 25, 40 and 300 kHz) [168]. In a newly developed apparatus, simultaneous US/MW irradiation was achieved by inserting a PEEK® horn in a multimode oven. Optimum extraction times were determined and yields were compared with those obtained by MAE (open- and closed-vessel) and conventional methods. The best oil yield was obtained with the cavitating tube (19 kHz, 80 W) and double sonication employing an additional immersion horn (25 kHz). Compared with conventional methods, much higher yields were also achieved with closed-vessel MW irradiation at 120˚C and simultaneous US/MW irradiation. Results were even more striking in the case of *seaweed* extraction, as the cell wall of the *microalga* is very tough. Extraction times were reduced up to 10-fold and yields increased by 50–500% in comparison with conventional methods. GC analyses showed only slight or negligible differences in methyl ester profiles of oils extracted using high-intensity US or Soxhlet. The obtained results indicate that US and MW, either alone or combined, can greatly improve the extraction of bioactive substances, achieving higher efficiency and shorter reaction times at low or moderate costs, with minimal added toxicity.

Canals *et al.* used UMAE to determine total *Kjeldahl* nitrogen [177]. The obtained results were compared with the obtained results of *Hach* method (a modification of the classical *Kjeldahl*) and an USAE method. Five pure amino acids and two certified reference materials (peach leaves and soil) were analyzed to assess the accuracy of UMAE method that was successfully applied to five real samples. Mean nitrogen recoveries for five pure amino acids were obtained in the range of 66-87%, 92-95% and 93-100% for *Hach*, USAE and UMAE methods, respectively. The significant reduction in digestion time (being 30 min, 25 min and 7 min for classical *Kjeldahl*, USAE and UMAE methods, respectively) and consumption of reagents show that UMAE is a powerful and promising tool for low-pressure digestion of solid and liquid samples.

Tang *et al.* used UMAE in order to maximize the yield and purity of polysaccharides from *Inonotus obliquus* [178]. Response surface methodology (RSM) was employed to optimize the UMAE conditions. Under the optimal conditions, the yield and purity of polysaccharides were 3.25% and 73.16%, respectively, which are above that of traditional hot water extraction and close to the predicted value (3.07% and 72.54%, respectively). These results confirmed that UMAE of polysaccharides had great potential and efficiency compared with traditional hot water extraction.

You *et al.* developed UMAE for simultaneous extraction of five organophosphate (OP) and eight pyrethroid insecticides from sediment [175]. Extracts were cleaned using solid phase extraction and analyzed by GC-MS. The newly developed UAME method was validated by comparing it to Soxhlet and sonication extraction methods. Better recoveries were achieved for most OPs by the novel UAME method, whereas there was no significant difference in recoveries for most of the pyrethroids.

Lu *et al.* studied ionic liquid-based UMAE (IL-UMAE) of five anthraquinones (physcion, chrysophanol, emodin, rhein, and aloe-emodin) from *rhubarb* [179]. Several parameters of UMAE were optimized, and the results were compared with of the heat-reflux extraction (HRE), USAE, and MAE. Compared with the conventional HRE, MAE and USAE techniques, the proposed approach exhibited higher efficiency (18.90–24.40% enhanced) and shorter extraction time (from 6 h to 2 min). This study suggests that IL-UMAE was an efficient, rapid, simple and green preparation technique.

Recently, Chai *et al.* have reported a UMAE coupled with HPLC-DAD/UV-TOF/MS system for evaluation of 7 marker compounds and 13 unknown chromatographic peaks from *Fructus Corni*, a commonly used traditional Chinese medicine [176]. The obtained recoveries were in the range of 97.3-102.7% for seven marker components. In summary, the developed method is generally applicable and easily expandable to include more quality evaluation of complex herbal matrices.

There are some reports about combination of US and MW but they are different from the studies mentioned above [180,181]. In these reports, sample exposure to both US and MW irradiation is done separately. It means that first, the sample is sonicated and then introduced to MW, and therefore, it is not exposed to US and MW irradiation at the same time (Fig. 6C).

7.2. Ultrasound assisted supercritical fluid extraction (USASFE)

Today, CO_2 based SFE has become a promising technique used in many areas. Some of the motivations for its employment are that the solvent is non-toxic, recyclable, cheap, relatively inert, non-flammable, and the process improves product quality and product recovery [182]. SFE has some drawbacks which caused new researches to overcome them. In recent years, particular attention have been paid to the combination of ultrasound and SFE. Ultrasound can be used as off-line or on-line in combination with SFE [183-188]. In on-line coupling of US and SFE, the use of high-intensity ultrasound represents an efficient manner of producing small scale agitation, enhancing mass transfer in supercritical fluids extraction processes. This is due to the effects produced by compressions and decompressions, as well as by radiation pressure, streaming, *etc* [183]. In addition, this is probably the unique practical way to produce agitation in SFE because the use of mechanical stirrers is not possible.

Riera *et al.* developed a supercritical CO_2 extraction of oil from particulate almonds using US power [183]. An overall scheme of a pilot plant is shown in Fig. 7A. Fig. 7B shows the installation of a piezoelectric sandwich transducer inside the extractor [183]. To examine the effect of the acoustic waves, all experiments were performed with and without ultrasound. The results showed that the kinetics and the extraction yield of the oil were enhanced by rate of 30% and 20% respectively when a power of about 50 W was applied to the transducer (Fig. 7C). As can be seen, the initial part of the efficiency curve was identical with and without US application; this suggests that this stage is mainly controlled by the solubility of the solute in the leachant, while it seems clear that the following stage is mainly determined by mass transfer mechanisms where US plays a key role. The average time of each extraction process was about 8 h and 30 min. In addition, the transducer was also used as a sensitive probe capable of detecting the phase behavior of supercritical fluids when it was driven at low power. In the other work, a new configuration device has been designed, implemented, tested and successfully validated for supercritical fluid extraction of oil from different vegetable substrates by the same authors [184]. In the extraction procedure, ultrasonic energy represents an efficient way of producing deep agitation enhancing mass transfer processes because of some mechanisms (radiation pressure, streaming, agitation, high amplitude vibrations, *etc*.). Previous work to this research pointed out the feasibility of integrating an ultrasonic field inside a supercritical extractor without losing a significant volume fraction. This pioneer method enabled to accelerate mass transfer and then, improving supercritical extraction times.

Luo *et al*. studied USAE of ginsenosides from ginseng in supercritical CO_2 reverse microemulsions formed by bis(2-ethylhexyl) sodium sulfosuccinate (AOT) [185]. It was found that ultrasound significantly enhanced supercritical CO_2 reverse microemulsion extraction.

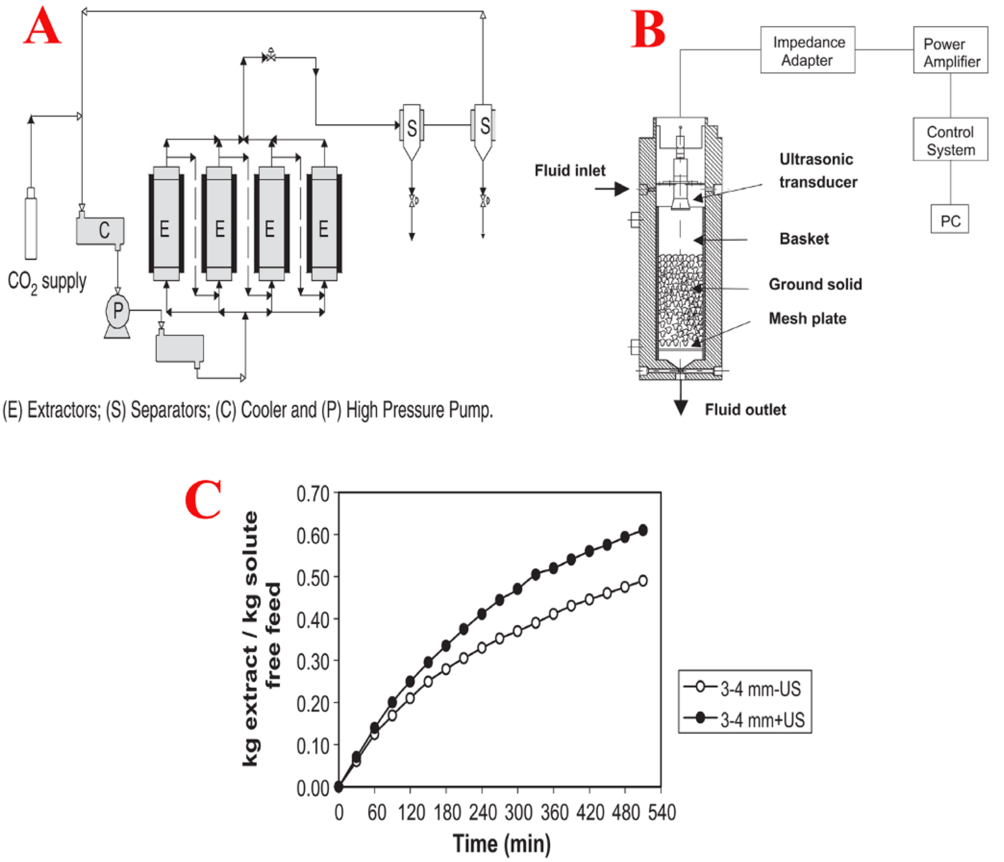


Figure 7. (A) Scheme of a typical basic experimental set-up used for SFE assisted by power ultrasound, (B) scheme of the extractor used for SFE and (C) Yield of the extracted oil from 3–4 mm particulate almond size with and without ultrasound (reproduced with permission of Elsevier [183]).

Gao *et al*. studied extraction of lutein esters from marigold using supercritical CO_2 extraction enhanced by ultrasound [189]. The mass transfer coefficient in the solid phase increased from 3.1×10^{-9} to 4.3×10^{-9} m s^{-1} due to presence of ultrasound. The results showed that the yield of lutein esters extraction increased significantly in the presence of ultrasound.

Kentish *et al.* examined the concurrent use of ultrasound power during the extraction of pungent compounds from a typical herb (*ginger*) using supercritical CO_2 [186]. The yield of pungent compounds from ginger is significantly increased in the presence of ultrasound up to 30%. The higher extraction rate can attributed to disruption of the cell structures and an increase in the accessibility of the solvent to the internal particle structure which enhances the intra-particle diffusivity. They analysed the ginger particles by field emission scanning electron microscopy (FESEM), and the obtained results showed that ultrasonic vibration indeed disturbed the cell walls and thereby facilitated removal of the cell contents.

Liang *et al.* studied USASFE of oil and coixenolide from *adlay* seed [187]. The results showed that supercritical fluid extraction with the assistance of US could reduce the operating conditions used in the process. Compared with SFE, USASFE could give a 14% increase in the yield for extracting oil and coixenolide from *adlay* seed with less severe operating conditions.

As mentioned before, ultrasound can be used in off-line combination with SFE. SFE often works more efficiently with matrices that were put to some pretreatment. Sonication is a simple and efficient way which can enhance the recovery. The trick is simple: SFE can be driven either by solubility or by the mass transfer. In real samples, all available analytes are extracted quite quickly, but some analytes that are strongly bound to the matrix or hidden deep in matrix particles are limited by the mass transfer process. During the sonication pretreatment, certain parts of matrix are damaged, and the SFE mass transfer takes place much more easily. Klejdus *et al.* used off-line combination of ultrasound as a pretreatment step with SFE for the extraction and determination of *isoflavones* in sea and fresh water algae and *cyanobacteria* [188].

7.3. Ultrasound assisted pressurized liquid extraction (USAPLE)

PLE is an extraction methodology which uses conventional solvents at elevated temperatures (100-180°C) and pressures (1500-2000 psi) to enhance the extraction of target analytes from their matrices. The combination of elevated pressures and temperatures affects the solvent, the sample and their interactions. For example, high pressure allows the solvent to penetrate deeper into the sample matrix, and at higher temperatures, analyte solubility increases, solvent viscosity and surface tension are reduced and the mass transfer is faster [5]. PLE has been applied to the extraction of organic compounds from different samples [5]. Solid samples were weighed and loaded into an extraction cell located inside the oven extractor. The oven was coupled to a heating device fitted on the upper part of the chamber and electronically controlled through a thermocouple. Extraction solvent was pumped through the system (dynamic extraction) to extract the analytes from the samples at a given flow rate and time (Fig. 8A).

In 2008, Richter *et al*. have reported a continuous PLE method assisted by ultrasound energy for the extraction of polychlorinated biphenyls from biosolids [190]. The PLE method was assisted by ultrasound showing a significant effect on the recoveries. The same procedure and manifold as implemented for PLE was used in this case, except for the oven, which was substituted with an ultrasonic bath at a temperature of 50ºC. US applied for 0–30 min at 35 kHz.

On the other hand, comparative studies were made in the same sample with the conventional Soxhlet extraction technique. In this case, the recovery obtained was 87.9%, showing that the ultrasound energy incorporated into the system USAPLE promotes efficient PCB desorption from the active sorption sites of the matrix.

7.4. Ultrasound assisted Soxhlet extraction (USASE)

Soxhlet leaching has been the most widely used technique over the years for isolating a variety of analytes from all types of samples. The most serious shortcomings of *Soxhlet* leaching are the long time involved, the large volumes of organic solvents released into the atmosphere; the *Soxhlet* procedure is far from clean and the process cannot be automated [191]. A variety of devices intended to circumvent these shortcomings while retaining the favorable characteristics of *Soxhlet* extraction have been developed, most of which use microwaves as auxiliary energy to accelerate leaching [192].

Luque-García *et al.* designed and constructed an USASE [193]. The device is based on the same principles as a conventional *Soxhlet* extractor but modified in order to allow location of the Soxhlet chamber in a thermostat bath through which ultrasounds are applied by means of an ultrasonic probe. The device used for the USASE (Fig. 8B) consisted of a thermostat water-bath modified by making an orifice at the bottom in order to enable connection of a conventional 50 mL *Soxhlet* chamber with a 100 mL distillation flask through a Teflon connector. An electrical isomantle with a rheostat was used to heat the distillation flask. A sonifier (20 kHz, 100 W) equipped with a cylindrical titanium alloy probe (2.54 cm diameter) was immersed in the thermostated water-bath and used to accelerate the extraction process. A rotary-evaporator was used to release the solvent after each conventional *Soxhlet* extraction. An electrically heated oven, an analytical balance and a desiccator were used to determine the sample moisture as well as for the gravimetric determination of the extracts.

The new device has been tested for the extraction of the total fat content from different *oleaginous* seeds such as sunflower, rape and soybean seeds followed by GC-FID. A quantitative comparison of the lipid extract obtained by both the official and the proposed method has been carried out. Efficiencies similar or even better than those provided by both conventional *Soxhlet* extraction and the official method have been achieved saving both time and sample manipulation. The composition of the fat extracts did not change after application of ultrasound, and the precision of the proposed approach was similar to that obtained by the reference method. Thus, it can be concluded that the present approach constitutes a valuable alternative for the extraction of easily compactable matrices such as seed samples.

7.5. Ultrasound assisted purge and trap system (USAPT)

Recently, Monteiro *et al*. simplified the total Kjeldahl nitrogen (TKN) using a manifold connected to a purge and trap system immersed into an ultrasonic (US) bath for simultaneous ammonia (NH_3) extraction [194]. A schematic of USAPT system is shown in Fig. 8C. A set consists of a reaction tube (RT), a NH_3 collection tube (CT), a u-tube and a manifold with 10 tips to connect to 10 sets and one more tip to connect to the vacuum pump.

The proposed method is faster, simpler and more sensitive than the classical Kjeldahl steam distillation method. The time for NH_3 extraction by the USAPT system (20 min) was half of that by the Kjeldahl steam distillation (40 min) for digested samples in this work. The detection limit was 9 µg g^{-1} N, while for the Kjeldahl classical/indophenol method was 58 µg g^{-1} N. Precision was always better than 13%. In the proposed method, carcinogenic reagents are not used, contrary to the indophenol method. Furthermore, the proposed method can be adapted for fixed NH_4^+ determination.

8. Ultrasound assisted microextraction methods

In the past two decades, a large number of modern sample preparation techniques including solvent free extraction techniques or extraction techniques with a very high sample to solvent ratio which leads to a high preconcentration factor of analytes have been introduced [195]. The application of ultrasound to the miniaturized sample preparation techniques has increased in the last years. This technique has been used in the development of methods for the analysis of numerous contaminants including organic and inorganic compounds.

These techniques are reviewed briefly below, focusing on their major advances which resulted from US coupling. US can be coupled with microextraction techniques by different modes. In simultaneous mode (SM), both ultrasound irradiation and microextraction take place in one-step. Other terminologies commonly encountered are those which ultrasound irradiation take place before (BM) or after (AM) microextraction.

8.1. Coupling of BM mode with different microextraction techniques

BM is especially suitable for solid samples including soil, sediment, plant, food *etc*. In this case; first, target analytes are extracted using ultrasound assisted liquid-solid extraction, therefore, a microextraction technique is used for producing more clean-up and high preconcentration factors. However, BM can be used for other purposes such as derivatization reactions (see Fig. 3) in order to sample pretreatment before microextraction. For example, Andruch *et al.* used US for conversion of boron to tetrafluoroborate before dispersive liquid–liquid microextraction (DLLME) [196].

8.1.1. Coupling of BM mode with DLLME

Bendicho *et al.* have used successfully combined USAE and ion pair-based DLLME for gold determination [197]. The expeditiousness of USAE for fast solid-liquid extraction (or USAL) along with the efficient liquid-liquid microextraction provided by DLLME allows improved sample preparation for determination of gold at ultratrace levels. This methodology could be easily adapted for the determination of other elements present at ultratrace levels in solid samples using suitable liquid-phase microextraction approaches after USAE. Also, USAE-DLLME has been reported for extraction of some organophosphorus pesticides residues in tomato [198] and polybrominated diphenyl ethers in sediment samples [199].

8.1.2. Coupling of BM mode with stir bar sorptive extraction (SBSE)

Llorca-Pórcel *et al.* developed a novel method based on ultrasonic solvent extraction and SBSE followed by thermal desorption gas chromatography (TD-GC-MS) for the analysis of phenolic pollutants in soil samples [200]. By comparison with classic Soxhlet extraction, the main advantage of this method is substantial solvent reduction (only 15 mL methanol instead of 100–200 mL of toxic solvents, generally hexane or dichloromethane). In addition, the method is very simple to perform and requires much less sample handling than the classic Soxhlet extraction method. Also, Kende *et al*. studied determination of some pesticides in fruits and vegetables using SBSE after extraction of analytes by ultrasound [201].

8.1.3. Coupling of BM mode with homogeneous liquid-liquid microextraction (HLLME) and electromembrane extraction (EME)

Milani Hoseini *et al*. reported a new method based on combining ultrasonic assisted miniaturized matrix solid-phase dispersion and HLLME for the determination of some organochlorinated pesticides in fish followed by GC-ECD [202].

Yamini *et al*. investigated EME for determination of thebaine in poppy capsules after ultrasound extraction [203]. Coupling of ultrasound as a pretreatment step with EME produced an efficient extraction and high degree of clean up.

8.1.4. Coupling of BM mode with cloud point extraction (CPE)

González *et al.* used cloud-point methodology to develop a new procedure for preconcentration of polycyclic aromatic hydrocarbons (PAHs) previously extracted from marine sediment with a micellar polyoxyethylene-10-lauryl ether medium by microwave- or USAE [204]. The efficiencies of extraction of both processes were similar, but the precision was considerably higher when the extraction was performed in the presence of US.

8.2. Coupling of SM mode with different microextraction techniques

Most of the microextraction techniques fall within the SM category.

8.2.1. Coupling of SM mode with DLLME, ultrasound assisted emulsification microextraction (USAEME) and solidified floating organic drop (SFO)

The first application of ultrasonic radiation in LLE methods (USALLE) has been reported by Luque de Castro *et al.* [1,2]. After that, Regueiro *et al*. applied a miniaturized

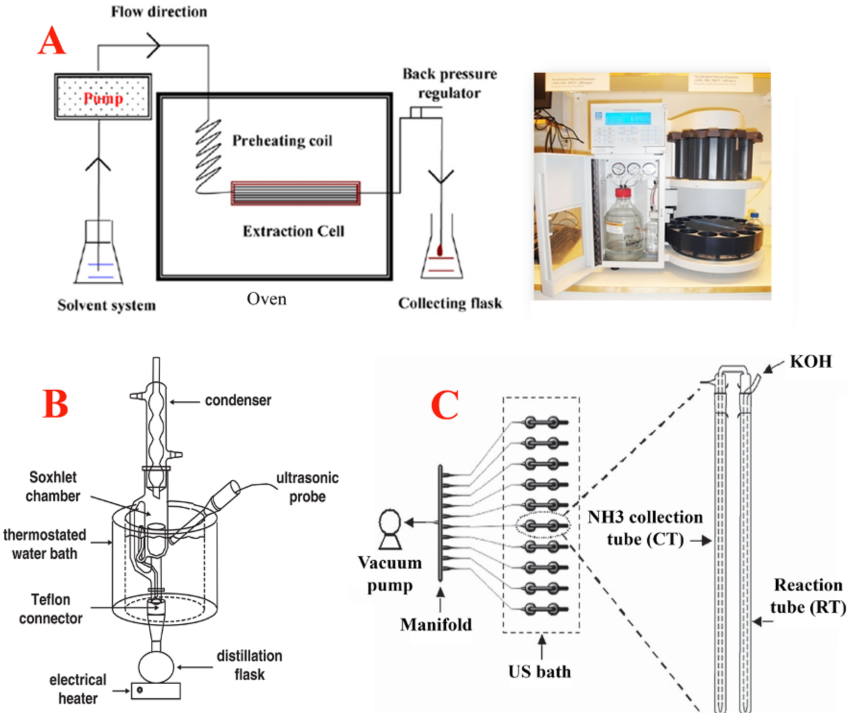


Figure 8. Scheme of (A) an accelerated solvent extraction system, (B) an ultrasound assisted Soxhlet leacher and (C) an ultrasound assisted purge and trap system (reproduced with permission of Elsevier [193,194]).

approach to USALLE by using a micro volume of organic phase to provide the advantages of both DLLME and USALLE [205]. They successfully applied ultrasound assisted emulsification microextraction (USAEME) to determine some emergent contaminants and pesticides in environmental waters. In this technique, micro volumes of the organic solvents were withdrawn into a microsyringe and injected slowly into the sample solution tube at the presence of ultrasound radiation. By this strategy, disperser solvent, which is used in DLLME for dispersion of extraction solvent, is removed. Consumption of disperser solvent in DLLME leads to decreasing of partition coefficients of analytes into the extracting solvent. Ultrasound irradiation has been also applied in DLLME technique. It causes to formation of more tiny droplets and increasing of mass transfer rate and extraction efficiency. More recently, Yamini *et al.* have summarized the updated developments and applications of DLLME [206]. This review covers almost all the publications related to the procedure from the beginning and also some limitations and an outlook on further developments. Both low and high density organic solvents are useable for USA-DLLME and USAEME methods. However, low density organic solvents have more variety than higher density organic solvents, and also, are more compatible with analytical instruments. Collection of organic solvents on the top of sample solution was the main problem in usage of these solvents. Recently, some efforts have been done for overcoming to this problem.

Solidified floating organic drop (SFO) is a microextraction technique in which a small volume of an organic solvent with melting point near room temperature (in the range of 10–30ºC) is floated on the surface of aqueous solution. The aqueous phase is stirred for a prescribed period of time, and then, the sample is transferred into an ice bath. When the organic solvent is solidified, it is transferred into a small conical vial, and the melted organic solvent is used for analyte determination [207]. Recently, this technique in combination with USAEME or DLLME (solely or assisted by US) has found noticeable popularity due to creating the possibility of low density organic solvents in these techniques. To the best of our knowledge, no reports exist for direct application of ultrasound in SFO, and it has been used more as a coupling technique with ultrasound assisted dispersive or emulsification techniques. But ultrasound can investigated directly (SM mode) in this technique for mass transfer during extraction instead of common magnetic stirring or used for back extraction SFO techniques (AM mode). Recently, Wang *et al*. used ultrasound for back extraction of Se(IV) from organic phase to aqueous phase in determination of hydride generation atomic fluorescence spectrometry (HG-AFS) [208]. It is based on solidified floating drops of 1-undecanol that are capable of extracting the target analyte after chelation with a water soluble ligand with subsequent ultrasound assisted back-extraction (UABE) into a aqueous solution.

However, the numbers of organic solvent with melting point near room temperature are narrow. Other ways have been proposed using a broad range of low density organic solvents in both USAEME and DLLME techniques.

Yamini *et al.* [209] proposed USAEME method based on applying low density organic solvents. Home-designed centrifuge glass vials containing an aqueous sample were immersed into an ultrasonic water bath. Micro volumes of the organic solvents were withdrawn into a microsyringe and injected slowly into the sample through the capillary tube at the top of the centrifuge vial. The conic top of the centrifuge vial attached to a capillary tube makes it suitable for easy collection of micro volumes of the floated organic solvents on the surface of the aqueous sample (Fig. 9A). Also, Jen *et al.* developed an in syringe-USAEME technique based on low density organic solvents for determination of organophosphorous pesticides in water samples followed by GC-ECD [210].

Chen *et al.* compared sonication and vigorous stirring as dispersion-assistance [211]. By stirring the solution vigorously for 5 min, the obtained relative responses of PAHs were found to be lower than following sonication. Sonication stirring produced smaller droplets of organic solvent in the aqueous bulk than vigorous stirring, as shown in Fig. 9B. During ultrasonic irradiation, implosion bubbles were generated due to the cavitation phenomenon, which produces intensive shock waves in the surrounding liquid and high-velocity liquid jets. Such microjets can cause droplet disruption in the vicinity of collapsing bubbles and thus, improve dispersion by generating a smaller droplet size of the dispersed phase right after disruption [1,2]. This leads to a rapid increase in the extraction efficiency of the USA-DLLME in a short period of time.

Also, a comparison between efficiency of ultrasound and shaking assisted DLLME was done for the determination of trace organoarsenic compounds in edible oil by Lee *et al.* [212]. The results show that extraction efficiency of analytes with ultrasound-assist is higher than with shake-assist (Fig. 9C). The clear difference between cloudy solutions is completely justifiable in investigations of Chen *et al.* [211].

Lavilla *et al.* investigated the presence of triclosan in cosmetics and wastewater samples using a simultaneous derivatization and IL based-USAEME technique followed by cuvetteless UV–Vis microspectrophotometry [213]. They compared no shaking (only centrifugation), magnetic shaking, bath sonication and cup-horn sonication in order to demonstrate the suitability of ultrasound energy in an IL based-USAEME procedure for achieving complete emulsification. The results showed that longer times are needed when magnetic or bath-sonication is used. When a 6 min time was fixed as shaking time for all systems, the sonoreactor achieved higher absorbances. Due to the viscosity of ILs, the cavitation threshold increases as a result of higher attractive forces between molecules [214] and therefore, longer sonication times or higher amplitudes can be needed to achieve complete emulsification. The effect of the sonication time was examined in the range of 3–15 min. Maximum absorbance was reached within 7 min for both cosmetic and wastewater samples. Sonication amplitude was also studied between 20 and 100%. An increase in the analytical signal was observed for amplitude up to 80%, while higher amplitudes gave rise to a decrease in the signal.

USA-DLLME and USAEME provide many merits such as excellent enrichment factors, simplicity, stability, easy to operate, short extraction time, low cost and low consumption of organic solvents. As can be seen from the literature, uses of these techniques have found noticeable importance among analytical scientists.

8.2.2. Coupling of SM mode with headspace liquid-phase microextraction technique

Xu *et al.* have developed a new sample pretreatment technique, ultrasound assisted headspace liquid-phase microextraction (UAHS-LPME) [215]. In this technique, the volatile analytes were headspace extracted into a small drop of solvent, which suspended on the bottom of a cone-shaped PCR tube instead of the needle tip of a microsyringe. More solvent could be suspended in the PCR tube than microsyringe due to the larger interfacial tension, thus the analysis sensitivity was significantly improved with the increase of the extractant volume. The method has been used to determine chlorophenols [215], phenols [216] in water samples and hexanal and heptanal in human blood [217]. Good recoveries were obtained and compared with traditional methods; the extraction efficiency is about ten times higher. It is a promising alternative for analyzing volatile or semivolatile pollutants in environmental samples due to its simplicity, rapidity and stability. A schematic diagram of the apparatus is showed in Fig. 9D.

Zhang *et al.* have introduced a novel method using simultaneous ultrasonic nebulization extraction and headspace single drop microextraction (UNE–HS-SDME) followed by gas chromatography-mass spectrometry for analysis of essential oil in *Cuminum cyminum L.* [218]. Compared with hydrodistillation (HD), UNE–HS-SDME provides the advantages of a small amount of sample, time-saving, simplicity, cheapness and low toxicity. In addition, UNE–HS-SDME provided higher enrichment efficiency and sensitivity compared with stirring extraction (SE)–HS-SDME, USAE and UNE. The results indicated that the UNE–HS-SDME is a simple and highly efficient extraction and enrichment technique. A schematic diagram of the system is shown in Fig. 9E.

Hashemi *et al.* successfully used headspace-solvent microextraction (HS–SME) with sample ultrasound irradiation for the study of the influence of nitrogen fertilization and plant density on the essential oil yield and composition of cumin (*Cuminum cyminum L.*) seeds [219].

8.2.3. Coupling of SM mode with hollow fiber based liquid phase microextraction (HF-LPME)

Among the emerging techniques, LPME techniques which are based on porous membranes, like hollow fibers (HF-LPME), are one of the most promising developments for preconcentration, separation and clean-up purposes. Nevertheless the potential capabilities of HF-LPME, the needed extraction time in this technique is usually high and common extraction times of 30-50 min have been reported [220,221]. Recently, Shrivas *et al.* have evaluated a simple, rapid and sensitive ultrasound assisted hollow fibre liquid-phase microextraction (USA-HF-LPME) method [222]. They have used this technique for extraction of nicotine in one-drop of nightshades vegetables and commercial food products [222] and selenium in vegetable and fruit samples [223]. The optimum extraction time in these samples were obtained 10 and 15 min, respectively. The ultrasound irradiation of donor phase accelerates the kinetics of extraction by decreasing the thickness of the Nernst diffusion film around the interface between two phases and thus enhances the analyte mass transfer rate from the donor to acceptor phase. The schematic diagram for the performance of USA-HFLPME is shown in Fig. 9F. They compared the results of this technique with the results of USA-SDME. The results showed that the performance of USA-HF-LPME was better than the UA-SDME for preconcentration of selenium in vegetable and fruit samples.

8.2.4. Coupling of SM mode with solvent bar microextraction (SBME)

Guo *et al.* have developed an ultrasound assisted solvent bar mcroextraction technique (USA-SBME) for the simultaneous trace analysis of benzene and toluene in beverages [224]. In this method, a piece of hollow fiber was filled with extraction solvent. Then two ends of the hollow fiber segment were closed by mechanical pressure. The filled hollow fiber segment was then placed in the glass bottle. During microextraction, the extraction system was placed on the ultrasonic probe to enhance the analyte mass transfer rate. After extraction, the acceptor phase was collected with a micro-syringe and analyzed by GC-FID. The equipment used for the extraction procedure is illustrated in Fig. 9G**.** The optimum extraction time in this technique was obtained at 10 min. A comparison between electromagnetic stirring and ultrasound agitation has been done in this work which confirms noticeable effect of ultrasound in reducing of extraction time (Fig. 9H).

8.3. Combination of AM mode with different microextraction techniques

The latter case of ultrasound mode is AM. AM is used in various type of microextraction techniques with different aims.

8.3.1. Coupling of AM mode with CPE

Cloud point extraction (CPE) consumes surfactants as extraction solvent but the use of the surfactants often brings some problems into the analysis of the analytes by many instruments such as GC and HPLC.

For the first time in 2005, Paleologos *et al.* developed CPE (by using both of ionic and non-ionic surfactants) coupled with microwave or ultrasonic assisted back extraction (MABE and UABE) prior to GC for determination of a mixture of six PAHs from water and soil samples [225]. Due to the high viscosity and low volatility of the surfactant rich phase, it cannot be injected directly into the GC. Therefore, after CPE extraction and before the injection, a supplemental stage was required in order to avoid clogging the injector and deteriorate the column. The UABE or MABE were carried out by adding a microliter amount of a water immiscible organic solvent into the resulting surfactant rich phase and sonicating or MW irriadating the system for a few minutes. After sonication or MW irradiation, two phases were formed: the surfactant rich and the water immiscible organic phase. In these conditions, the analytes remained in the water immiscible phase. The proper amount of the organic phase was injected into the GC-MS for analysis.

Fontana *et al.* used CPE-UABE to extract the target polybrominated diphenyl ethers (PBDEs) from water and soil samples [226] and organophosphates pesticides from honey samples [227] followed by GC-MS.

Generally, type and volume of organic solvent which use for back extraction; ultrasonic power and also sonication time are important parameters in success of back extraction process and should be optimized.

8.3.2. Coupling of different modes of US with solid phase microextraction (SPME) technique

Solid phase microextraction (SPME) is a solvent-free extraction technique, originally developed by Pawlyszin *et al.* [228]. The basic principles and technical aspects of this technique have been summarized by Vas *et al*. [229]. SPME consists of two steps including adsorption/absorption of analyte on the fiber surface and analyte desorption. The analytes can be released from the surface of fiber thermally into the injection port of GC or by solvent elution into HPLC or CE instruments. Agitation method is one of the most important factors among different variables that can affect on SPME [229]. It affects the efficiencies of both adsorption and desorption steps during SPME procedure. An efficient agitation system not only can reduce the needed extraction time for analyte adsorption/absorption on the surface of fiber but also, reduce standard deviations. The required time to reach equilibrium is directly proportional to the thickness of the polymer coating whereas it has inverse relation with the diffusion coefficient of the analyte in the coating [5]. It should be noticed that these relations are true for well-agitated solutions. In the case of improper agitation systems, the needed time to reach equilibrium is essentially determined by the diffusion rate through the static aqueous layer adjacent to the fiber [5]. According to the literatures, the main aims for application of sonication in the SPME are improvement of extraction procedure in both direct and headspace formats of SPME as well as reduction the equilibrium and desorption times [5].

Therefore, all of the three mentioned modes of ultrasound application in microextraction techniques including BM, SM and AM are applicable in SPME technique. In 1993, the effect of three different agitation systems including magnetic stirring, intrusive mixing and sonication on SPME were studied by Pawliszyn *et al.* [230]. These studies showed that sonication is the best agitation system in comparison with two other options providing higher extraction efficiencies in shorter times. Against the fact that stirring is the most common agitation method it provided lower mixing efficiency. Good agitation was obtained by application of intrusive mixing, however this system causes to significant sample heating and therefore analyte losing during extraction. Also, different sonication powers were investigated in the range of 0 to 150 W. The results showed better applicability for low sonication powers. The mentioned phenomenon can be related to the drawbacks of high sonication powers including heating, high pitched noise and sample decomposition.

The effect of ultrasound to accelerate the extraction of chlorinated pesticides from water samples was investigated by Boussahel *et al.* [231]. In fact, an appropriate decision about the effect of ultrasound in this work is not possible because no study has been done in the absence of ultrasound. Therefore, the observed results could be attributed to heating effect or ultrasonic power [5].

A new fast SPME procedure followed by gas chromatography mass spectrometry was developed by Rial-Otero *et al.* for determination of acaricides (amitraz, bromopropylate, coumaphos and fluvalinate) from honey [232]. A comparison was done between magnetic stirring and sonication using a new ultrasonic bath technology that could provide different sonication frequencies (35 and 130 kHz) as well as different working modes (Sweep, Standard and Degas). In the Standard mode, the ultrasonic frequency is regulated against the chemical resonance of the ultrasound transformer which optimizes the performance in the distributed maxima. The Sweep function causes a continued shifting of the sound pressure maxima, which ensures that the sound field distribution is more homogeneous in the bath than during Standard operation. During the Degas function, the set power is interrupted for a short period so that the air bubbles are not retained by the ultrasonic forces, and the liquid is degassing which optimizes the ultrasonic effect. In addition, the possibilities given by the three modes in which the ultrasonic bath can be used, Sweep, Standard and Degas, are fully exploited in this work for first time in analytical literature. The results showed that the use of low ultrasonic frequency, 35 kHz, provide worst results than the utilization of the high frequency, 130 kHz, especially in the case of amitraz. It was stated that amitraz was the most unstable compound in this study conditions. Therefore, it can be easily concluded that the cavitation effects produced by the ultrasonic bath at 35 kHz were enough to decompose amitraz in the acidic media. Thus, the recovery obtained for amitraz was significantly different, when the 130 kHz is compared with 35 kHz, both in the Standard operation mode and with 15 min of ultrasonic application. It must be pointed out that the cavitation effects are directly linked to the sonication frequency. The lower frequency creates the higher cavitation effects for the same amplitude [233]. It must be also stressed that, for the same extraction time, 15 min, the recoveries obtained at 130 kHz for bromopropylate and coumaphos were higher than using the 35 kHz frequency. Moreover, the Sweep mode was the best way to use the ultrasonic bath for those compounds. However, for fluvalinate, the best mode was the standard one, with which twice more was recovered than with the other modes. For this reason, the Standard mode was selected for further experiences, since in this mode, all the compounds showed good recoveries. Finally, the sonication time was studied also for 30 min, showing an increase of 100%, for all compounds except fluvalinate, for which the maximum recovery is achieved in 15 min. In addition, when extraction with sonication was compared with extraction with magnetic stirring, the recoveries obtained for sonication were higher and statistical differences were observed. For this reason, extraction with sonication for 30 min was selected as the optimum agitation condition for further experiments.

In the headspace SPME, agitation improves the extraction efficiency with decreasing depletion of analytes concentration in the headspace of sample solution. It has no effect on the diffusion rate of analytes to the fiber surface because this step is very fast [234]. Sonication is the most efficient agitation method evaluated to date for SPME applications because it can release the volatile physically trapped anlytes from the sample matrix into the headspace with breaking down the structure of matrix [235]. The effect of sonication time (0-60 min) on the headspace extraction of volatile compounds of *Parmesan* cheese was studied by Lee *et al.* [236]. Sonication showed significant improvement on increasing of peak areas of *Parmesan* cheese volatile components by 70% with passing time from 10 min up to 40 min in comparison with extraction in the absence of sonication. A noticeable decrease was observed after 40 min which can be attributed to the increase of water vapor pressure in the headspace of sample solution. The positive effect of sonication is due to breaking the sample matrix and releasing of physically trapped analytes. Forty minutes of sonication was chosen for the rest of work. Also, the simultaneous effect of sonication and salt (NaH_2PO_4) on the total peak areas of the volatile components of cheese was studied. No significant difference was observed in comparison with samples which only contained salt. However, only salting with 25% NaH_2PO_4 solution was recommended due to time efficiency effect.

The effects of magnetic stirring and sonication on the extraction of volatile compounds using HS-SPME from *Kimchi* (a traditional Korean fermented vegetable product) were investigated by the same authors [237]. The method sensitivity increased about 16% in comparison with only heating due to application of ultrasonic bath at 40ºC. However, magnetic stirring showed better results by 68% improvement in this study.

Kusch *et al.* have studied application of ultrasonic bath and different temperatures in the range of 25-80ºC to speed out the extraction of residual styrene monomer and other organic compounds in expanded polystyrene by HS-SPME [237]. Acceptable and repeatable results were obtained after 15 min sonication at 60ºC.

Increasing of extraction temperature has bilateral effects on the extraction efficiency of HS-SPME. On the one hand, it provides the needed energy for analyte molecules to overcome the energy barriers that bind them to the matrix as well as enhancement of mass transfer and vapor pressure of the analytes whereas it decreases the analyte partition coefficients and subsequent extraction due to the exothermic nature of the adsorption [238].

In 2004, Huang *et al.* designed a new headspace solid phase microextraction (HS-SPME) system to overcome this limitation. This system contains a cooling device on the upper part of the sample vial and a heating and ultrasonic activating device. This system was successfully applied for extraction and determination of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in soil samples [238]. This sterategy increased the efficiency of extraction because the mass transfer is accelerated and a temperature gap is created between cold-fiber coating and the hot headspace, which significantly increase the distribution coefficients. The cooled SPME device is shown in Fig. 9I. The solid-phase microextraction method developed was shown to be a fast, efficient and economical technique for the rapid screening of PCDDs/PCDFs in soil samples.

Biazon *et al.* studied extraction of volatiles of beer using SPME [239]. The application of ultrasound improved the extraction efficiency. After 30 min of application, most of the compounds exhibited an enhancement in the detected signal of at least 100%. The increase in percentage was proportional to the relative amount in the matrix. For instance, ethyl octanoate and ethyl decanoate, which were preponderant among the six target molecules, reached values of around 200% and 300% in enhancement after 30 min of ultrasound. The effect of salt addition and presence of silica based adsorbents were investigated. The results showed that the presence of sorbents to affect the analytes signals was more than the addition of NaCl or the use of ultrasound.

Ghiasvand *et al.* used ultrasound assisted headspace solid phase microextraction (UA-HS-SPME) coupled to GC–MS for analysis of volatile compounds in dry *Tagetes minuta L.* Comparison of the method with the commonly used hydrodistillation (HD) method showed that the proposed method is simpler, needs much less sample, requires shorter extraction time and lower temperature, has high trapping ability, and extracts more volatile and thermally sensitive compounds [240].

As mentioned before, analyte desorption in the SPME can be done thermally into the injection port of GC or by solvent elution for further HPLC or CE analysis. In the case of desorption by solvent elution, selection of the appropriate solvent and desorption time are two important factors can noticeably affect extraction efficiency. Desorption yield can be improved by magnetic stirring or sonication. This effect was investigated by Battle *et al.* to accelerate desorption of aliphatic isocyanates derivatized from the fiber into a mixture of acetonitrile/water (85 : 15, v/v) using a 48 KHz ultrasonic bath [241].

Yang *et al.* [242] employed an ultrasonic bath during 30 min to desorb chlorophyll from a chitosan membrane, used as SPME membrane, into 5% NaOH. Also, Xu *et al.* applied a 60 Hz ultrasonic bath at 40ºC to desorb aldehydes from a novel SPME frit based on polymer monolith [243]. The analytes were desorbed into 60 µL acetonitrile during 5 min and analyzed by HPLC.

8.3.3. Coupling of AM mode with SBSE

Stir bar sorptive extraction (SBSE) was introduced as an extraction technique for enrichment of volatile and semi-volatile organic compounds from aqueous and gaseous media by Baltussen *et al.* [244]. Similar to SPME, SBSE is not an exhaustive extraction technique. However, the extraction recoveries in SBSE are greater than SPME due to large volumes of sorbent phase (50-200 µL) which are used in this technique in comparison with SPME (0.5 µL) [5]. For a typical extraction, the stir bar which is covered with a layer of polymeric coating, exposure to sample solution for a given time. After that, the sorbent is removed and the analytes desorbed thermally and analyzed by GC or desorbed by means of a proper solvent. In the last case, analysis is done by HPLC or CE instruments. Desorption using organic solvent can use for improving selectivity or for interfacing to an LC system. Recently, the current states of SBSE including the most recent developments have been summarized by Sánchez-Rojas *et al.* [245]. Two main purposes have been mentioned for application of ultrasound in the SBSE including accelerating of analyte desorption from the stirrers as well as avoiding carryover problems.

As it can be seen, AM mode has an important role in SBSE. Also, some works have been reported about application of BM and SM modes in this extraction technique [200,246].

Popp *et al.* applied a 35 KHz ultrasonic bath to accelerate desorption of PAHs from two different types of sorbents namely PDMS stir bars [247] and polysiloxane rods [248]. An optimum sonication time of 10 min was obtained for different levels of this factor in the range of 5 to 20 min. The obtained results by both PDMS stir bars and polysiloxane rods were comparable. However, the extraction procedure based on polysiloxane rods is not fully automated and need to longer extraction time in comparison with SBSE (3 h using silicon rods *vs.* 1 h using SBSE).

Sulistyorini *et al.* used sonication to desorb phenanthrene from the surface of PTFE stir bars into 3 mL of acetonitrile which was placed in a glass vial during 15 min [249].

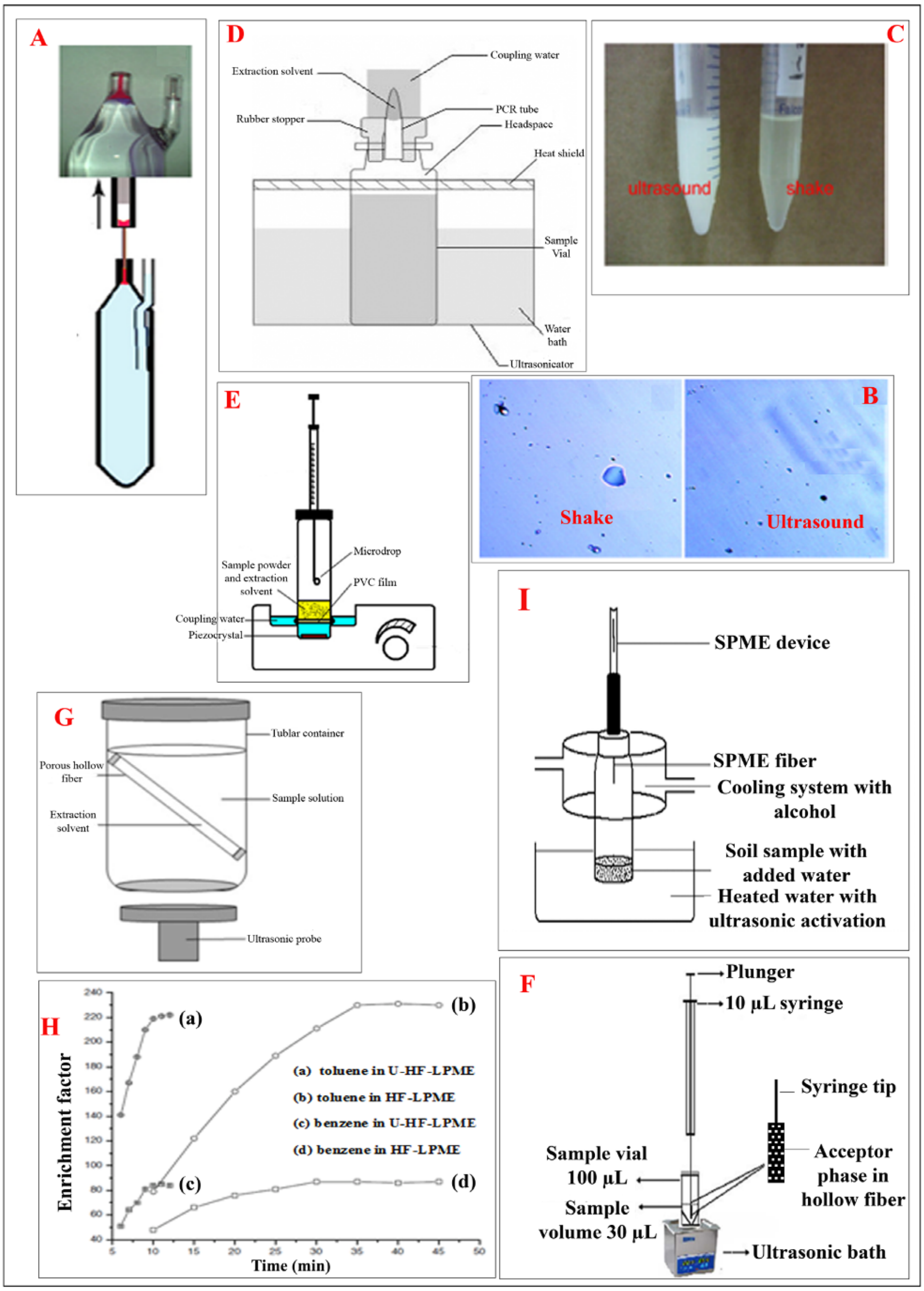


Figure 9. Different types of ultrasound assisted microextraction methods; (A) USAEME, (B) microphotographs of tetrachloroethylene droplets attained by vigorously stirring and sonication after 5 min, (C) comparison of ultrasound assisted DLLME and shake assisted DLLME, (D) schematic diagram of UA-HS-LPME apparatus, (E) UNE–HS-SDME system, (F) schematic diagram for the operation of UA-HF-LPME, (G) schematic illustration of the set-up for ultrasound assisted SBME, (H) comparison of extraction time of ultrasound assisted SBME and HF-LPME and (I) schematic diagram of extraction apparatus for SPME (reproduced with permission of Elsevier and Springer, Springer, -modified [209,211,212,215,218,222,224,238]).

Table 5. Different ultrasound assisted microextraction techniques (Before and after sonication modes, BM and AM) for determination of organic and inorganic compounds from different matrices.

Extraction method	Determination technique	Analyte	Matrix	Sonication conditions					LOD	Ref.
				Time (min)	Temp. (˚C)	Type	Frequency kHz	Mode		
CME or CPE-UABE	GC-MS	OPPs	Honey	5	-	UB	40	AM	0.03-0.47 ng g^{-1}	[227]
SFO-UABE	HG-AFS	Se(IV)	Water	30	-	UB	40	AM	7.0 ng L^{-1}	[208]
USAE-DLLME	GC-FPD	OPPs	Tomato	35	-	UB	-	BM	0.1- 0.5 μg kg^{-1}	[198]
USAC-DLLME	UV–Vis spectrophotometry	Boron	Water	10	-	UB	-	BM	0.015 mg L^{-1}	[250]
USAE-DLLME	ETAAS	Au	Water Sediment Soil	20	-	CHSR	24±1	BM	42 ng L^{-1} 1.5 ng g^{-1}	[197]
USA-HS-LPME	HPLC-UV	Hexanal Heptanal	Human blood	20	40	UB	-	SM	0.79 nmol L^{-1} 0.80 nmol L^{-1}	[217]
USAL-DSPE-DLLME	GC-MS/MS	PBDEs	Sediment	30	35±2	UB	40	BM	0.02–0.06 ng g^{-1}	[199]
USA-SPME	HPLC-UV	Hexanal Heptanal	Urine Blood	5	40	UB	60	AM	0.81 nmol L^{-1} 0.76 nmol L^{-1}	[245]
USAE-SPME	HPLC-FLD	Less polar HAs	Meat	4.5	45	UB	-	BM	0.28–1.1 ng g^{-1}	[251]
USAE-IL based-DLLME	HPLC-FLD	Pesticides and metabolites	Soil	10	-	UB	42	BM	0.02-90.2 ng g^{-1}	[252]
USAE-SPME	GC-MS/MS	PBDEs	Sewage sludge River sediment	10	-	UB	-	BM	0.01-1.2 ng g^{-1}	[253]
USAE-PMME	CE-UV	Sulfonamides	Chicken meat	1	-	UB	-	BM	3.49–16.7 ng g^{-1}	[254]
USAE-EME	HPLC-UV	Thebaine	Poppy capsule	30	40	UB	40	BM	<15 μg L^{-1}	[203]
HS-SPME	GC-MS	Volatile compounds	Delipidated protein powder	15	-	UB	47±6	BM	-	[255]
USA-MSPD-HLLME	GC-ECD	OPPs	Fish	10	40	UB	37	BM	0.4–1.2 ng g^{-1}	[202]
CPE-UABE	GC-MS	PBDEs	Water and soil	5	-	UB	40	AM	1.0-2.0 pg mL^{-1}	[226]
USAE-SBSE	GC-MS	Pesticide	Fruits and vegetables	10	-	-	-	BM	-	[201]
SBSE	HPLC-UV	Chlorpromazine Trifluoperazine	Human serum	20	50	UB	-	AM	0.7-1.5 μg L^{-1}	[246]

Abbreviations: AFS: atomic fluorescence spectrometry, CHSR: cup-horn sonoreactor, CME: Coacervative microextraction, CPE: cloud point extraction,, DLLME: dispersive liquid liquid microextraction, DSPE: dispersive solid-phase extraction, ECD: electron-capture detector, EME: electromembrane extraction, ETAAS: electrothermal atomic absorption spectrometry, FAAS FLD: fluorescence detector, FPD: flame photometric detection, GC: gas chromatography, HF-LPME: hollow fiber liquid phase microextraction, HG: hydride generation, HLLME: homogeneous liquid liquid microextraction, HPLC: high performance liquid chromatography, LOD: limit of detection, SPME: solid phase microextraction, MS: mass spectrometry, MSPD: matrix solid phase dispersion, OCP: organochlorine pesticides, OPPs: organophosphates pesticides, PBDEs: polybrominated diphenyl ethers, PMME: polymermonolith microextraction, SBSE: stir bar sorbtive extraction, SFO: solidified organic drop, UABE: ultrasound assisted back-extraction, UB: ultrasonic bath, UP: ultrasonic probe, USA: ultrasound assisted, USAC: ultrasound assisted conversion, USAE: ultrasound assisted extraction, USAL: ultrasound assisted leaching.

The effect of vial type used for analyte desorption in SBSE applying ultrasound has been studied by Popp *et al.* [247]. No significant difference was observed. Moreover, it was found that sonication into an appropriate solvent can remove carryover problem from one sample to another in SBSE [247]. In this study, 1.0 mL solution of methylene chloride and methanol (1:1, v/v) and 5 min of sonication time were selected for desorption of PAHs from the surface of stir bars. To avoid carryover problem in SBSE, purification of stir bars should be realized before next sample pretreatment.

Table 6. Different ultrasound assisted microextraction techniques (simultaneous mode, SM) for determination of organic and inorganic compounds from different matrices.

Extraction method	Determination technique	Analyte	Matrix	Sonication conditions					LOD	Ref.
				Time (min)	Temp. (°C)	Type	Frequency kHz	Mode		
USAEME	GC-MS	SCs	Wine	20 s	25±2	UB	42	SM	0.36-1.67 ng mL^{-1}	[256]
USAEME-SFO	HPLC-UV	Antidepressant drugs	Urine Plasma	20	25	UB	35	SM	3 mg L^{-1}	[257]
USA-DLLME	GC-FID	Pyrethroids	Domestic wastewater	2	-	UB	40	SM	0.2–0.7 mg L^{-1}	[258]
IL based-USAEME	HPLC-UV	BUPs	Water	15	20	UB	-	SM	0.21-0.45 mg L^{-1}	[259]
USA-SBME	GC-FID	Benzene Toluene	Beverage	10	25	UP	40	SM	0.34 μg L^{-1} 0.18 μg L^{-1}	[260]
USAEME-SFO	FAAS	Au	Water	3	-	UB	-	SM	0.45 ng mL^{-1}	[261]
HS-SDME	GC-MS	Essential Oil	Plant seed	4 min extraction time (15 min preconditioning time)	60	UB	22	SM and BM	-	[219]
USAEME	GC-MS	PAHs	Seawater	5	35 ± 2	UB	40	SM	1.0–10.0 ng L^{-1}	[211]
USAEME	HPLC-UV	Propoxur	Water Soil Beverages	15	60	UB	40	SM	1 ng mL^{-1}	[262]
USAEME-SFO	FAAS	Zn	Water	20	40	UB	53	SM	0.79 μg L^{-1}	[263]
Silica-based adsorbents-HS-SPME	GC-MS	Volatile compounds	Beer	30	40	-	-	SM	-	[239]
USA-HS-SPME	GC-MS	Volatile compounds	Plant	40 min extraction time (15 min for equilibration)	70	UB	18	SM	-	[240]
USAEME-SFO	FAAS	Cu	Water	15	45	UB	59	SM	0.76 μg L^{-1}	[264]
IL based-USAEME	HPLC-DAD	Fungicides	Red wine	5	-	UB	40	SM	2.8-16.8 μg L^{-1}	[265]
USA-HS-LPME	HPLC-UV	Phenols	Water	10	50	UB	-	SM	0.45-0.76 mg L^{-1}	[216]
USAEME-SFO	FAAS	Pd	Water	2	-	UB	-	SM	0.60 ng mL^{-1}	[266]
USAEME	GC-MS	Fragrance allergens	Water	2	25 ± 3	UB	40	SM	<1 ng mL^{-1}	[267]
USAEME-SFO	HPLC-DAD	Phthalate esters	Water	12	25	UB	35	SM	0.005-0.01 μg L^{-1}	[268]
USAEME	GC-MS	Strobilurin Oxazole	Juices Fruits	4	25	UB	50	SM	<0.075 ng mL^{-1}	[269]
IL based-USAEME	ETAAS	Cd	Water	60 s	-	UP	-	SM	7.4 ng L^{-1}	[270]
IL based-USAEME	Microvolume UV–Vis spectrophotometry	Triclosan	Cosmetics Wastewater	7	-	UB CHSR	- 24	SM	0.018 μg g^{-1} 0.005 μg mL^{-1}	[213]
USA-HF-LPME	ETAAS	Se	Vegetable Fruit	15	RT	UB	50/60	SM	0.08 ng mL^{-1}	[223]
USA-DLLME	HPLC-UV	Fluoroquinolones	Wastewater	2	25	UB	40	SM	0.14-.081 μg L^{-1}	[271]
USAEME	GC-MS	Emergent contaminants Pesticides	Water	10	25±3	UB	40	SM	10 pg mL^{-1}	[205]
USAEME	Fibre optics-based cuvetteless UV–vis micro-spectrophotometry	Formaldehyde	Cosmetics	5	-	Cup horn shaped UP	24	SM	0.02 μg g^{-1}	[272]
USAEME	GC-MS/MS	Phenolic preservatives	Water	5	25±3	UB	40	SM	3.9-27.5 pg mL^{-1}	[273]
USA-HS-SDME	HPLC-UV	Chlorophenols	Water	20	50	UB	-	SM	6-23 ng mL^{-1}	[215]
USAEME	FAAS	Cd	Water	20	50	UB	59	SM	0.91 μg L^{-1}	[274]
USAEME	GC-MS	PCBs	Water	10	25	UB	35	SM	14-30 ng L^{-1}	[275]
USAEME	GC-MS	PAHs	Water	15	25	UB	35	SM	0.001-0.036 μgL^{-1}	[276]
USAEME	HPLC-FLD	Nitric oxide	PC12 cells	2.5	-	-	-	SM	2.5×10^{-13} mol L^{-1}	[277]
USAEME	GC-MS	2,4,6-TCAN	Water	5	30±2	UB	40	SM	0.2 ng L^{-1}	[278]
USAEME	GC-FID	PAHs	Water	30 s	25±3	UB	40	SM	0.02–0.05 μg L^{-1}	[209]
USAEME	GC-MS	PBDEs	Water	5	35±2	UB	40	SM	1–2 pg mL^{-1}	[279]
USA-DLLME	HPLC-FLD	Biogenic amines	Rice wine	1	20	-	-	SM	0.02–5 ng mL^{-1}	[280]
USA-DLLME	LC-MS	Organoarsenic compounds	Edible oil	5	-	UB	-	SM	1-5.8 ng g^{-1}	[212]
USAEME	HPLC-DAD	Carbamate pesticides	Water	3	25±2	UB	-	SM	0.1–0.3 ng mL^{-1}	[281]
USAEME	GC-MS	Geosmin 2-methylisoborneol	Water Wine	3	20	UB	-	SM	2-9 ng L^{-1}	[282]
UASEME	HPLC-DAD	OPPs	Water	3	23	UB	59	SM	0.1-0.3 ng mL^{-1}	[283]
USA-DLLME	GC-FID	Cypermethrin Permethrin	Pear juice	2	-	UB	-	SM	2.2-3.1 μg kg^{-1}	[284]

Continued **Table 6.** Different ultrasound assisted microextraction techniques (simultaneous mode, SM) for determination of organic and inorganic compounds from different matrices.

Extraction method	Determination technique	Analyte	Matrix	Sonication conditions					LOD	Ref.
				Time (min)	Temp. (˚C)	Type	Frequency kHz	Mode		
UASEME	HPLC-FLD	PAHs	Water	1	25±2	UB	40	SM	0.6–62.5 ng L^{-1}	[285]
USA-HS-LPME	HPLC-UV	Hexanal Heptanal	Human blood	20	40	UB	-	SM	0.79 nmol L^{-1} 0.80 nmol L^{-1}	[217]
IL based-USAEME	FAAS	Rh(III)	Water	2	-	UB	35	SM	0.37 ng mL^{-1}	[286]
USA-DLLME	HPLC-UV	Pyrethroids	River water	2	-	-	-	SM	0.11-0.3 μg L^{-1}	[287]
IL based-USAEME	HPLC-FLD	Biogenic amines	Beer	1	-	UB	40	SM	0.25–50 ng mL^{-1}	[289]
USA-HF-LPME	GC-MS	Nicotine	Nightshades vegetables Food	10	-	UB	50/60	SM	0.2–0.5 ng g^{-1}	[222]
SPE-USAEME	HPLC-UV	Clenbuterol	Porcine tissues	5	25	UB	40	SM	0.07 μg kg^{-1}	[289]
In syringe-USAEME	GC-μECD	OPPs	Water	30 s	-	UB	43	SM	1-2 ng L^{-1}	[210]
Surfactant enhanced-USAEME	HPLC-DAD LC-MS	Diethofencarb and pyrimethanil fungicides	Water and fruit juice	3	25±2	UB	40	SM	0.01 μg L^{-1}	[290]
IL based-USAEME	HPLC-UV	Lovastatin and simvastatin	Water	400 s	-	UB	-	SM	0.17-0.29 μg L^{-1}	[291]
USAEME	GC-FID	OPPs	Water and juice	5	25	UB	40	SM	5.3-10.0 ng L^{-1}	[292]
IL based-USAEME	HPLC-UV	Aromatic amines	Water	5	-	UB	-	SM	0.17-0.49 μg L^{-1}	[293]
USAEME	HPLC-DAD	CPAs	River water	9	25±2	UB	40	SM	0.67-1.5 μg L^{-1}	[294]
USAEME	HPLC-DAD	Triazine herbicides	Soil	3	25±2	UB	40	SM	0.1-0.5 ng g^{-1}	[295]
USAEME	GC-μECD	OCPs	Water	5	25	UB	35	SM	0.002-0.016 μg L^{-1}	[296]

Abbreviations: BUPs: benzoylureas pesticides, CPAs: chlorinated phenoxyacetic acids, DAD: diode array detection, ECD: electron-capture detector, ETAAS: electrothermal atomic absorption spectrometry, FAAS: flame atomic emission spectroscopy, FID: flame ionization detection, FLD: fluorescence detector, GC: gas chromatography, HPLC: high performance liquid chromatography, HS-SDME: head space single drop microextraction, HS-SPME: head space solid phase microextraction, LOD: limit of detection, MS: mass spectrometry, OPPs: organophosphates pesticides, PAHs: polycyclic aromatic hydrocarbons, PBDEs: polybrominated diphenyl ethers, PCBs: polychlorinated biphenyls, RT: room temperature, SCs: sulfur compounds, TCAN: trichloroanisole, UB: ultrasonic bath, UP: ultrasonic probe.

Talebpour *et al.* used a sensitive and reproducible stir bar sorptive extraction and HPLC-UV detection method for the therapeutic drugs monitoring of chlorpromazine and trifluoperazine in human serum [246]. They investigated the effect of both magnetic stirring and sonication on desorption efficiency and the obtained results showed that sonication is more effective for desorption of analytes.

The present review covers almost all the publications related to the procedure from the beginning that summarized in Tables 5 and 6.

9. Beyond analytical chemistry

There are close to 20 different methods for the fabrication of nanomaterials [3] however, power ultrasound provides one of the most exciting ways to synthesise pure and supported nanomaterials for research and industry. Jing *et al.* published an article about sonochemical synthesis of polyaniline nanofibers [297]. These fibers can be used for different purposes such as SPME in analytical chemistry. It is demonstrated that ultrasonic synthesis is a unique way in preparing polyaniline nanofibers and represents a facile and scalable one, which is of great importance in production and applications of the polyaniline nanofibers.

Proteomics has become one of the more interesting fields in science which study the complete set of proteins. Proteomics is currently applied to the discovery of new protein biomarkers of disease, toxicity, drug efficiency and clinical diagnosis [298]. Although noticeable improvements have been achieved in the analytical instruments used in proteomics studies during the past decade, the sample treatments used in proteomics remain one of the main limiting factors because it is time consuming and multiple steps are needed in sample handling [299]. Sample handling for protein identification usually requires long times as 24-48 h in order to complete [5]. However, application of US reduced this tedious treatment time to 8 min as well as reduced the needed steps for sample handling. Therefore, US has a special place in proteomics.

Also, US has been used in organic and inorganic synthesis in many reported publications [5]. Also, US has become a tool in polymer sciences with various aims including as an initiator for polymer synthesis, to study polymer degradation mechanism and as a fast sample treatment method before characterization of polymer with MS-based techniques such as MALDI-TOF-MS [5]. Also, molecular imprinting polymer (MIP) is a method that used for creating selectivity in analytical chemistry. Ultrasonication could be used for preparation of MIP with different purposes including (1) to aid in the initiation, (2) to increase the solubility of template and the monomers and (3) to achieve efficient degassing through the polymerization. It is also expected to alter the binding sites population distribution as well as the morphology of the finished polymers [5].

Ultrasound has found many applications in pharmaceutical, medical and biomedical sciences. For example, transdermal drug delivery constitutes a key advance in painless delivery of drugs to be frequently given to patients [300,301]. Sonophoresis has received special attention on account of its characteristics and has so far provided very promising results. Recently, the use of "reverse sonophoresis" has opened up new avenues for sampling with monitoring and (or) diagnostic purposes [302]. US also provides an effective tool for different purposes in industry [303] and food technology [8,304,305].

Therefore, US energy is a constantly growing tool which has found a special place in different areas and as can be seen, some of the applications described are directly with those in analytical chemistry such as MIPs. Worthwhile information about some mentioned applications of US in this section has been written by different authors that they have been assembled in a book with the title of "*Ultrasound in Chemistry*" by Prof. Capelo-Martinez [5].

10. Limitations and future trends

Most applications of ultrasound assisted operations are discrete in nature as can be seen in the literature. Probably, the main reason for this fact is that the development of laboratory-made continuous systems for ultrasound assisted sample preparation requires more complex material and skilled designers than do batch systems. Thus, a propulsion device, usually a peristaltic pump, is mandatory for propelling the fluids through the dynamic system. In addition, switching and/or injection valves may be required for proper functioning of the system.

As mentioned before, in the case of liquid samples, emulsification is the main problem which exists in dynamic systems and should be avoided. So, US cannot always be a favored system for mass transferring between two immiscible phases.

In both discrete and continuous ultrasound assisted methods, selection of the type and characteristics of the US device need to high precision as it can be the key to successful development of these techniques.

As mentioned before, combination of ultrasound with other auxiliary techniques can result in noticeable and interesting improvements in extraction efficiencies and times. However, there are a few reports in this case and this subject that can be made to further development of US for the extraction of various compounds from different matrices.

To the best of our knowledge, there is no report about application of ultrasound in microextraction techniques in a continuous way and further research is still needed to complete the experiences in this area. Regarding the advantages of automatic systems and application of US in microextraction methods, using US in these techniques can show good performances especially for liquid phases that are based on emulsification. Finally, other efforts can be made to further develop the application of US in different aspects of sample preparation methods as well as the other fields of analytical chemistry.

Conclusions

At the time of writing there can be no doubt that the development of ultrasound makes an excellent tool in analytical chemistry. In order to give a general view of the potential of ultrasound, a brief description of the theoretical understanding of this method as well as the different steps which can be aided by this energy have been reviewed. These steps range from those widely used by the analytical community to those that scarcely known by analytical chemists. The major aim of this review focused on ultrasound assisted sample preparation techniques in both micro and macro-scale modes. The main advantage of US in the preparation of samples versus traditional extraction techniques is the reduction of the preparation time. In addition, other advantages such as the low reagent consumption under milder conditions of temperature and pressure, relative low cost of ultrasonic equipment and its simple use have also to be taken into account. Although, up to now the most applications of US in sample preparation have been focused on macro-scale mode, recently, it has found noticeable interests for micro-scale mode due to many advantages which resulted from application of this energy in different microextraction techniques. Also, different instrumentation modes (discrete and dynamic) of US for sample preparation as well as the possibility of coupling ultrasound with other analytical techniques discussed. An overview of more recent applications of ultrasound in different environmental and biological samples such as food, soil and water were presented.

At the end, it attempted to show that there are links that can be made across many of the ultrasound "disciplines" and that these links can serve to strengthen research in the general area of ultrasound. Regarding the mentioned points, US can find an important place in different areas of sciences including analytical chemistry in the future.

Acknowledgment

Financial support from Tarbiat Modares University is gratefully acknowledged. Also, the authors would like to announce their advanced thanks from Mrs. M. Ghambarian (Ph.D.), Miss E. Tahmasebi (Ph.D. student), Miss F. Rezaei (Ph.D. student), Miss M. Rezazadeh (M.Sc.), Mr. A. Esrafili (Ph.D. student) and Mr. M. Moradi (Ph.D. student) for their gracious helps.

Abbreviations

AAA: amino acid analyzer;
ACN: acetonitrile;
AES: atomic emission spectroscopy;
AFS: atomic fluorescence spectrometry;
AOT: Sulphosuccinic acid bis (2-ethylhexyl) ester sodium salt;
ASE: accelerated solvent extraction;
ATR: attenuated total reflectance;
BBI: Bowman-Birk inhibitor;
BCA: bicinchoninic acid;
BPA: bisphenol-A;
BUPs: benzoylureas pesticides;
CBBM: Coomassie brilliant blue method;
CCD: central composite design;
CE: capillary electrophoresis;
CHSR cup-horn sonoreactor;
CME: Coacervative microextraction;
CPAs: chlorinated phenoxyacetic acids;
CPE: cloud point extraction;
CZE: capillary zone electrophoresis;
3D: three dimentional;
DAD: diode array detection;
DCM: dichloromethane;
D2EHPA: bis(2-ethylhexyl)phosphoric acid;
DLLME: dispersive liquid liquid microextraction;
DMA: dimethylarsinic acid;
DPTA: diethylenetriamine pentaacetic acid;
DSPE: dispersive solid-phase extraction;
ECD: electron-capture detector;
EDCs: endocrine disrupting compounds;
EDTA: ethylenediaminetetracetic acid;
EME: electromembrane extraction;
ESI: electrospray ionization;
ETAAS: electrothermal atomic absorption spectrometry;
EtOH: ethanol;
FAAS: flame atomic emission spectroscopy;
FESEM: field emission scanning electron microscopy;
FID: Flame ionization detector;
FLD: fluorescence detector;
FPIA: fluorescence polarization immunoassay;
FTIR: fourier transform infrared spectrometry;

FQ: fluoroquinolones;
GC: gas chromatography;
GD: gravimetric detection;
GPC: gel permeation chromatography;
HF-LPME: hollow fiber based liquid phase microextraction;
HD: hydro distillation;
HG: hydride generation;
HLLME: homogeneous liquid-liquid microextraction;
HPLC: high performance liquid chromatography;
HRE: heat-reflux extraction;
HS-SDME: head space single drop microextraction;
HS-SPME: head space solid phase microextraction;
IC: Ion chromatography;
ICP: inductively coupled plasma;
LC: liquid chromatography;
LOD: limit of detection;
LOQ: limit of quantification;
MABE: microwave assisted extraction;
MAE: microwave assisted extraction;
MeHg+: methyl mercury;
MeOH: methanol;
MIP: microwave induced plasma;
MIPs: molecularly imprinted polymers;
MMA: monomethylarsonic acid;
MS: mass spectrometry;
MSPD: matrix solid-phase dispersion;
MQL: method quantification limit;
MW: microwave;
NCI: negative chemical ionization;
OCP: organochlorine pesticides;
OES: optical emission spectroscopy;
OP: organophosphate;
OPPs: organophosphates pesticides;
PAHs: polycyclic aromatic hydrocarbons;
PBS: phosphate buffer solution;
PBDEs: polybrominated diphenyl ethers;
PCBs: polychlorinated biphenyls;
PDA: photo diode array;
PFOA: perfluorooctanoic acid;
PFOS: perfluorooctane sulphonate;
PFPD: pulsed flame photometric detector PhACs: pharmaceuticals;
PMAE: pressurized microwave assisted extraction;
PMME: polymermonolith microextraction;
PSE: pressurized solvent extraction;
PTFE: poly tetrafluoroethylene;
QU: quinolones;
RSM: response surface methodology;
RT: room temperature;
SAESC: sonication assisted extraction in small columns;
SBME: solvent bar microextraction;
SCs: sulfur compounds;
SCP: stripping chronopotentiometry;
SFO: solidified organic drop;

SPE: solid phase extraction;
TBBPA: tetrabromobisphenol-A;
TCA: trichloroacetic acid;
TCAN: trichloroanisole;
TCBPA: tetrachlorobisphenol-A;
TKN: total Kjeldahl nitrogen;
TLC: thin layer chromatography;
TMAH: tetramethylammonium hydroxide;
UAB: ultrasound assisted back-extraction;
UB: ultrasonic bath;
UMAE: ultrasonic/microwave assisted extraction;
UP: ultrasonic probe;
UPLC: ultra performance liquid chromatography;
UR: ultrasonic reactor;
US: ultrasound;
USA: ultrasound assisted;
USAPLE; ultrasound assisted pressurized liquid extraction;
USAC: ultrasound assisted conversion;
USAE: ultrasound assisted extraction;
USAEME: ultrasound assisted emulsification microextraction;
USAD: ultrasound assisted digestion;
USAL: ultrasound assisted leaching;
USA-LPME: ultrasound assisted liquid phase microextraction;
USAPT: ultrasound assisted purge and trap;
USASE: ultrasound assisted Soxhlet extraction;
USASFE: ultrasound assisted supercritical fluid extraction;
XRF: X-ray fluorescence.

References

[1] M.D. Luque de Castro, F. Priego-Capote, Talanta 72, 321 (2007)
[2] M.D. Luque de Castro, F. Priego-Capote, Analytical application of ultrasound (Elsevier, Amsterdam, 2007)
[3] T.J. Mason, Ultrason. Sonochem.10, 175 (2003)
[4] P. Linares, F. Lizaro, M.D. Luque de Castro, M. Valcircel, J. Autom. Chem.10, 88 (1988)
[5] J. Capelo-Martinez, Ultrasound in chemistry (Wiely-VCH Verlag Gmbh, Weinheim, 2009)
[6] T.J. Mason, Prog. Biophys. Mol. Biol. 93, 166 (2007)
[7] J.L. Luche, C. Petrier, J.P. Lansard, A.E. Greene, J. Org. Chem. 48, 3837 (1983)
[8] A.C. Soria, M. Villamiel, Trends Food Sci. Technol. 21, 323 (2010)
[9] C.E. Banks, R.G. Compton, Analyst 129, 678 (2004)
[10] K.S. Suslick, The Year Book of Science and Future (Encyclopedia Britannica, Chicago, 1994)
[11] H.J. Kim, M.H. Chi, I.K. Hong, J. Ind. Eng. Chem. 15, 919 (2009)
[12] M.D. Luque de Castro, F. Priego-Capote, Anal. Chim. Acta 583, 2 (2007)
[13] F. Priego-Capote, M.D. Luque de Castro, Anal. Bioanal. Chem. 387, 249 (2007)
[14] X. Gu, J. Cai, X. Zhu, Q. Su, J. Sep. Sci. 28, 2477 (2005)
[15] A. Caballo-López, M.D. Luque de Castro, Anal. Chem. 2297, 78 (2006)
[16] M.D. Luque de Castro, F. Priego-Capote, A. Peralbo-Molina, J. Chromatogr. B 879, 1189 (2011)
[17] T. Nguyen, K.P. McNamara, Z. Rosenzweig, Anal. Chim. Acta, 400, 45 (1999)
[18] L. Zhang, J. Liu, P. Zhang, S. Yan, X. He, F. Chen, Chromatographia 73, 129 (2011)
[19] E. Anastasaki, C. Kanakis, C. Pappas, L. Maggi, C.P. del Campo, M. Carmona, G.L. Alonso, M.G. Polissiou, Eur. Food Res. Technol. 229, 899 (2009)
[20] E. Alissandrakis, E. Mantziaras, P.A. Tarantilis, P.C. Harizanis, M. Polissiou, Eur. Food Res. Technol. 231, 21 (2010)
[21] Z. Zhang, Z. Zhang, X. Zhang, J. Li, Y. Wang, C. Zhao, Front. Agric. China 4, 69 (2010)

[22] Z. Ming, H. Ke-long, Z. Jian-guo, L. Shuang, Z. Li, J. Cent. South Univ. Technol. 17, 472 (2010)

[23] J. Li-jia, L. Si-yang, C. Zui, W. Yang, Y. Xiu-feng, J. For. Res. 22, 239 (2011)

[24] R. Guoyan, L. Bafang, Z. Xue, Z. Yongliang, Y. Mingyan, H. Hu, Z. Xiukun, C. Li, J. Ocean Univ. China 8, 83 (2009)

[25] H. Hu, L. Bafang, Z. Xue, J. Ocean Univ. China 10, 85 (2011)

[26] J. Pan, X. Xia, J. Liang, Ultrason. Sonochem. 15, 25 (2008)

[27] Y.A. Hammel, R. Mohamed, E. Gremaud, M.H. LeBreton, P.A. Guy, J. Chromatogr. A 1177, 58 (2008)

[28] J. He, S. Wang, G. Fang, H. Zhu, Y. Zhang, J. Agric. Food Chem. 56, 2919 (2008)

[29] N. Tokman, C. Soler, M. Farré, Y. Picó, D. Barceló, J. Chromatogr. A 1216, 3138 (2009)

[30] V. Nania, G.E. Pellegrini, L. Fabrizi, G. Sesta, P. De Sanctis, D. Lucchetti, M. Di Pasquale, E. Coni, Food Chem. 115, 951 (2009)

[31] N. Yan, L. Zhou, Z. Zhu, X. Chen, J. Agric. Food Chem. 57, 807 (2009)

[32] K. Ghafoor, Y.H. Choi, J.Y. Jeon, I.H. Jo, J. Agric. Food Chem. 57, 4988 (2009)

[33] S. Chemat, A. Lagha, H.A. Amar, P.V. Bartels, F. Chemat, Flavour Fragr. J. 19, 188 (2004)

[34] Y. Liu, J. Yu, X. Wang, Int. J. Food Sci.Technol. 43, 763 (2008)

[35] R. Fernandez-Torres, M.A. Bello Lopez, M. Olias Consentino, M. Callejon Mochon, J.L. Perez-Bernal, Anal. Chim. Acta 675, 156 (2010)

[36] C.K. Zacharis, F.S. Kika, P.D. Tzanavaras, P. Rigas, E.R. Kyranas, Talanta 84, 480 (2011)

[37] L. Anta, M.L. Marina, M.C. García, J. Chromatogr. A 1217, 7138 (2010)

[38] T. Jerman, P. Trebše, B. Mozetič Vodopivec, Food Chem. 123, 175 (2010)

[39] B.L. Batista, J.L. Rodrigues, S.S. de Souza, V.C.O. Souza, F.B. Jr, Food Chem. 126, 2000 (2011)

[40] L. Maggi, A.M. Sánchez, M. Carmona, C.D. Kanakis, E. Anastasaki, P.A. Tarantilis, M.G. Polissiou, G.L. Alonso, Food Chem.127, 369 (2011)

[41] S. Goscinny, V. Hanot, J.F. Halbardier, J.Y. Michelet, J.V. Loco, Food Control 22, 226 (2011)

[42] M.K. Khan, M. Abert-Vian, A.S. Fabiano-Tixier, O. Dangles, F. Chemat, Food Chem. 119, 851 (2010)

[43] Z. Pan, W. Qu, H. Ma, G.G. Atungulu, T.H. McHugh, Ultrason. Sonochem. 18, 1249 (2011)

[44] A.L-S. Eh, S-G. Teoh, Ultrason. Sonochem.19, 151 (2012)

[45] Z. Lou, H. Wang, M. Zhang, Z. Wang, J. Food Eng. 98, 13 (2010)

[46] Y. Zou, C. Xie, G. Fan, Z. Gu, Y. Han, Innov. Food Sci. Emerg. Technol. 11, 611 (2010)

[47] J. Li, Y. Yue, T. Li, X. Hu, H. Zhong, Anal. Chim. Acta 650, 221 (2009)

[48] B.Á. Sánchez, F.P. Capote, M.D. Luque de Castro, J. Chromatogr. A 1201, 21 (2008)

[49] J. Wang, B. Sun, Y. Cao, Y. Tian, X. Li, Food Chem. 106, 804 (2008)

[50] J. Kuligowski, G. Quintás, F.A. Esteve-Turrillas, S. Garrigues, M. de la Guardia, J. Chromatogr. A 1185, 71 (2008)

[51] A. Bacaloni, C. Cavaliere, F. Cucci, P. Foglia, R. Samperi, A. Laganà, J.Chromatogr. A 1179, 182 (2008)

[52] K.X. Zhu, X.H. Sun, H.M. Zhou, J. Cereal Sci. 50, 266 (2009)

[53] D. Hernanz, V. Gallo, Á.F. Recamales, A.J. Meléndez-Martínez, F.J. Heredia, Talanta 76 929, (2008)

[54] A. Sharma, S.C. Verma, N. Saxena, N. Chadda, N.P. Singh, A.K. Sinha, J. Sep. Sci. 29, 613 (2006)

[55] M. Díaz-Alvarez, E. Turiel, A. Martín-Esteban, Anal. Bioanal. Chem. 393, 899 (2009)

[56] J. Raich-Montiu, J.L. Beltrán, M.D. Prat, M. Granados, Anal. Bioanal. Chem. 397, 807 (2010)

[57] V.G. Samaras, N.S. Thomaidis, A.S. Stasinakis, T.D. Lekkas, Anal. Bioanal. Chem. 399, 2549 (2011)

[58] K. Skalicka-Woźniak, K. Głowniak, Chromatographia 68, 85 (2008)

[59] R. Fernández-González, E. Martínez-Carballo, C. González-Barreiro, R. Rial-Otero, J. Simal-Gándara, Environ. Sci. Pollut. Res. 18, 1139 (2011)

[60] Q. Zhou, Y. Sang, L. Wang, S. Ji, J. Ye, X. Wang, Front. Agric. China 4, 489 (2010)

[61] M. Villalobos, A.P. Avila-Forcada, M.E. Gutierrez-Ruiz, Water Air Soil Pollut. 194, 151 (2008)

[62] C. Sánchez-Brunete, E. Miguel, B. Albero, J.L. Tadeo, Span. J. Agric. Res. 6, 7 (2008)

[63] J.J. Ramos, R. Rial-Otero, L. Ramos, J.L. Capelo, J. Chromatogr. A 1212, 145 (2008)

[64] M.C. Yebra, S. Cancela, R.M. Cespón, Food Chem. 108, 774 (2008)

[65] C. Sánchez-Brunete, E. Miguel, J.L. Tadeo, J. Chromatogr. A 1216, 5497 (2009)

[66] X. Esparza, E. Moyano, M.T. Galceran, J. Chromatogr. A 1216, 4402 (2009)

[67] E. Rodríguez-Gonzalo, R. Carabias-Martínez, E. Miranda-Cruz, J. DomínguezÁlvarez, J. Hernández-Méndez, J. Sep. Sci. 32, 575 (2009)
[68] L. Rey-Salgueiro, E. Martínez-Caballo, M.S. García-Falcón, C. González-Barreiro, J. Simal-Gándara, Food Chem. 115, 814 (2009)
[69] J. Zhou, X. Xue, Y. Li, J. Zhang, F. Chen, L. Wu, L. Chen, J. Zhao, Food Chem. 115, 1074 (2009)
[70] H. Zhang, Y. Ren, X. Bao, J. Pharm. Biomed. Anal. 49, 367 (2009)
[71] J. Zhou, X. Xue, F. Chen, J. Zhang, Y. Li, L. Wu, L. Chen, J. Zhao, J. Sep. Sci. 32, 955 (2009)
[72] X.M. Xu, Y.P. Ren, Z.X. Cai, J.L. Han, B.F. Huang, Y. Zhu, Anal. Chim. Acta 650, 39 (2009)
[73] P. Navarro, J. Bustamante, A. Vallejo, A. Prieto, A. Usobiaga, S. Arrasate, E. Anakabe, E. Puy-Azurmendi, O. Zuloaga, J. Chromatogr. A 1217, 5890 (2010)
[74] B. Klejdus, L. Lojková, M. Plaza, M. Šnóblová, D. Štěrbová, J. Chromatogr. A 1217, 7956 (2010)
[75] A.R. Fontana, A.Camargod, L.D. Martinez, J.C. Altamirano, J. Chromatogr. A 1218, 2490 (2011)
[76] M. Orozco-Solano, J. Ruiz-Jiménez, M.D. Luque de Castro, J. Chromatogr. A 1217, 1227 (2010)
[77] Y. Tao, H. Yu, D. Chen, Z.Y. Liu, D. Yang, Y. Pan, Y. Wang, L. Huang, Z. Yuan, J. Chromatogr. B 878, 3415 (2010)
[78] M. Asensio-Ramos, J. Hernandez-Borges, T.M. Borges-Miquel, M.A. Rodriguez-Delgado, Anal. Chim. Acta 647, 167 (2009)
[79] G. Zgórka, J. Sep. Sci. 32, 965 (2009)
[80] E.G. Karageorgou, V.F. Samanidou, J. Sep. Sci. 33, 2862 (2010)
[81] L.H. Reyes, G.M. Mizanur Rahman, T. Fahrenholz, H.M. Skip Kingston, Anal. Bioanal. Chem. 390, 2123 (2008)
[82] S. Pereira, L.P. Fonseca, J.L. Capelo, T. Armas, F. Vilhena, A.P. Pinto, M.L.S. Gonçalves, A.M. Mota, Anal. Bioanal. Chem. 398, 2315 (2010)
[83] A. Pourhosseina, M. Madani, M. Shahlaei, K. Fakhri, P. Alimohamadi, M. Amiri, Cent. Eur. J. Chem. 7, 382 (2009)
[84] F.A. Silva, C.C.F. Padilha, G. Rocha de Castro, P. dos Santos Roldan, A.R. de Araujo Nogueira, P.M. Moraes, P.M. Padilha, Cent. Eur. J. Chem. 9, 119 (2011)
[85] S.M. Stanišić, L.M. Ignjatović, D.D. Manojlović, B.P. Dojčinović, Cent. Eur. J. Chem. 9, 481 (2011)
[86] C. Güler, M. Alpaslan, M.A. Kurt, A. Temel, Environ. Earth Sci. 60, 203 (2010)
[87] I. Pumure, J.J. Renton, R.B. Smart, Environ. Geol. 56, 985 (2009)
[88] D. Remeteiová, S. Ružičková, R. Rusnák, Microchim. Acta 163, 257 (2008)
[89] I. Lavilla, P. Vilas, C. Bendicho, Food Chem. 106, 403 (2008)
[90] J.C. Cypriano, M.A. Costa Matos, R. Camargo Matos, Microchem. J. 90, 26 (2008)
[91] M.N. Matos Reyes, M.L. Cervera, R.C. Campos, M. de la Guardia, Talanta 75, 811 (2008)
[92] C. Sola-Larrañaga, I. Navarro-Blasco, Food Chem. 115, 1048 (2009)
[93] R.C.F. Neves, P.M. Moraes, M.A.D. Saleh, V.R. Loureiro, F.A. Silva, M.M. Barros, C.C.F. Padilha, S.M.A. Jorge, P.M. Padilha, Food Chem. 113, 679 (2009)
[94] A. Gonzálvez, A. Llorens, M.L. Cervera, S. Armenta, M. de la Guardia, Food Chem. 115, 360 (2009)
[95] I. López, S. Cuello, C. Camara, Y. Madrid, Talanta 82, 594 (2010)
[96] M. Costas-Rodríguez, I. Lavilla, C. Bendicho, Spectrochim. Acta Part B 664, 121 (2010)
[97] M. Costas, I. Lavilla, S. Gil, F. Pena, I. de la Calle, N. Cabaleiro, C. Bendicho, Anal. Chim. Acta 679, 49 (2010)
[98] T.G. Kazi, N. Jalbani, J.A. Baig, M.B. Arain, H.I. Afridi, M.K. Jamali, A.Q. Shah, A.N. Memon, Food Chem. 119, 1313 (2010)
[99] C. Li, F. Xie, Y. Ma, T. Cai, H. Li, Z. Huang, G. Yuan, J. Hazard. Mater. 178, 823 (2010)
[100] M. Chiha, O. Hamdaoui, F. Ahmedchekkat, C. Pétrier, Ultrason. Sonochem. 17, 318 (2010)
[101] I.D.L. Calle, N. Cabaleiro, M. Costas, F. Pena, S. Gil, I. Lavilla, C. Bendicho, Microchem. J. 97, 93 (2011)
[102] A. Bellido-Martín, J.L. Gómez-Ariza, P. Smichowsky, D. Sánchez-Rodas, Anal. Chim. Acta 649, 191 (2009)
[103] B.L. Batista, J.L. Rodrigues, V.C. de Oliveira Souza, F.B. Jr., Forensic Sci.Int.192, 88 (2009)
[104] M.B. Arain, T.G. Kazi, M.K. Jamali, N. Jalbani, H.I. Afridi, J.A. Baig, J. Hazard. Mater. 154, 998 (2008)
[105] M.L. Prat, A. López-Gonzálvez, M.A. Ruiz, C. Barbas, J. Pharm. Biomed. Anal. 49, 1040 (2009)
[106] W.P.C. Santos, J.T. Castro, M.A. Bezerra, A.P. Fernandes, S.L.C. Ferreira, M.G.A. Korn, Microchem. J. 91,153 (2009)
[107] I.D.L. Calle, N. Cabaleiro, I. Lavilla, C. Bendicho, Spectrochim. Acta Part B 64, 874 (2009)
[108] M.M. Santoyo, J.A.L. Figueroa, K. Wrobel, K. Wrobel, Talanta 79, 706 (2009)

[109] S.F.O. de Vallejuelo, A. Barrena, G. Arana, A. de Diego, J.M. Madariaga, Talanta 80, 434 (2009)
[110] J. Kuligowski, A. Breivogel, G. Quintás, S. Garrigues, M. de la Guardia, Anal. Bioanal. Chem. 392, 1383 (2008)
[111] J.P. Lamas, L. Sanchez-Prado, J. Regueiro, M. Llompart, C. Garcia-Jares, Anal. Bioanal. Chem. 394, 2231 (2009)
[112] H. Liu, Q. Li, Y. Zhang, Y. Zhou, Chromatographia 69, 339 (2009)
[113] W. GuiHua, S. Ping, Z. Fan, H. XiangYan, Y. Yi, G. ZhenKu, Sci. China Chem. 54, 231 (2011)
[114] M.A.D. Saleh, R.C.F. Neves, P.M. Moraes, P.M. Lima, F.A. dos Santos, F.A. Silva, P.M. Padilha, Sens. Instrumen. Food Qual. 3, 108 (2009)
[115] M.L. Hladik, K.M. Kuivila, J. Agric. Food Chem. 56, 2310 (2008)
[116] M.S. Kim, T.W. Kang, H. Pyo, J. Yoon, K. Choi, J. Hong, J. Chromatogr. A 1208, 25 (2008)
[117] V.S. Morozova, S.A. Eremin, P.N. Nesterenko, N.A. Klyuev, A.A. Shelepchikov, I.V. Kubrakova, J. Anal. Chem. 63, 127 (2008)
[118] J.P. Bossio, J. Harry, C.A. Kinney, Chemosphere 70, 858 (2008)
[119] C. Sánchez-Brunete, E. Miguel, M.D. Delgado, J.L. Tadeo, Fresenius Environ. Bull. 17, 1601 (2008)
[120] J. Xu, L. Wu,W. Chen, A.C. Chang, J. Chromatogr. A 1202, 189 (2008)
[121] G. Bianco, G. Novario, D. Bochcchio, G. Anzilotta, A. Palma, T.R.I. Cataldi, Chemosphere 73, 104 (2008)
[122] L. Nuñez, J.L. Tadeo, A.I. Garcia-Valcarcel, E. Turiel, J. Chromatogr. A 1214, 178 (2008)
[123] S. Cantarero, A. Zafra-Gómez, O. Ballesteros, A. Navalón, J.L. Vílchez, G. Crovetto, C. Verge, J.A. de Ferrer, Talanta 82, 1548 (2010)
[124] A.M. Rojano-Delgado, F. Priego-Capote, M.D. Luque de Castro, R. De Prado, Talanta 82, 1757 (2010)
[125] J. García-Lavandeira, E. Blanco, C. Salgado, R. Cela, Talanta 82, 261 (2010)
[126] M. Olivares, A. Vallejo, M. Irazola, X. Murelaga, J.I. Baceta, A. Tarriño, N. Etxebarria, Talanta 83, 605 (2010)
[127] J.P. Lamas, L. Sanchez-Prado, C. Garcia-Jares, M. Llompart, J. Chromatogr. A, 1217, 1882 (2010)
[128] M.L. Feo, E. Eljarrat, D. Barceló, J. Chromatogr. A, 1217, 2248 (2010)
[129] S.T. Cargnin, J. de Matos Nunes, J.S. Haas, L.F. Baladão, E. Cassel, R.F. Vargas, S.B. Rech, G.L. von Poser, J. Chromatogr. B 878, 83 (2010)
[130] A.P. Louppis , D. Georgantelis , E.K. Paleologos, M.G. Kontominas, Food Chem. 121, 907 (2010)
[131] Z. Ying, X. Han, J. Li, Food Chem. 127, 1273 (2011)
[132] J. Liu, J.W. Li, J. Tang, Food Bioprod. Process. 88, 215 (2010)
[133] J. Londoño-Londoño, V.R. de Lima, O. Lara, A. Gil, T.B.C. Pasa, G.J. Arango, J.R.R. Pineda, Food Chem. 119, 81 (2010)
[134] J. Dong, Y. Liu, Z. Liang, W. Wang, Ultrason. Sonochem.17, 61 (2010)
[135] E.Q. Xia, X.X. Ai, S.Y. Zang, T.T. Guan, X.R. Xu, H.B. Li, Ultrason. Sonochem. 18, 549 (2011)
[136] S. Zhao, O.D. Baik, Ultrason. Sonochem. 19, 22 (2012)
[137] Y. Sun, Z. Liu, J. Wanga, Sep. Purif. Technol.78, 49 (2011)
[138] D.T. Santos, P.C. Veggi, M.A.A. Meireles, J. Food Eng. 101, 23 (2010)
[139] M.L. Feo, A. Ginebreda, E. Eljarrat, D. Barceló, J. Hydrol. 393, 156 (2010)
[140] S. Orecchio, Atmos. Environ. 45, 1888 (2011)
[141] P.A. Machado, H. Fu, R.J. Kratochvil, Y. Yuan, T.S. Hahm, C.M. Sabliov, C.I Wei, Y. M. Lo, Bioresource Technol. 101, 1091 (2010)
[142] I. Novak, P. Janeiro, M. Serug, A.M. Oliveira-Brett, Anal. Chim. Acta 630, 107 (2008)
[143] L. Rey-Salgueiro, X. Pontevedra-Pombal, M. Álvarez-Casas, E. Martínez-Carballo, M.S. García-Falcón, J. Simal-Gándara, J. Chromatogr. A 1216, 5235 (2009)
[144] A.R. Fakhari, S. Nojavan, S.N. Ebrahimi, C.J. Evenhuis, J. Sep. Sci. 33, 2153 (2010)
[145] L. Chen, H. Jin, L. Wang, L. Sun, H. Xu, L. Ding, A. Yu, H. Zhang, J. Chromatogr. A 1192, 89 (2008)
[146] J.P. Lamas, L. Sanchez-Prado, C. Garcia-Jares, M. Llompart, J. Chromatogr. A 1216, 5755 (2009)
[147] N. Sánchez-Ávila, J.M. Mata-Granados, J. Ruiz-Jiménez, M.D. Luque de Castro, J. Chromatogr. A 1216, 6864 (2009)
[148] S. Schneider, E. Sibille, M. Yegles, H. Neels, R. Wennig, A. Mühe, J. Chromatogr. B 877, 2589 (2009)
[149] L.S. Foteeva, N.V. Stolyarova, A.R. Timerbaev, B.K. Keppler, J. Pharm. Biomed. Anal. 48, 218 (2008)
[150] J.M. Roldán-Gutiérrez, J. Ruiz-Jiménez, M.D. Luque de Castro, Talanta 75, 1369 (2008)
[151] J. Heroult, T. Zuliani, M. Bueno, L. Denaix, G. Lespes, Talanta 75, 486 (2008)

[152] C. Qi-he, F. Ming-liang, L. Jin, Z. Hai-feng, H. Guo-qing, R. Hui, Ultrason. Sonochem. 16, 599 (2009)
[153] C. Mardones, D. von Baer, A. Hidalgo, A. Contreras, C. Sepffllveda, J. Sep. Sci. 31, 1124 (2008)
[154] L. Zhang, Y. Geng, W. Duan, D. Wang, M. Fu, X. Wang, J. Sep. Sci. 32, 3550 (2009)
[155] L, Zhang, X, Wang, J. Sep. Sci. 33, 2035 (2010)
[156] C. Sánchez-Brunete, R.A. Perez, E. Miguel, J.L. Tadeo, J. Chromatogr. A 823, 17 (1998)
[157] S. Ozcan, A. Tor, M.E. Aydin, Clean 37, 811 (2009)
[158] M.C. Yebra, A. Moreno-Cid, R. Cespon, S. Cancela, Talanta 62, 403 (2004)
[159] Q. Yang, X.L. Zhang, X.Y. Li, W.K. Tang, J.X. Zhang, C.X. Fang, C.Y. Zheng, Anal. Chim. Acta 589, 231 (2007)
[160] S. Chemat, A. Lagha, H.A. Amar, P.V. Bartels, F. Chemat, Flavour Fragr. J. 19, 188 (2004)
[161] S. Sporring, S. Bøwadt, B. Svensmark, E. Björklund, J. Chromatogr. A 1090, 1 (2005)
[162] W. GuiHua, S. Ping, Z. Fan, H. XiangYan, Y. Yi1, G. ZhenKu, Sci. China Chem. 54, 231 (2011)
[163] A. Caballo-López, M.D. Luque de Castro, Anal. Chem. 78 (2006) 2297
[164] M. Galesio, M. Mazzarino, X. de la Torre, F. Botrè, J.L. Capelo, Anal. Bioanal. Chem. 399, 861 (2011)
[165] A. Moreno-Cid, M.C. Yebra, Anal. Bioanal. Chem. 379, 77 (2004)
[166] C. Brunori, I. Ipolyi, L. Macaluso, R. Morabito, Anal. Chim. Acta 510, 101 (2004)
[167] S. Chemat, A. Lagha, H.A. Amar, F. Chemat, Ultrason. Sonochem. 11, 5 (2004)
[168] G. Cravotto, L. Boffa, S. Mantegna, P. Perego, M. Avogadro, P. Cintas, Ultrason. Sonochem. 15, 898 (2008)
[169] K. Ganzler, A. Salgo, K. Valko, J. Chromatogr. 371, 299 (1986)
[170] V. Camel, Trends Anal. Chem. 19, 229 (2000)
[171] J. Szpunar, V.O. Schmitt, O.F.X. Donard, R. Lobifiski, Trends Anal. Chem. 15, 181 (1996)
[172] Y.Y. Shu, T.L. Lai, H.S. Lin, T.C. Yang, C.P. Chang, Chemosphere 52, 1667 (2003)
[173] J.R. Dean, Sci. Total Environ. 15, 2914 (2000)
[174] Z. Lianfu, L. Zelong, Ultrason.Sonochem. 15, 731 (2008)
[175] H. Li, Y. Wei, J. You, M.J. Lydy, Talanta 83, 171 (2010)
[176] Z. Liu, Z. Zhu, H. Zhang, G. Tan, X. Chen, Y. Chai, J. Pharm. Biomed. Anal. 55, 557 (2011)
[177] C. Domini, L. Vidal, G. Cravotto, A. Canals, Ultrason. Sonochem. 16, 564 (2009)
[178] Y. Chena, X. Gu, S.Q. Huang, J. Li, X. Wang, J. Tang, Int. J. Biol. Macromol. 46, 429 (2010)
[179] C. Lu, H. Wang, W. Lv, C. Ma, P. Xu, J. Zhu, J. Xie, B. liu, Q. Zhou, Chromatographia DOI 10.1007/s10337-011-2023-5
[180] Y. Hu, T. Wang, M. Wang, S. Han, P. Wan, M. Fan, Chem. Eng. Process. 47, 2256 (2008)
[181] Z.L.Wu, B. Ondruschka, G. Cravotto, Environ. Sci. Technol. 42, 8083 (2008)
[182] Q. Lang, C.M. Wai, Talanta 53, 771 (2001)
[183] E. Riera, Y. Golás, A. Blanco, J.A. Gallego, M. Blasco, A. Mulet, Ultrason. Sonochem. 11, 241 (2004)
[184] E. Riera, A. Blanco, J. García, J. Benedito, A. Mulet, J.A. Gallego-Juárez, M. Blasco, Ultrasonics 50, 306 (2010)
[185] D. Luo, T. Qiu, Q. Lu, J. Sci. Food Agric. 87, 431 (2007)
[186] S. Balachandran, S.E. Kentish, R. Mawson, M. Ashokkumar, Ultrason. Sonochem. 13, 471 (2006)
[187] A.J. Hu, S. Zhao, H. Liang, T.Q. Qiu, G. Chen, Ultrason. Sonochem. 14, 219 (2007)
[188] B. Klejdusa, L. Lojková, M. Plaza, M. Šnóblová, D. Štěrbová, J. Chromatogr. A 1217 7956, (2010)
[189] Y. Gao, B. Nagy, X. Liu, B. Simándi, Q. Wang, J. Supercrit. Fluids 49, 345 (2009)
[190] G. Rocco, C. Toledo, I. Ahumada, B. Sepúlveda, A. Cañete, P. Richter, J. Chromatogr. A 1193, 32 (2008)
[191] M.D. Luque de Castro, F. Priego-Capote, J. Chromatogr. A 1217, 2383 (2010)
[192] M.D. Luque de Castro, J.L. Luque-García, Acceleration and Automation of Solid Sample Treatment, (Elsevier, Amsterdam, 2002)
[193] J.L. Luque-García, M.D. Luque de Castro, J. Chromatogr. A 1034, 237 (2004)
[194] F.V.M. Pontes, M.C. Carneiro, D.S. Vaitsman, G.P. da Rocha, L.I.D. da Silva, A.A. Neto, M.I.C. Monteiro, Anal. Chim. Acta 632, 284 (2009)
[195] S. de Koning, H.G. Janssen, U.A.T. Brinkman, Chromatographia 69, S33 (2009)
[196] L. Rusnáková, V. Andruch, I.S. Balogh, J. Škrlíková, Talanta 85, 541 (2011)
[197] I.D.L. Calle, F. Pena-Pereira, N. Cabaleiro, I. Lavilla, C. Bendicho, Talanta 84 (2011) 109
[198] A. Bidari, M.R. Ganjali, P. Norouzi, M.R.M. Hosseini, Y. Assadi, Food Chem. 126, 1840 (2011)
[199] A.R. Fontana, N.B. Lana, L.D. Martinez, J.C. Altamirano, Talanta 82, 359 (2010)

[200] J. Llorca-Pórcel, M. Martínez-Parreño, E. Martínez-Soriano, I. Valor, J.Chromatogr. A 1216, 5955 (2009)

[201] A. Kende , Z. Csizmazia, T. Rikker, V. Angyal, K. Torkos, Microchem. J. 84, 63 (2006)

[202] F. Rezaei, M.R.M. Hosseini, Anal. Chim. Acta 702, 274 (2010)

[203] S. Seidi, Y. Yamini, A. Heydari, M. Moradi, A. Esrafili, M. Rezazade, Anal. Chim. Acta 701, 181 (2011)

[204] V. Pino, J.H. Ayala, A.M. Afonso, V. González, Fresenius J. Anal. Chem. 371, 526 (2001)

[205] J. Regueiro, M. Llompart, C. Garcia-Jares, J.C. Garcia-Monteagudo, R. Cela, J. Chromatogr. A 1190, 27 (2008)

[206] M. Rezaee, Y. Yamini, M. Faraji, J. Chromatogr. A 1217, 2342 (2010)

[207] M.R.K. Zanjani, Y. Yamini, S. Shariati, J.Å. Jönsson, Anal. Chim. Acta 585, 286 (2007)

[208] Y. Wang, X. Luo, J. Tang, X. Hu, Microchim. Acta 173, 267 (2011)

[209] A. Saleh, Y. Yamini, M. Faraji, M. Rezaee, M. Ghambarian, J. Chromatogr. A 1216, 6673 (2009)

[210] Y.S. Su, J.F. Jen, J. Chromatogr. A 1217, 5043 (2010)

[211] X. Song, J. Li, C. Liao, L. Chen, Chromatographia, DOI 10.1007/s10337-011-2048-9

[212] W.X. Wang, T.J. Yang, Z.G. Li, T.T. Jong, M.R. Lee, Anal. Chim. Acta 690, 221 (2011)

[213] N. Cabaleiro, F. Pena-Pereira, I. de la Calle, C. Bendicho, I. Lavilla, Microchem. J. (2011), doi:10.1016/j.microc.2011.05.010

[214] O. Behrend, K. Ax, H. Schubert, Ultrason. Sonochem. 7, 77 (2000)

[215] H. Xu, Y. Liao, J. Yao, J. Chromatogr. A 1167, 1 (2007)

[216] H. Xu, J. Yao, J. Cheng, Y. Cui, D. Song, Y. Feng, Chromatographia 68, 235 (2008)

[217] H. Xua, L. Lva, S. Hub, D. Songa, J. Chromatogr. A 1217, 2371 (2010)

[218] L. Wang, Z. Wang, H. Zhang, X. Li, H. Zhang, Anal. Chim. Acta 647, 72 (2009)

[219] P. Hashemi, A. Yarahmadi, K. Azizi, B. Sabouri, Chromatographia 67, 253 (2008)

[220] H. Ugland, M. Krogh, K. Rasmussen, J. Chromatogr. B 749, 85 (2000)

[221] R. Zhao, J. Yuan, H. Li, X. Wang, T. Jiang, J. Lin, Anal. Bioanal. Chem. 387, 2911 (2007)

[222] K. Shrivas, D. K. Patel, Food Chem. 122, 314 (2010)

[223] K. Shrivas, D.K. Patel, Food Chem. 124, 1673 (2011)

[224] Q. Yang, Y. Guo, L. Wang, S. Liang, X. Liu, Chromatographia 72, 1157 (2010)

[225] T.I. Sikalos, E.K. Paleologos, Anal. Chem. 77, 2544 (2005)

[226] A.R. Fontana, M.F. Silva, L.D. Martínez, R.G. Wuillou, J.C. Altamirano, J. Chromatogr. A 1216, 4339 (2009)

[227] A.R. Fontana, A.B. Camargob, J.C. Altamirano, J. Chromatogr. A 1217, 6334 (2010)

[228] C.L. Arthur, J. Pawliszyn, Anal. Chem. 62, 2145 (1990)

[229] G. Vas, K. Vekey, J. Mass Spectrom. 39, 233 (2004)

[230] S. Motlagh, J. Pawliszyn, Anal. Chim. Acta 284, 265 (1993)

[231] R. Boussahel, S. Bouland, K.M. Moussaoui, M. Baudu, A. Montiel, Water Res. 36, 1909 (2002)

[232] R. Rial-Otero, E.M. Gasper, I. Moural, J.L. Capelo, Talanta 71, 1906 (2007)

[233] J.T. Mason, Sonochemistry (Oxford University Press, Oxford, UK, 1999)

[234] R. Eisert, J. Pawliszyn, Crit. Rev. Anal. Chem. 27, 103 (1997)

[235] J. Pawliszyn, Solid-Phase Microextraction: Theory and Practice (Wiely-VCH Verlag Gmbh, Weinheim, 1997)

[236] J.H. Lee, R. Diono, G.Y. Kim, D.B. Min, J. Agric. Food Chem. 51, 1136 (2003)

[237] P. Kusch, G. Knupp, J. Sep. Sci. 25, 539 (2002)

[238] K.J. Chia, T.Y. Lee, S.D. Huang, Anal. Chim. Acta 527, 157 (2004)

[239] C.L. Biazon, R. Brambilla, A. Rigacci, T.M. Pizzolato, J.H.Z. dos Santos, Anal. Bioanal. Chem. 394, 549 (2009)

[240] A.R. Ghiasvand, M. Nasseri, S. Farsizaeh, M.H. Meshkatalsadat, R. Sadeghi-Sarabi, S. Shadabi, M. Borzoei, Chromatographia 73, 1031 (2011)

[241] R. Batlle, A. Colmsjo, U. Nilsson, Frensenius J. Anal. Chem. 371, 514 (2001)

[242] H.L. Yang, Y.R. Wang, Z.X. Zhuang, X.R. Wang, Spectrosc. Spect. Anal. 27, 103 (1977)

[243] H. Xua, S. Wang, G. Zhangb, S. Huang, D. Song, Y. Zhou, G. Long, Anal. Chim. Acta 690, 86 (2011)

[244] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcolumn Sep. 11, 737 (1999)

[245] F. Sánchez-Rojas, C. Bosch-Ojeda, J.M. Cano-Pavón, Chromatographia 69, S79 (2009)

[246] S. Bazhdanzadeh, Z. Talebpour, N. Adib, H.Y. Aboul-Enein, J. Sep. Sci. 34, 90 (2011)

[247] P. Popp, C. Bauer, L. Wennrich, Anal. Chim. Acta 436, 1 (2001)
[248] P. Popp, C. Bauer, A. Paschke, L. Montero, Anal. Chim. Acta 504, 307 (2004)
[249] D. Sulistyorini, M.D. burford, D.J. Weston, D.W.M. Arrigan, Anal. Lett. 35, 1429 (2002)
[250] L. Rusnáková, V. Andruch, I.S. Balogh, J. Škrlíková, Talanta 85, 541 (2011)
[251] A. Martín-Calero, J.H. Ayala, V. González, A.M. Afonso, Anal. Chim. Acta 582, 259 (2007)
[252] M. Asensio-Ramos, J. Hernández-Borges, T.M. Borges-Miquel, M.Á. Rodríguez-Delgado, J. Chromatogr. A 1218, 4808 (2010)
[253] C. Salgado-Petinal, M. Llompart, C. García-Jares, M. García-Chao, R. Cela, J. Chromatogr. A 1124, 139 (2006)
[254] T. Li, Z.G. Shi, M.M. Zheng, Y.Q. Feng, J. Chromatogr. A 1205, 163 (2008)
[255] B.A. Romero, E. Bou-Maroun, J.M. Reparet, J. Blanquet, N. Cayot, Food Chem. 119, 459 (2010)
[256] V.P. Jofré, M.V. Assof, M.L. Fanzone, H.C. Goicoechea, L.D. Martínez, M.F. Silva, Anal. Chim. Acta 683, 126 (2010)
[257] H. Ebrahimzadeh, Z. Saharkhiz, M. Tavassoli, F. Kamarei, A.A. Asgharinezhad, J. Sep. Sci. 34, 1275 (2011)
[258] H. Yan, J. Du, X. Zhang, G. Yang, K.H. Row, Y. Lv, J. Sep. Sci. 33, 1829 (2010)
[259] Q. Zhou, X. Zhang, J. Sep. Sci. 33, 3734 (2010)
[260] Q. Yang, Y. Guo, L. Wang, S. Liang, X. Liu, Chromatographia 72, 1157 (2010)
[261] S. Tajik, M.A. Taher, Microchim. Acta 173, 249 (2011)
[262] J. Wu, B. Xiang, J. Xia, Microchim. Acta 166, 157 (2009)
[263] J. Ma, J. Zhang, X. Du, X. Lei, J. Li, Microchim. Acta 168, 153 (2010)
[264] Q. Chang, J. Zhang, X. Du, J. Ma, J.L. Front. Environ. Sci. Engin. China, 4, 187 (2010)
[265] S. Wang, L. Ren, Y. Xu, F. Liu, Microchim. Acta 173, 453 (2011)
[266] M. Mohamadi, A. Mostafavi, Talanta 81, 309 (2010)
[267] E. Becerril-Bravo, J.P. Lamas, L. Sanchez-Prado, M. Lores, C. Garcia-Jares, B. Jimenez, M. Llompart, Chemosphere 81, 1378 (2010)
[268] F. Kamarei, H. Ebrahimzadeh, Y. Yamini, Microchem. J. 99, 26 (2011)
[269] P. Viñas, N. Martínez-Castillo, N. Campillo, M. Hernández-Cordóba, J. Chromatogr. A 1217, 6569 (2010)
[270] S. Li, S. Cai, W. Hu, H. Chen, H. Liu, Spectrochim. Acta Part B 64, 666 (2009)
[271] H. Yana, H. Wang, X. Qin, B. Liu, J. Du, J. Pharm. Biomed. Anal. 54, 53 (2011)
[272] I. Lavilla, N. Cabaleiro, F. Pena, I. de la Calle, C. Bendicho, Anal. Chim. Acta 674, 59 (2010)
[273] J. Regueiro, M. Llompart, E. Psillakis, J.C. Garcia-Monteagudo, C. Garcia-Jares, Talanta 79, 1387 (2009)
[274] J.J. Ma, X. Du, J.W. Zhang, J.C. Li, L.Z. Wang, Talanta 80, 980 (2009)
[275] S. Ozcan, A. Tor, M.E. Aydin, Anal. Chim. Acta 647, 182 (2009)
[276] S. Ozcan, A. Tor, M.E. Aydin, Anal. Chim. Acta 665, 193 (2010)
[277] K.J. Huang, H. Wang, M. Ma, M.L. Sha, H.S. Zhang, J. Chromatogr. A 1103, 193 (2006)
[278] A.R. Fontana, J.C. Altamirano, Talanta 81, 1536 (2010)
[279] A.R. Fontana, R.G. Wuilloud, L.D. Martínez, J.C. Altamirano, J. Chromatogr. A 1216, 147 (2009)
[280] K.J. Huang, C.Y. Wei, W.L. Liu, W.Z. Xiea, J.F. Zhang, W. Wang, J. Chromatogr. A 1216, 6636 (2009)
[281] Q. Wu, Q. Changa, C. Wu, H. Rao, X. Zeng, C. Wang, Z. Wang, J. Chromatogr. A 1217, 1773 (2010)
[282] C. Cortada, L. Vidal, A. Canals, J. Chromatogr. A 1218, 17 (2011)
[283] C. Wu, N. Liu, Q. Wu, C. Wang, Z. Wang, Anal. Chim. Acta 679, 56 (2010)
[284] J. Du, H. Yan, D. She, B. Liu, G. Yang, Talanta 82, 698 (2010)
[285] J. Cheng, G. Matsadiq, L. Liu, Y.W. Zhou, G. Chen, J. Chromatogr. A 1218, 2476 (2011)
[286] E. Molaakbari, A. Mostafavia, D. Afzali, J. Hazard. Mater. 185, 647 (2011)
[287] H. Yan, B. Liu, J. Du, G. Yang, K.H. Row, J. Chromatogr. A 1217, 5152 (2010)
[288] K.J. Huang, C.X. Jin, S.L. Song, C.Y. Wei, Y.M. Liu, J. Li, J. Chromatogr. B 879, 579 (2011)
[289] B. Liu, H. Yan, F. Qiao, Y. Geng, J. Chromatogr. B 879, 90 (2011)
[290] J. Cheng, Y. Xia, Y. Zhou, F. Guo, G. Chen, Anal. Chim. Acta 701, 86 (2010)
[291] T. Mao, B. Hao, J. He, W. Li, S. Li, Z. Yu, J. Sep. Sci. 32, 3029 (2009)
[292] C. Jia, X. Zhu, L. Chen, M. He, P. Yu, E. Zhao, J. Sep. Sci. 33, 244 (2010)
[293] Q. Zhou, X. Zhang, J. Xiao, J. Chromatogr. A 1216, 4361 (2009)
[294] S.L. Lin, M.R. Fuh, J. Chromatogr. A 1217, 3467

(2010)
[295] Q. Wu, Z. Li, C. Wu, C. Wang, Z. Wang, Microchim. Acta 170, 59 (2010)
[296] S. Ozcan, A. Tor, M.Emin Aydin, Water Res. 43, 4269 (2009)
[297] X. Jing, Y. Wang, D. Wu, J. Qiang, Ultrason. Sonochem. 14, 75 (2007)
[298] L.F. Steel, B.B. Haab, S.M. Hanash, J. Chromatogr. B 815, 275 (2005)
[299] G.B. Smejkal, A. Lararev, Separation Methods in Proteomics (Taylor & Francis, Boca Raton, 2006)
[300] S. Mitragotri, J. Kost, Adv. Drug Deliver. Rev. 56, 589 (2004)
[301] G.T. Haar, Eur. J. Ultrasound 9, 3 (1999)
[302] J. Kost, S. Mitragotri, R.A. Gabbay, M. Pishko, R. Ranger, Nat. Med. 6, 347 (2000)
[303] C. Leonelli, T.J. Mason, Chem. Eng. Process. 49, 885 (2010)
[304] F. Chemat, Z.E. Huma, M.K. Khan, Ultrason. Sonochem. 18, 813 (2011)
[305] K. Vilkhu, R. Mawson, L. Simons, D. Bates, Innov. Food Sci. Emerg. Technol. 9, 161 (2008)