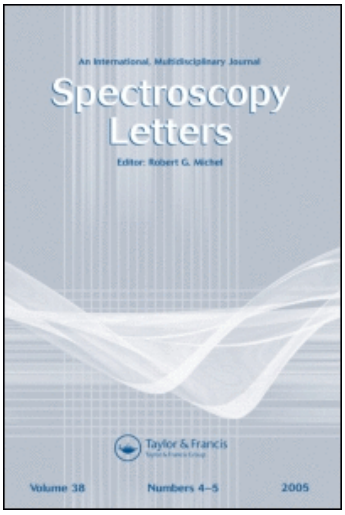
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Alternative Solid Sample Pretreatment Methods in Green Analytical Atomic Spectrometry

Antonio Moreda-Piñeiro[a]; María del Carmen Barciela-Alonso[a]; Raquel Domínguez-González[a]; Elena Peña-Vázquez[a]; Paloma Herbello-Hermelo[a]; Pilar Bermejo-Barrera[a]
[a] Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, Santiago de Compostela, Spain

Online publication date: 01 December 2009

To cite this Article Moreda-Piñeiro, Antonio , Barciela-Alonso, María del Carmen , Domínguez-González, Raquel , Peña-Vázquez, Elena , Herbello-Hermelo, Paloma and Bermejo-Barrera, Pilar(2009) 'Alternative Solid Sample Pretreatment Methods in Green Analytical Atomic Spectrometry', Spectroscopy Letters, 42: 6, 394 — 417
To link to this Article: DOI: 10.1080/00387010903187393
URL: http://dx.doi.org/10.1080/00387010903187393

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Spectroscopy Letters, 42:394–417, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903187393

Taylor & Francis
Taylor & Francis Group

Alternative Solid Sample Pretreatment Methods in Green Analytical Atomic Spectrometry

Antonio Moreda-Piñeiro, María del Carmen Barciela-Alonso, Raquel Domínguez-González, Elena Peña-Vázquez, Paloma Herbello-Hermelo, and Pilar Bermejo-Barrera

Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, Santiago de Compostela, Spain

Downloaded At: 02:47 30 January 2011

ABSTRACT A review of recent literature utilizing alternative sample pretreatment methods for solid environmental and biological materials analysis to assess total metals content by atomic spectrometry is provided. All the selected treatments coincide with all or some of the fundamentals of Green Chemistry policy such as prevention of waste generation; safer and less toxic solvents and reagents; and designs for energy efficiency. The review covers the classic slurry sampling technique, mainly, its current trends, as well as developments based on the use of diluted acids, chelating agents solutions, or even water for leaching (extraction) methods assisted by ultrasounds, microwave energy, or pressurization. In addition, the use of conventional or assisted enzymatic hydrolysis procedures is also discussed.

KEYWORDS atomic spectrometry, green chemistry, sample pretreatment, trace elements

INTRODUCTION

Although the introduction of the concept of Green Chemistry[1] and the establishment of the Twelve Principles of Green Chemistry[2] were mainly focused on industrial process and synthetic chemistry, most of these fundamentals were rapidly applied to analytical procedures leading to the concept of Green Analytical Chemistry (GAC).[3] From these twelve principles, four top priorities concerning the elimination or reduction of organic solvents and/or highly toxic or ecotoxic reagents, the prevention of waste generation, and the reduction of energy consumption, were first identified in the analytical laboratory by Namieśnik.[4]

Nowadays, aspects involving none or simple sample preparation, or little or no sample destruction, have also been introduced as principles of GAC[5] and the sample pretreatment stage has received special attention to make it greener.[5–7]

Concerning spectrometric determinations, acid digestion procedures, mainly microwave assisted methods, are the most used methodologies as sample pretreatment to assess major and trace elements. A variety of procedures, as well as concentrated acids, commonly nitric acid (HNO_3) and

An invited paper submitted to a special issue on Green Spectroscopy and Analytical Techniques, organized by Professor Miguel de la Guardia, of the Department of Chemistry, University of Valencia, Spain, and Professor Arabinda Kumar Das, of the Department of Chemistry, University of Burdwan, West Bengal, India.

Received 14 December 2008; accepted 9 March 2009.

Address correspondence to Antonio Moreda-Piñeiro, Department of Analytical Chemistry, Nutrition and Bromatology, Faculty of Chemistry, University of Santiago de Compostela, Avenida das Ciencias, Santiago de Compostela, s/n. E-15782, Spain. E-mail: amoreda@usc.es

hydrochloric acid (HCl), have been described and applied to digest biological, environmental, and geological materials. All these procedures require the use of highly toxic reagents as concentrated hydrogen peroxide (H_2O_2) and/or concentrated acids (HNO_3, HCl) when treating biological samples, and even forbidden reagents as hydrofluoric acid (HF) when preparing geological material and samples with a high silicate content, with the subsequent generation of toxic wastes. Another drawback that these treatments offers is the nitrous vapor generated as a consequence of organic matrix destruction, vapors that require safety considerations.

Sample pretreatment for elemental analysis can be minimized or even omitted when using spectrometric methods based on laser ablation or glow discharge coupled to plasma techniques. However, these analytical methods can only be applied to limited kinds of samples[5] and therefore, the sample pretreatment for spectrometric analysis is still an active research field and the development of green methodologies for these treatments is a current trend in analytical chemistry.

In this article we have revised the most useful and greenest sample pretreatments for atomic spectrometric determinations in solid samples. All these methods are considered as alternative methodologies to conventional wet digestions procedures. The revised sample pretreatments comprise the well-established slurry sampling technique, first applied in the 1970s,[8] and modern pretreatments based on certain physical/chemical mechanisms to make more efficient the interaction between the solid phase (the sample) and the liquid phase (the extracting). Because of a more efficient contact between sample and extracting, diluted acids and/or non-toxic reagents can be used. The main mechanisms involve the use of ultrasounds (ultrasound assisted extraction, UAE) or microwave irradiation (microwave assisted extraction, MAE) and pressurization (pressurized liquid extraction, PLE). In addition, enzymatic hydrolysis procedures have been also considered as environmentally friendly methods because of the mild operating conditions required and the avoidance of concentrated acids for trace elements extraction. At this point it is worth mentioning that the action of enzymes, mainly proteolytic enzymes, on biological matrices can be efficiently speeded up by ultrasounds,[9] pressurization,[10] and even microwave irradiation.[11]

SLURRY SAMPLING TECHNIQUES IN ATOMIC SPECTROSCOPY

The slurry sampling technique is a well-established methodology for direct determination of trace metals in solid samples by Atomic Spectrometry. The use of this approach provides good analytical results with some advantages over conventional procedures including: (1) reduced sample preparation time; (2) decreased possibility of loss of analyte through volatilization prior to analysis; (3) reduced possibility of sample contamination, (4) it prevents the use of dangerous and corrosive reagents and (5) applicability to both organic and inorganic samples; and (6) the same atomizers that are used for liquid sampling can be used for the atomization. Moreover, the slurry technique overcomes some of the problems associated with direct solid sampling as it allows sample introduction using conventional autosamplers.

Slurry Sampling Techniques in ETAAS and FAAS

Most of the applications of slurry sampling technique make use of Electrothermal Atomic Absorption Spectrometry (ETAAS). In this way, Bendicho and de Loos-Vollebregt[12] published in 1991 a review reporting the different aspects of solid sampling in ETAAS (direct solid sampling and slurry sampling). Later, Kürfust[13] summarized the literature about solid and slurry sampling up to the mid 1990 s and Cal-Prieto et al.[14] published a review of the literature about slurry sampling for ETAAS from 1990 to 2000. Recently, Vale et al.[15] published a review about the current status of direct solid sampling for ETAAS including the developments between 1995 and 2005.

The most critical factor in slurry sampling technique is the need for maintaining stable the slurry during the time required for sample introduction. This is especially important when using ETAAS, being the particle size distribution is a most critical parameter for any technique that involves sample introduction by nebulization such as FAAS or ICP–OES/MS. Different techniques have been proposed for homogenization of slurry, including manual shaking, mechanical agitation (magnetic stirring and vortex mixing), gas bubbling, ultrasonic homogenization (ultrasonic baths or ultrasonic probes either hand-held or assembled to the

Downloaded At: 02:47 30 January 2011

autosampler tray).[16] The advantages and disadvantages of these systems have been evaluated by different authors and were reported in the cited reviews.

Other drawbacks of slurry methods are associated with the particle size, grinding time, and sedimentation error.[17,18] In these cases, these problems are avoided with the addition of special agents (thixotropic or surfactant agents) to the liquid medium. In low-density materials the main problem is the flotation of light and finely ground material on the surface of the slurry. Therefore, wetting and dispersing agents must be used and ethanol, Triton X-100, and glycerol are the most commonly reported.[14,15]

Another important factor is the liquid media used to obtain the slurry. The liquid acts as a suspension media but also as an extracting medium, improving the accuracy and the precision. In many cases, the use of H_2O was good enough to obtain satisfactory results, being a good contribution to the Green Chemistry.[14,19,20] Various authors have used concentrated acids, including HNO_3, HF, or a combination of HNO_3 and H_2O_2[21] or H_2O_2.[14,15] The use of these acids results in similar corrosive waste problems as with conventional sample digestion.

The minimum number of particles that should be introduced into the graphite tube in order to ensure the representativity of the aliquot of sample analyzed is another factor that has to be taken into account. Some authors have concluded that a minimum of 50 particles have to be introduced.[22] In this sense, Miller-Ihli[23] developed an equation to calculate the representative sample mass. In this equation the author takes in to consideration the percentage of analyte extracted to the liquid media during the slurry preparation.

Slurry methods using FAAS are more limited because of the restriction of the particle size. Usually the developed methods require an acid medium to prepare the slurry. In this way, Alves et al.[24] developed a method for Cu, Zn, and Pb in river sediments using acidified slurries (6.0 mol L-1 HNO_3 and 2% (m/v) NH_4Cl) sonicated for 15 min in an ultrasonic bath. Mn and Zn in chocolate samples were determined by da Silva et al.[25] using multi-element flame atomic absorption spectrometry. Also, in this case, the slurry was prepared in an acid medium (2.0 mol L-1 HNO_3) under sonication (15 min). The same acid medium but with a sonication time of 20 min was used by Ferreira et al.[26] for Zn and Cu determination in human hair. The authors compared the results obtained using this acid slurry and after complete digestion in a closed system showed no significant differences. Recently, a comparison of slurry sampling and microwave-assisted digestion for Ca, Mg, Fe, Cu, and Zn determination in fish was reported by Alonso et al.[27] The treatment of slurried samples in nitric acid by microwave irradiation permitted achievement of efficient recoveries for Ca, Fe, Mg, and Zn; however, it was necessary to use hydrochloric acid as a suspension medium for Cu determination.

Slurry Sampling Techniques in ICP

The application of slurries as sample introduction in inductively coupled plasma OES and MS have been reported by several authors for the determination of different elements mainly in inorganic materials such as cement clay and ceramic and geological materials. Different works dealing with this topic are compiled in a first review published by Ebdon et al.[28] in 1997 about slurry nebulization in ICP. Recently, Santos and Nóbrega[29] published in 2006 a new review about the slurry nebulization in plasmas for analysis of inorganic materials. Although most of the applications were devoted to inorganic samples,[29] some authors have used the slurry technique combined to plasmas for elemental analysis in biological and organic samples. Therefore, Cernohorsky et al.[30] have analyzed flour-based ready-oven foods; Krejcova et al.[31] have determined macro and trace elements in multivitamins preparations; Baralkiewicz et al.[32] have developed a simple and rapid method for Pb, Mg, and Ca in plant roots; and Zachariadis and Valianou[33] have studied different nebulizers systems for multi-element analysis of infant milk powders.

A critical factor in direct analysis of slurries by ICP–OES is the stability and homogeneity of the slurry. High stable and homogeneous slurry is necessary in order to achieve a homogeneous and reliable aerosol for introduction into the plasma and to obtain precise and accurate results.[29] Therefore, different suspending or dispersing agents such as Triton X-100, poly(acrylate amine), NH_3, HNO_3, HCl have been used for several samples.[29,30,32] Usually, the slurry is stirred before the introduction in the plasma using the same systems reported earlier.[29] However,

Downloaded At: 02:47 30 January 2011

the use of surfactant agent does not avoid problems related to particle size distribution, a parameter that affects the efficiency on transport and atomization-excitation. In general, a mean particle size of 5–10 μm is essential to ensure that the slurry has similar transport properties than an aqueous solution[29] and therefore, an efficient grinding process is needed. For samples such as porcelain material,[34] the effect of the particle size was found as negligible for sizes less than 57 μm.

Chemical Vapor Generation from Slurry Sampling

The method of cold vapor (CV)/hydride generation (HG) is a well-established sample introduction technique in atomic spectroscopy. The technique is applicable to the determination of trace levels of As, Hg, Sb, Se, Sn (and other hydride forming elements) in different matrixes. However, the application of these techniques to solid samples requires the complete digestion (usually acid digestions with HNO_3, HCl) of the sample prior to the analysis. To overcome this limitation, different authors have proposed the use of slurries as an alternative technique of sample preparation before the vapor generation and recently, Matusiewicz[35] reviewed the use of this approach. The main problem associated with this technique is the low vapor generation efficiency from the metals trapped in the solid particles. To avoid this problem, several authors have prepared the slurry sample in acid medium such as HCl,[35] HCl + HF, HNO_3,[36,37] aqua regia,[38] aqua regia + HCl,[39,40] aqua regia + HF[41] in combination with a mechanical agitation or sonication process. The use of these acids improved the vapor generation efficiency due to the analyte's mobilization from the solid particle to the liquid phase. The disadvantages of these procedures are the time required to complete the acid slurry preparation (10 min–hours) and in some cases, the high acid concentrations used, which are not environmentally friendly. For certain matrixes such as coal fly ash and urban dust, it was possible the determination of these elements using aqueous slurry sampling. In this way, Moreda-Piñeiro et al.[42] have developed a method for As, Sb, and Se determination in aqueous slurries of coal fly ash samples by hydride generation-atomic fluorescence spectrometry. The same authors compared the results obtained for As, Sb, and Sn in urban dust samples, using aqueous and acidified slurry sampling.[43] These authors concluded that the chemical composition and the mean particle size of the samples determine the accuracy of the results. The use of aqueous slurries is enough to obtain accurate results from samples with low particle size and high carbon content when As and Sn were determined. However, the use of acidified slurries (in this case, diluted nitric acid) is necessary to achieve accurate results for samples with high mean particle size and low gypsum and low carbon content.

On the other hand, vapor generation from slurries samples has been used for speciation studies. In this way, several works have been published for Sb, As, and Se speciation in different samples such as sediments, liver tissue, or garlic. Some of these works have been included in the review by Matusiewicz.[35]

LEACHING (EXTRACTION) METHODS

Leaching methods, also referred as lixiviation methods, are based on the use of diluted reagents, mainly acids (acid leaching or acid lixiviation), to extract or leach the target trace elements from solid samples. In general, leaching procedures do not involve the total matrix sample destruction but the breakdown of certain chemical bonds between the trace elements and the matrix sample constituents.[44] However, it has been established that a partial dissolution of the solid sample is unavoidable, especially when biological matrices are being treated with diluted oxidizing acids such as nitric acid and the sample dissolution ratio is expected to be increased when assisting the process with ultrasounds, microwaves, or pressurization. Therefore, the mechanisms through which the targets reach the solution can be considered as partial sample decomposition.[45] Because leaching does not lead to a total solubilization of sample, leachable recoveries of some elements can be lower than total concentrations and recoveries can only achieve total values if the elements are completely soluble in the leaching solvent.[45] This is important for some elements such as aluminum, which is normally associated to the silicate fraction in the sample and it is not easily leached, leading to non-quantitative extractions.

The procedure that can be considered as the first application of an acid leaching process can be

Downloaded At: 02:47 30 January 2011

attributed to Westöö[46] who used concentrated hydrochloric acid to break down the chemical bonds between methyl-mercury and the protein thiol groups in biological matrices prior to the solvent extraction of this mercury specie in an organic solvent. Based on this early work, there have been many applications of different assisted or not assisted acid leaching procedures to isolate methyl-mercury from different biological and environmental matrices, as well as other leaching methods using non-acidic solutions for organometallic speciation studies.[47] In addition, the sequential selective extraction techniques commonly used to fractionate the solid-phase forms of metals, mainly in contaminated soils and sediments (BCR and Tessier methods) can be also considered as leaching procedures.[48]

This section will only be devoted to those leaching methods developed to assess the total metal content in a solid sample. In this sense, the first reference on using an acid leaching method for total metal extraction can be attributed to Puchyr and Shapiro.[49] These authors used concentrated acids (a 9/1 HCl/HNO_3 mixture, as a leaching solution) and heating to extract quantitatively Al, Cd, Cr, Cu, Fe, K, Mg, Ni, Sn, and Zn from foods. A similar application has been proposed by Torstensen et al.[50] to leach trace elements from thermomechanical pulps from paper industries with a chelating agent as diethylenetriaminepentaacetic acid disodium salt (DTPA) and sulfurous acid at a pH 2.5; and by Vidal et al.[51] for releasing trace elements from diet feed samples.

Downloaded At: 02:47 30 January 2011

Ultrasound-Assisted Leaching

The application of ultrasound energy by means of ultrasonic water baths or ultrasonic probes for assisting or accelerating both organic and inorganic compounds extraction from solid materials is nowadays a current practice.[52,53] This is especially significant for some spectrometric techniques such as electrothermal atomic absorption spectrometry (ETAAS), which are available with ultrasonic probes coupled to the autosampler device.[54] As commonly reported,[52,53] the induced cavitations process occurring in a medium containing suspended particles promotes asymmetric collapses of bubbles leading high-speed microjets toward the solid phase. Under these conditions analyte transport from the solid particles to the liquid phase is more efficient and quantitative extractions in short times can be expected. In addition, due to a best interaction between the solid sample and the extracting solution, chemical bonds between the analytes and the matrix components can be broken by the action of diluted acids. As recently reviewed by Santos Júnior et al.,[53] two ultrasound generator devices are available: ultrasounds water-baths (ultrasonic baths, ultrasonic cleaning devices) and ultrasonic probes. The next sections will be devoted to reported applications by using both ultrasounds assisting systems (see Table 1).

Ultrasound Water Bath–Assisted Leaching

The first device consists of a tank, with or without temperature control, in which the ultrasound transducer (normally placed at the bottom of the tank) transfers the ultrasound energy to the liquid, normally ultrapure water, contained in the tank. By this way, the ultrasound energy is partially dissipated in both the reaction vessels placed in the bath and also through the water contained into the tank. In addition, considerations on the position in which the sample vessel is situated inside the bath (vertical and horizontal position) must be taken into account. Therefore, the intensity of the ultrasound energy is not constant in all points of the bath, neither inside all reaction vessels.[55] This fact, together with the different ultrasound frequencies and powers depending on the specific transducers used in the different commercial ultrasonic baths, makes the attempts to compare experimental conditions difficult. These drawbacks are avoided when using ultrasonic probes, in which the ultrasound transducer is coupled to metal probes (tips), or to pure titanium or even glass probes[54,56,57] to minimize metal contamination. These probes are then directly immersed into the reaction vessels and the ultrasound energy is completely absorbed by the reaction medium, increasing the sonication efficiency.

Some papers using ultrasound water baths were published early but most of these developments used concentrated acids in order to acid digest the sample.[58–61] The first reference using ultrasounds (water-bath device) and a diluted acid as an extracting solution can be attributed to Kumina et al.[62] who extract Ca, Cu, Fe, K, Mg, Mn, Na, and Zn from plant samples with 1.5 M HCl. Other applications involving

TABLE 1 **Applications of Ultrasound Assisted Leaching Methods (Ultrasonic Bath and Probe)**

Analyte	Sample	Processor	Leaching solution (atomic spectrometric technique)	Temperature	Leaching time	Ref.
Ca, Cu, Fe, K, Mg, Mn, Na, Zn	Plants	Bath	1.5 M HCl	Room temperature	4.0 min[a]	62
Cd. Cu, Fe, Pb, Zn	Plants	Bath	1.0 M HCl	Room temperature	15.0 min	63
Total Cr (Cr(III) and Cr(VI))	Welding fumes	Bath	2.0%(w/v) NaOH +3.0%(w/v) Na_2CO_3 (pH 12.7)	70°C	30.0 min	64
Se	Bovine liver and seafood	Bath	4.0%(v/v) HNO_3(ETAAS)	Room temperature	18.0 min	65
Cd	Sludge, ash, krill, and human hair	Bath	6.0 M HCl (CVAAS)	Room temperature	20.0 min	66
Ca, Mg, Mn, Zn Fe	Vegetables	Bath	0.14 M HNO_3 (FAAS) 1.4 M HNO_3 (FAAS)	Room temperature	10.0 min	67
Ge	Soils	Probe	Concentrated HF (ETAAS)	Room temperature	10.0 min	68
Cd, Pb	Foods	Bath	2.8 M HNO_3 (FAAS)		5.0–10.0 min	
Ca, Cd, Cu, K, Mg, Mn, Na, V, Zn	Mussels	Bath	1.6 M HNO_3 +1.2 M HCl +1.5 M H_2O_2 (FAAS/ETAAS)	Room temperature	120.0 min	69
Cd, Cu, Mn, Pb	Biological materials	Bath	0.5 M HNO_3 (ETAAS)	Room temperature	5.0 min	70
As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Pb, Se, Zn	Mussels, clams, tuna	Bath	(0.5–4.5)M HNO_3 + (2.0–4.0)M HCl +1.5 M H_2O_2 (FAAS/ETAAS/CVAAS)	Room temperature except for Se (90°C)	10.0 min except for Se (35.0 min)	71
As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Pb, Se, Zn	Certified reference materials (seafood)	Bath	(0.5–4.5)M HNO_3 + (2.0–4.0)M HCl +1.5 M H_2O_2 (FAAS/ETAAS/CVAAS)	Room temperature except for Se (90°C)	10.0 min except for Se (35 min)	44
Ca, Cu, Fe, Mg, Mn, Zn	Human hair	Bath	4.0 M HNO_3 +3.5 M HCl (FAAS/ETAAS)	80–90°C	10.0 min	72
Cd, Cr, Pb, Se	Human hair	Bath	4.8 M HNO_3 +4.8 M HCl +0.5 M H_2O_2 (ETAAS)	90°C	10.0 min	73
Hg (Me-Hg)			0.5 M HNO_3 +4.8 M HCl +0.5 M H_2O_2 (CVAAS)	Room temperature		
Ca, Cu, K, Mg, Mn, Na, Zn	Edible seaweed	Bath	3.7 M HNO_3 +3.0 M HCl +3.0 M H_2O_2 (FAAS/FAES)	65°C	35.0 min	75
Fe			Step 1: 6.0 M HCl Step 2: 3.7 M HNO_3 +3.0 M HCl +3.0 M H_2O_2 (FAAS)	Room temperature 65°C	10.0 min 35.0 min	
As, Ca, Cd, Cu, Fe, K, Mn, Mg, Na, Ni, Zn	Edible seaweed	Bath	Step 1: 6.0 M HCl Step 2: 3.7 M HNO_3 +3.0 M HCl +3.0 M H_2O_2 (ICP-OES)	Room temperature 65°C	10.0 min 35.0 min	76

(*Continued*)

Downloaded At: 02:47 30 January 2011

TABLE 1 Continued

Analyte	Sample	Processor	Leaching solution (atomic spectrometric technique)	Temperature	Leaching time	Ref.
Ba, Ca, Cd, Cu, Mg, Mn, Ni, Pb, Sr, Zn	Plants	Bath	Diluted HNO_3 and HCl (ICP-OES)[b]	Room temperature	40.0 min	79
Ca, Cu, Fe, K, Mn, Zn	Vegetables	Bath	5%(v/v) HNO_3 (FAAS)	70°C	30.0 min	80
Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, P, Pb, Sr, Ti, Zn	Plants	Bath	1.0 M HCl +surfactants (ICP-OES)	Room temperature	40.0 min	81
Cr, Cu, Pb, Zn	Sludge	Bath	1.0 M HNO_3 +2.0 M HCl (FAAS)	Room temperature	10.0 min	82
As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Pb, Se, Zn	Certified reference materials (seafood)	Bath	(0.5–4.5)M HNO_3 + (2.0–4.0)M HCl +1.5 M H_2O_2 (FAAS/ETAAS/CVAAS)	Room temperature except for Se (90°C)	10.0 min except for Se (35.0 min)	83
Cd, Cu, Zn	Fish and mussel	Bath	4.0 M HNO_3 +4.0 M HCl +0.5 M H_2O_2 (FAAS/ETAAS)	56°C	30.0 min	84
As	Seafood (TORT-2)	Bath	80% MeOH	Room temperature	60.0 min	85
Cd			2.0%(v/v) HNO_3 (ICP-MS)			
Al, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ti, Zn	Quartz	Bath	Stage 1: Treatment at 700°C			92
			Stage 2: 10%(v/v) HF (ICP-OES)	Room temperature	65.0 min	
Cd	Aquatic plant, mussel	Probe	3.0%(v/v) HNO_3 (ETAAS)	Room temperature	1.0 min	93
Cd	Mussel	Probe	3.0%(v/v) HNO_3 (ETAAS)	Room temperature	15 s	94
Pb					3.0 min	
Cd, Pb	Biological materials	Probe	1.0 M HNO_3 (ETAAS)	Room temperature	1.0–5.0 min	95
Cd, Cu, Pb	Biological materials sediments	Probe	0.5–5.0%(v/v) HNO_3 (ETAAS)	Room temperature	2.0–5.0 min	96
Pb	Biological materials	Probe	3.0%(v/v) HNO_3 (ETAAS)	Room temperature	3.0 min	97
Cu	Biological materials	Probe	3.0%(v/v) HNO_3 (ETAAS)	Room temperature	3.0 min	98
As	Seafood	Bath	3.0%(v/v) HNO_3 (ETAAS)	Room temperature	3.0 min	99
		Probe			30.0 min	
As, Ni, Se, V	Fish and shellfish	Probe	0.5–3.0%(v/v) HNO_3 (ETAAS)	Room temperature	3.0 min	100
Ni, V	Mussel	Probe	3.0%(v/v) HNO_3 (ETAAS)	Room temperature	3.0 min	101
Se	Seafood	Probe	0.5%(v/v) HNO_3 (ETAAS)	Room temperature	3.0 min	102

(*Continued*)

Downloaded At: 02:47 30 January 2011

TABLE 1 Continued

Analyte	Sample	Processor	Leaching solution (atomic spectrometric technique)	Temperature	Leaching time	Ref.
Se	Breast cancer biopsies	Probe	0.5%(v/v) HNO_3 +4.4%(v/v) H_2O_2 (ETAAS)	Room temperature	3.0 min	103
Hg	Fish	Probe	2.0 M HCl (CVAAS)	Room temperature	3.0 min	104
Cu, Mn, Pb, Zn	Aquatic plants	Probe	Stage 1: 1.0%(w/w) HCl +15%(w/w) HNO_3	Room temperature	3.0 min	105
			Stage 2: 1.0%(w/w) HCl +15%(w/w) HNO_3(FAAS)		3.0 min	
Mg, Mn, Zn	Vegetables	Probe	0.3%(v/v) HNO_3 (FAAS)	Room temperature	3.0 min	106
Ca, Cd, Cr, Cu, Fe, Mg, Pb, Zn	Animal tissues	Probe[c]	15.0%(v/v) HNO_3 (FAAS/ETAAS)	Room temperature	10.0 min	107
Ca, Cd, Mg, Mn, Pb, Zn	Plants, aquatic moss	Probe	0.1 M EDTA pH 10 (FAAS/ETAAS)	Room temperature	3.0 min	108
Hg	Fish	Probe	5.0%(v/v) HNO_3 +0.02%(w/v) thiourea	Room temperature	3.0 min	109
	Plants		10.0%(v/v) HNO_3 +0.02%(w/v) thiourea		3.0 min	
	Coal fly ash		20.0%(v/v) HNO_3 +0.2%(w/v) thiourea (CVAAS)		4.0 min	

[a]3 cycles for extracting Fe.
[b]Concentrations not available.
[c]Sample into the extraction chamber is immersed into a water bath at room temperature and the ultrasound probe is placed 1 mm from the top surface of the extraction cell.

Downloaded At: 02:47 30 January 2011

the use of diluted acids and leaching at room temperature[63–69] for extracting different trace elements from biological materials are summarized in Table 2. From these data, quantitative recoveries were achieved for most of the elements, except for Se in bovine liver and mollusk soft tissue[65,69] and for Cd in human hair.[66]

To improve metal recovery, some authors have proposed the combined effect of ultrasound energy and moderate high temperature.[70] After a systematic study of the effect of temperature and the acid leaching composition, it could be concluded that metal releasing from the solid particles was dependent on the trace element and the nature of sample. Therefore, several trace elements (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, Mg, Mn, Pb, and Zn) could be leached from seafood products (mussel, clam, and tuna soft tissues) by sonicating at room temperature, while a temperature of 90°C was needed to quantitatively extract Se.[44,71] These results agree with those obtained by Mierzwa et al.[65] and El Azouzi et al.[69] However, similar approaches applied to human hair samples required high temperature (80–90°C) for extracting Ca, Cu, Fe, Mg, Mn, and Zn[72] and Cd, Cr. Hg, Pb, and Se.[73]

The effectiveness of the extraction was also found dependent on the composition of the acid leaching solution, and 2.5 M/0.5 M HCl/HNO_3 mixture was adequate to extract Co and Hg from seafood products, while higher acid concentrations (up to 3.8 M) were required for extracting other elements.[71] In addition, quantitative Fe recoveries from seafood products were only achieved in the presence of H_2O_2 at 1.5 M in acid leaching solution.[71] A similar result has been obtained by Melo et al.[74] when extracting Fe from fish muscle tissue by sonication with a water soluble tertiary amines (50%(v/v)) and H_2O_2 at 30%(m/m). In general, the acid leaching composition required higher HCl/HNO_3 concentrations for human hair than those needed for mollusk and fish soft tissues.[72,73]

When treating seaweed samples, some major elements such as Ca, Cu, K, Mg, Mn, Na, and Zn

TABLE 2 Applications of Continuous on-line Ultrasound Assisted Leaching Methods (Ultrasonic Bath and Probe)

Analyte	Sample	Processor	Leaching solution (atomic spectrometric technique)	Temperature	Leaching time	Ref.
Cu	Mussels	Bath	3.0 M HNO_3 +3.0 M HCl (FAAS)	Room temperature	5.0 min	114
Ca, Cu, Fe, Mg, Zn	Animal feeds	Probe	10.0%(w/w) HNO_3 (FAAS)	40°C	18.0 min	115
Ca	Mussels and clams	Bath	3.0 M HNO_3 (FAAS)	Room temperature	0.5 min	116
Cr	Mussels	Bath	3.0 M HNO_3 +3.0 M HCl (FAAS)	Room temperature	5.0 min	117
Cu	Mussels and clams	Bath	3.0 M HNO_3 (FAAS)	Room temperature	1.0 min	118
Fe					3.0 min	
Fe	Mussels	Bath	3.0 M HNO_3 +3.0 M HCl (FAAS)	Room temperature	5.0 min	119
Mn	Mussels and clams	Bath	1.5 M HNO_3 (FAAS)	Room temperature	0.5 min	120
Fe	Meat	Bath	3.0 M HNO_3 +3.0 M HCl (FAAS)	Room temperature	5.0 min	121
Zn	Meat	Bath	0.75 M HNO_3 or 0.75 M HCl (FAAS)	Room temperature	0.5 min	122
Cd	Human hair	Bath	3.0 M HNO_3 (FAAS)	80°C	4.0 min	123
Pb					2.0 min	
Cu, Fe, Mn	Human hair	Bath	3.0 M HNO_3 (FAAS)	80°C	3.0 min	124
Zn				70°C	2.0 min	
Cd	Mussels	Bath	3.0 M HNO_3 (FAAS)	Room temperature	2.0 min	125
Pb					3.0 min	
Cd	Vegetables, fruits	Bath	3.0 M HNO_3 (FAAS)	Room temperature	2.0 min	126
Cd	Meat	Bath	3.0 M HNO_3 (FAAS)	Room temperature	2.0 min	127
Cd	Legumes	Bath	2.0 M HNO_3 (FAAS)	Room temperature	2.5 min	128
	dried fruits		3.0 M HNO_3 (FAAS)		1.0 min	
Cd	Cheese, yogurt	Bath	3.0 M HNO_3 (FAAS)	Room temperature	0.5 min	129
Ni	Food	Bath	1.5–3.0 M HNO_3 (FAAS)	Room temperature	0.5–3.0 min	130
Co	Seafood	Bath	3.0 M HNO_3 (FAAS)	Room temperature	2.0 min	131
Cr					2.5 min	
Zn	Welding fumes	Bath	3.0 M HNO_3 (FAAS)	Room temperature	4.0 min	132
Cd	Welding fumes	Bath	3.0 M HNO_3 (FAAS)	50°C	1.0 min	133
Ni				80°C	4.0 min	
Pb				70°C	2.0 min	
Cr(VI)	Welding fumes	Bath	10.0%(w/v) Na_2CO_3 +2.0%(w/v) $NaHCO_3$ (FAAS)	40°C	5.0 min	134

Downloaded At: 02:47 30 January 2011

could be easily leached at 65°C and 17 kHz with an acid leaching solution containing HCl and HNO_3, and also H_2O_2.[75] However, it has been reported that a previous sonication stage with 6.0 M HCl at room temperature for Fe[75] or at 65°C for Cd, Cr, Ni, and Pb[76] was needed for destroying cellular walls and allowing the completeness of the extraction. These results agree with similar studies when extracting different arsenic species from seaweed samples.[77,78] Similarly, the combined effect of diluted nitric and hydrochloric acids with ultrasounds and high temperature was also tested to assess trace elements in plant materials, showing quantitative recoveries for some target elements (Ba, Ca, Cd, Cu, Mg, Mn, Ni, Pb, Sr, and Zn) although lack of accuracy for Al, Cr, Fe, Ti, and V.[79] Finally, other recent applications for biological materials, also summarized in Table 2, comprise the application of ultrasounds to treat plants and vegetables[80,81] or sludge samples,[82] and ultrasounds and temperature for trace elements leaching from seafood products.[83–85] Therefore, the nature of the sample and/or the bonds between the analytes and the matrix constituents' influences the acid leaching composition and the need of the use of high temperature during sonication.

Although ultrasound-assisted acid leaching methods have shown great potential for extracting trace elements from biological materials, applications for geological and environmental (mainly sediments and soils) samples are scarce to assess total element contents. Most of the applications dealing with marine sediments, soils, and particulate matter both using ultrasound water baths[86–90] or probes[91] have required concentrated acids in order to digest or

partially digest the sample. Therefore, although using ultrasounds, these methodologies can not be considered as green. However, there is one application involving the use of diluted acids and ultrasound water bath and probe to leach trace impurities from quartz samples.[92] The authors conclude that diluted HF leads to quantitative recoveries for some elements (Cu, Mn, K, and Na) for both ultrasound water bath and probe, but the number of metal quantitatively recovered can be increased when performing a previous thermal treatment of quartz samples at 700°C before the sonication stage.

Ultrasound Probe–Assisted Leaching

As commented before, high ultrasound intensities and a better repeatability among different ultrasound acid leaching procedures can be achieved when using ultrasound probes.[53–57] These applications normally require smaller amounts of sample and smaller volumes of leaching solution than those used for ultrasound water baths, typically 10–30 mg and 1 mL, respectively. Table 2 lists the published methods, mainly to assess total metal contents in biological samples by ETAAS. In these cases, the sample is placed directly in the autosampler cups (commonly 1.5–2.0 mL of capacity) and after adding the diluted acid solution the resulting slurry is sonicated for a certain time, placed in the autosampler tray, and allowed to stand without further stirring. Finally, the acidic supernatant, normally 20 μL, is injected into the graphite tube. Quantitative metal extractions can be achieved after short sonication times, less than 5 min, due to a high ultrasound intensity provided by ultrasonic probes. This implies an important advantage over ultrasonic baths. This methodology has been reported to assess trace elements such as Cd,[93–96] Pb,[62–64,97] Cu,[64,98] As,[99,100] V and Ni[67,101] and Se[66,102,103] from seafood products (Table 2). Higher sample masses and acid leaching volumes were used to extract Hg from fish tissues for flow injection cold vapor–atomic absorption spectrometry detection[104] or to leach Pb, Mn, and Zn from aquatic plants,[105] or Mg, Mn, and Zn from plants[106] before flame atomic absorption spectrometry (FAAS). Animal tissues (raw pig ham and bovine liver) were also treated by ultrasonic probe to leach several elements for FAAS and ETAAS determinations.[107] Finally, a similar procedure has also been reported for the determination of Cd, Ca, Mg, Mn, Pb, and Zn in plant and aquatic moss after ultrasound assisted leaching with EDTA at alkaline pH as an extracting solution[108] or for the extraction of total mercury from fish, plants, and coal fly ash with thiourea-nitric acid as an extracting solution.[109] It must be noted that lack of accuracy (low analyte recoveries) has been reported for Cu when using ultrasound probes and diluted nitric acid.[96,98,105]

Continuous On-Line Ultrasound–Assisted Leaching

Since the development and implementation of flow injection analysis systems (FIAS) in the analytical laboratories, the samples and/or solutions introduction could be automated in most of the analytical instruments. This fact allowed the sample pretreatment just before analyte determination, shortening the pretreatment times and mainly decreasing analyte losses and sample contamination. On-line ultrasound–assisted extraction methods by means of a FIAS were developed early to assess trace metals from solid samples by coupling the system to a UV-Vis spectrometer.[110,111] From these first works, some approaches have been developed for interfacing either ultrasounds-assisted leaching or microwave- assisted leaching procedures[112] to atomic spectrometry instruments. The approaches imply mainly the use of a single leaching solution to extract a certain number of analytes, but applications using different extracting solutions that are sequentially passed through the solid sample enclosed in a chamber (column or cell) have also been described.[113]

Both ultrasound water bath and ultrasound probe devices have been used for continuous ultrasound-assisted leaching procedures. In the first case, the solid sample enclosed in the extraction chamber is immersed in the ultrasonic water bath and after loading the leaching solution in the circuit the system is sonicated for a certain time.[114] When using an ultrasonic probe, similar operations regarding extraction chamber filling and leaching solution loading are applied but the extraction chamber is immersed in a water bath and the ultrasound irradiation is applied with the probe placed 1 mm from the top surface of the extraction cell.[115]

Extraction chambers containing the solid sample consist of glass minicolumns (50 mm × 3 mm i.d.) or of stainless-steel cylinders (10 cm × 10 mm i.d.),

Downloaded At: 02:47 30 January 2011

closed with screws at either end. The screw caps are plugged with filter paper or cellulose filters to ensure that the sample remained in the extraction unit.[114,115]

There are described in the literature two main approaches for the continuous on-line ultrasound–assisted acid leaching of trace elements from solid samples. In the first one, after immersing the extraction cell containing the sample into the ultrasonic bath, the system is loaded with a certain volume of the leaching solution (for instance 1.3 mL of 3.0 M/3.0 M HNO_3/HCl in Ref. 114), the circuit is then closed and this volume of leaching solution is pumped, at a fixed flow rate, through the extraction cell for a certain time under sonication conditions. After this extraction time, the leachate passes to a mixing coil and a small volume (around 250 μL) is injected by means of an injection valve into a carrier (ultrapure water) stream through the detection system.[114]

When using the second operation mode, after the extraction chamber containing the sample is immersed in the water bath, the leaching solution (for instant 10%(w/w) HNO_3 in Ref. 115) is continuously circulated through the solid sample for a certain time under ultrasound irradiation. Finally, after extraction was completed, the extract is collected and conveniently diluted before analyte determination. For either operation modes, the direction of the flow of the leaching solution during the extraction is changed after a fixed period of time (commonly between 30 and 80 s) to avoid compactness of the sample at the extraction chamber ends that could cause overpressure in the system.

Table 3 lists the continuous on-line ultrasound acid leaching procedures described in the literature. Moreover, the methods described earlier for the acid leaching of Cu from mussel[114] and Ca, Cu, Fe, Mg, and Zn from animal feeds,[115] there are reported several applications for extracting Ca,[116] Cr,[117] Cu,[114,118] Fe,[117,119] and Mn[120] from seafood products, and Fe and Zn from meat.[121,122] Nitric acid at a concentration of 3.0 M was enough for leaching Ca, Cu, Fe, and Mn from seafood at room temperature,[114,116–120] while a nitric acid/hydrochloric acid mixture was needed to treat meat samples.[121,122] Human hair samples were also subjected to continuous on-line acid leaching to extract Cd and Pb[123] and Cu, Fe, Mn, and Zn.[124] Sonication at a relative high temperature (70–80°C) was needed to obtain accurate results. These results agree with those previously reported for discontinuous (off-line) acid leaching methods to treat hair samples.[72,73]

Further applications (Table 3) were developed to combine the continuous on-line ultrasound–assisted acid leaching procedure with on-line pre-concentration of the leached analytes using chelating resins prior to FAAS determination. In such cases, after the acid extraction was completed, the leachate was mixed with a buffer solution stream (to obtain the optimum pH for the analyte complexation/retention ention in the resin), and then was passed through the pre-concentration column. Finally, the analyte was eluted with an acid solution and swept to the spectrometric detector. Following this general approach, trace elements present at low levels in food samples (seafood, meat, legumes, fruits) were conveniently on-line extracted, pre-concentrated, and determined by FAAS.[125–131]

Finally, some applications of continuous ultrasound-assisted acid leaching procedures have been developed for environmental samples (welding fumes).[131–134] In these cases, nitric acid at a concentration of 3.0 M was found adequate as an acid leaching. Some elements such as Zn can be quantitatively leached from the solid particles after sonication at room temperature.[132] However, other trace elements, such as Cd, Ni, and Pb, were efficiently leached at temperatures between 50 and 80°C[133] and hexavalent chromium extraction in alkaline medium was only possible by sonicating at 40°C.[134]

Microwave-Assisted Leaching

The use of microwave energy for sample preparation has been widely accepted for assessing inorganic and organic compounds in different biological and environmental samples.[135,136] Regarding elemental analysis by spectrometry techniques, since the first reported application by Abu-Samra et al.[137] to acid digestion of biological materials, microwave-assisted acid digestion is now a well-established methodology for treating biological, environmental, and geological samples and it is by far the chosen sample pretreatment for routine analysis.[138,139] The rapid heating achieved by microwave irradiation as consequence of ionic migration (dissolved salts in the solvent) and/or dipolar

Downloaded At: 02:47 30 January 2011

Downloaded At: 02:47 30 January 2011

TABLE 3 Applications of Microwave Assisted Leaching Methods

Analyte	Sample	Microwave oven	Leaching solution (atomic spectrometric technique)	Power/ Temperature/Pressure	Leaching time	Ref.
Cr, Cu, Pb, Zn	Sludge	Household microwave oven	0.5 M HNO_3 +0.7 M HCl (FAAS)	75 W + 170 W	0.5 min +2.0 min	82
Co, Cu, Fe, Mg, Mn	Apple leaves	High pressure microwave oven	14.0%(v/v) HNO_3 (FAAS/ETAAS)	1104 KPa	30.0 min	140
Ca, Cd, Cr, Mn, Pb	Seafood	Household microwave oven	4.5 M HNO_3 +2.8 M HCl +0.5 M H_2O_2	64 W	2.0 min	141
Cu, Fe, Mg, Zn			4.0 M HNO_3 +3.3 M HCl		1.5 min	
As			0.5 M H_2O_2 +4.5 M HCl		2.0 min	
Co			1.0 M HNO_3 +0.5 M HCl +4.5 M H_2O_2		2.0 min	
Se			4.5 M HNO_3 +4.5 M H_2O_2		2.0 min	
Hg			0.5 M HNO_3 +3.3 M HCl +0.5 M H_2O_2 (FAAS/ETAAS/CVAAS)		1.75 min	
B, Cd, Ni, Pb, Sr, Zn	Plants	High pressure microwave oven	0.02 M EDTA	250 W + 400 W + 550 W + 250 W	5.0 min +10.0 min +5.0 min +5.0 min	142
B, Ba, Cd, Cu, Mn, Ni, Pb, Sr, Zn			1.0 M HCl (ICP-OES)			
Ba, Cd, Cr, Cu, Fe, Mn, Pb, V, Zn	Mussels	High pressure microwave oven	2.5 M HNO_3 +3.0 M HCl +0.5%(m/v) H_2O_2(ICP-OES)	From room temperature to 65°C	2.5 min[a]	143
As	Fish	High pressure microwave oven	0.075%(w/v) TMAH (ETAAS)	From room temperature to 50°C	10.0 min[b]	144
As	Seafood (TORT-2)	High pressure microwave oven	2.0%(v/v) HNO_3 or 80% MeOH	From room temperature to 75°C	6.0 min	85
Cd			2.0%(v/v) HNO_3(ICP-MS)			
Cu, Fe, Mn, Zn	Multimineral supplements	High pressure microwave oven	0.7 M HNO_3 (FAAS)	360 W	15.0 min	145
Al, Ca, Mg, Mn	Tea leaves	Focused microwave oven	1.4 M HNO_3(ICP-OES/FAAS)	From room temperature to 95°C	2.0 min[c]	146
As, Hg, Se[e]	Coal	Focused microwave oven	6.0–8.0%(w/w) HNO_3(H-GAFS/CVAFS)	65% maximum power[d]	3.0 min[f]	147
Cd, Pb[g]	Beech leaves	Focused microwave oven	1%(v/v) HNO_3(ETAAS)	300 W	10–15 min	112

[a]0.5 min at 65°C.
[b]5.0 min at 50°C.
[c]3.0 min at 95°C.
[d]Maximum power 300 W.
[e]Focused microwave Soxhlet acid leaching.
[f]Each irradiation cycle (total cycle time 9 min).
[g]Continuous microwave assisted acid leaching.

rotation (molecular solvents) and the new developments using closed reaction vessels under controlled pressure and temperature, are some of the main advantages offered by microwave-assisted procedures.

Microwave-assisted acid digestion procedures require the use of concentrated acids to totally destroy the sample, but as proposed by Lorentzen and Kingston,[45] there is the possibility of extracting (leaching) trace elements without total sample decomposition. In such cases, the term microwave-assisted acid leaching is preferred, although the mechanisms through which the elements reach the solution must be considered as partial sample decomposition due to diluted oxidizing and relatively high temperature and pressure are used.[45] However, it must be mentioned that a total digestion of a sample can be obtained using diluted acids and microwave irradiation.

Table 4 summarizes the application of microwave-assisted leaching procedures involving the use of diluted acids/reagents. The first approach can be attributed to Zhou et al.[140] who used a high pressure microwave oven and 14%(v/v) HNO_3 as a extracting solution for leaching Ca, Cu, Fe, K, Mg, Mn, Ni, and Zn from apple leaves. Good accuracy was achieved with the exception of Ni (analytical recovery lower than 90%). Then, other applications using household microwave ovens,[82,141] as well as high pressure[142–145] and focused microwave ovens,[146] were developed to treat sludge,[49] seafood products (mussels and fishes and CRM of marine origin),[85,141,143,144] plants (leaves of spinach beet and onion),[142] multimineral supplements[145] or tea leaves.[146] It must be noticed that non-quantitative recoveries for Al from mussel soft tissue[143] and plant leaves[142,146] have been reported.

Finally, Table 4 lists two additional applications involving acid leaching by means of a focused microwave Soxhlet device[147] and a continuous microwave-assisted acid leaching procedure.[112] In the first approach, a quartz vessel containing the sample (coal) and the extracting solution, is connected to a glass piece provided with three orifices to fit a refrigerant supply, to purge off the evaporated extracting solution, and to fit a glass tube (with a PTFE tube inside) connected to a cellulose cartridge, which was located 15 cm above the sample–nitric acid surface.[147] The leaching procedure consists of different cycles, each involving sequential stages such as a filling step with acid leaching solution, microwave irradiation, and immersion of the cartridge into the nitric acid solution–solid sample suspension to filter the solution toward the interior of the cartridge through its walls by aspiration.[147] In the second approach, the sample (beech leaves) is placed into an extraction cell connected to an extraction loop that is filled with the acid leaching solution (2.0 mL). The extraction cell is then placed in the vessel of the focused microwave oven, which contains water and it is irradiated at 300 W for 10–15 min.[147]

Pressurized Liquid Extraction and Pressurized Hot Water Extraction

Pressurized liquid extraction (PLE), also called pressurized fluid extraction (PFE), pressurized solvent extraction (PSE) or accelerated solvent extraction (ASE), is a well-established methodology for the extraction of organic compounds.[148–150] The technique is based on using solvents at a high pressure and/or high temperature without reaching the critical point. Under these conditions, the properties of the solvent, mainly the dielectric constant and the surface tension, are modified and the solubility of analytes in the extracting is increased. When using water as a solvent, the technique is commonly called pressurized hot water extraction (PHWE),[151] but the instrumentation as well as critical parameters controlling the extraction process are similar to PLE. In general, the system comprises a stainless-steel extraction cell, in which the sample, previously dispersed in an inert support, is placed and for which parameters such as temperature, pressure, static extraction time, and extraction cycles are programmed by electronically controlled heaters and pumps. The sample must be dispersed in an inert dispersion medium prior to extraction to assure good solvent sample contact within the extraction cell.[150]

Because the transfer of analytes from the solid sample to the extracting solution is enhanced at the used temperature and pressure, the treatment can be carried out with small amounts of solvents and generation of wastes are reduced. In addition, the use of water or modified water (water with certain modifiers or additives to enhance the solubility of analytes in water or to increase interactions of water with the analytes)[151] makes the technique environmentally friendly.

Downloaded At: 02:47 30 January 2011

TABLE 4 Applications of Pressurized Hot Water Extraction and Pressurized Liquid Extraction

Analyte	Sample	Pressurized device	PHWE/PLE conditions	Atomic spectrometry technique	Leaching time	Ref.
Se	Sludge	Laboratory-made extractor	Water, 50–250°C, 200 bar	HG-AFS	15.0 min	153
As, Hg, Se	Coal	Laboratory-made extractor	Acidified water (4.0%(v/v) HNO_3), 80–250°C, 50 bar	GF/CV-AFS	15.0 min	154
Al, Ca, Fe, K, Mg, Na	Coal	Laboratory-made extractor	Acidified water (1.0%(v/v) HNO_3), 50–300°C, 20–150 bar	FAAS/FAES	120.0–300.0 min	155
Cd, Pb	Plants	Laboratory-made extractor	Acidified water (1.0%(v/v) HNO_3), 100–250°C	ETAAS	5.0 min	157
Cd, Cr, Cu, Ni, Pb, V	Industrial oils	Laboratory-made extractor	Acidified water (4.0%(v/v) HNO_3 +0.1 M KCl), 150°C	ETAAS		158
Cu, Fe, Ni, V, Zn	Industrial oils	Laboratory-made extractor	Acidified water (20.0%(v/v) HNO_3 +1.0 M KCl), 175°C	FAAS		159
Cl^-, F^-, SO_4^{2-}	Industrial oils	Laboratory-made extractor	Acidified water (5.0%(v/v) HNO_3), 200°C	IC		160
Al, As, B, Ba, Cd, Cu, Fe, Mn, Pb, Se, Zn	Particulate matter	Laboratory-made extractor	Acidified water (0.1%(v/v) HNO_3), 150°C, 1500 psi	ICP-OES/ICP-MS/HG-AAS	15.0 min (30.0 min)[a]	161
Cd, Cu, Zn	Squid waste	Laboratory-made extractor	Water, 170–380°C, 0.79–30 MPa	FAAS	1.0–40.0 min	162
B	Soils	Espresso machine	Water, 90°C	ICP-OES	1.0 min	163
Cd, Cr, Cu, Ni, Pb, Zn	Sediments	Supercritical fluid extractor	Water or water-+CO_2, 80°C, 27 MPa	ICP-OES/ICP-MS	5.0 h	165
As	Seafood	Supercritical fluid extractor	Water, 125–150°C,376–2188 psi	ICP-MS	20.0 min	85
Mo	(TORT-2)		Water, 100–150°C,376–2188 psi			
Se			Water, 150°C,376–2188 psi			
Cu, Mn, Pb	Sludge, river sediment, coal fly ash	Dionex ASE-200	0.02 M $EDTA^-$, 150°C, 14 Mpa, 5 cycles	ETAAS	30.0 min	166
Ca, Cd, Co, Cr, Cu, Mg, Mn, Na, Ni, Pb, Sr, V, Zn	Particulate matter	Dionex ASE-200	40.0 mM EDTA[b], 100°C, 1000 psi, 1 cycle	ICP-OES	10.0 min	167
Cd, Zn	Plants	Dionex ASE-200	0.01 M CDTA[c], 75°C, 1500 psi, 1 cycle	FAAS/ETAAS	5.0 min	168
Al, As, Cd, Co, Cu, Fe, Hg, Li, Mn, Pb, Se, Sr, V, Zn	Seafood	Dionex ASE-200	1.0 M formic acid, 125°C, 500 psi, 1 cycle	ICP-OES	10.0 min	169

(*Continued*)

Downloaded At: 02:47 30 January 2011

TABLE 4 Continued

Analyte	Sample	Pressurized device	PHWE/PLE conditions	Atomic spectrometry technique	Leaching time	Ref.
As, Cd, Cr, Ni, Pb	Marine sediments, soils	Dionex ASE-200	8.0 M acetic acid, 100°C, 1500 psi, 2 cycles	ICP-OES	15.0 min	170
As, Ca, Cd, Co, K, Li, Mg, Na, Ni, Sr	Human hair	Dionex ASE-200	0.75 M acetic acid, room temperature, 140 atm, 1 cycles	ICP-OES	5.0 min	171
As, Ca, Cd, Co, Cr, K, Mg, Mn, Na, Pb, Sr, Zn	Seaweed	Dionex ASE-200	0.75 M acetic acid, room temperature, 10.3 MPa, 1 cycle	ICP-OES	5.0 min	172

[a]30 min dynamic extraction time.
[b]EDTA, ethylendiaminotetraacetic acid.
[c]CDTA, 1,2-diaminocyclohexane-N,N,N′N″-tetraacetic acid.

Downloaded At: 02:47 30 January 2011

Therefore, besides the several applications of PLE and PHWE for extracting organic compounds, methods for extracting organometallic species, mostly arsenicals and organotin species, from environmental and biological materials were developed with great success[152] and also PLE/PHWE has been proposed to leach metals as a green alternative to acid digestion procedures.[152] The first applications for extracting metals (Table 5) were developed by Luque de Castro and colleagues using subcritical water[153] or acidified subcritical water[154,155] with an extractor made of stainless steel and designed and patented by Salvador and Merchán.[156] The methods comprise the continuous extraction of Se from sludge samples[153] or As, Hg, and Se from coal[154] and HG/CV–AFS determination, or an off-line procedure to extract Al, Ca, Fe, K, Mg, and Na from coal before FAAS or ETAAS measurement.[155] For acidified subcritical water extraction, the leaching solution consists of water modified with 1.0 to 4.0%(v/v) HNO_3.[154,155,157] Similar composition of the extracting solutions was also used for a continuous pressurized liquid-liquid extraction of Cd, Cr, Cu, Ni, Pb, and V[158] or Cu, Fe, Ni, V, and Zn[159] from used industrial oils and even for extracting non-metal species (chlorine, fluorine, and sulphur).[160] Laboratory-made prototypes for subcritical water extractions were also used by Morales-Riffo and Richter to treat airborne particulate matter[161] and by Tavakoli and Yoshida to remove trace elements from solid (squid) wastes.[162] Finally, it is worth mentioning the application by Webb et al. for the pressurized hot water extraction of boron from soils by using household devices such as different espresso machines from different manufacturers.[163]

A commercial supercritical extractor, designed for supercritical carbon dioxide extractions (SFE),[164] was also used by Heltai et al.[165] for a combined BCR three-steps sequential method involving supercritical carbon dioxide, subcritical water, and a subcritical mixture of water (90%) and carbon dioxide (10%). The procedure was applied in ecotoxicological studies of contaminated sediments by Cd, Cr, Cu, Ni, Pb, and Zn. A similar system was used for the subcritical water extraction of As, Mo, and Se from TORT-2 CRM (non-quantitative recoveries were obtained for Cd and Co).[85]

The first application of a commercial PLE piece of equipment (Dionex ASE-200 system) for leaching metals is attributed to Wanekaya et al.[166] who investigated the use of chelating agents (EDTA) in aqueous solution as extracting under pressurized conditions. These authors called the methodology pressurized assisted chelating extraction (PACE) and quantitatively extracted Cu, Mn, and Pb from sludge, coal fly ash, and river sediments (Table 5). Other applications of diluted solutions of chelating agents as extracting for PLE (40 mM EDTA) were led to leach major and trace elements from atmospheric particulate matter (PM10), previously collected on quartz fiber filters.[167] The quantitative

TABLE 5 Applications of Enzymatic Hydrolysis for Total Metal Extraction

Analyte	Sample	Enzyme	Enzymatic hydrolysis conditions	Atomic spectrometry technique	Leaching time	Ref.
Cd, Cu, Pb, Tl	Human liver, human kidney	Subtilisin Carlsberg	Trizma base (pH unknown), 55°C	FAAS	60 min	175
Se	Blood serum	Pronase E	37°C	ICP-MS	overnight	177
As, Cd, Cu	Mussels	Pronase E	37°C, buffer 0.1 M/0.1 M TRIS/HCl, pH 7.4	FAAS/ETAAS	5.0 h	178
Se	Plant and animal tissues	Protease type XIV/lipase/ cellulase	37°C, 0.03 M TRIS	ETAAS	4.0–8.0 h	179
Se	Plant and animal tissues	Protease type XIV	60°C, 0.03 M TRIS	ETAAS	4.0 h	180
Cd, Pb	Konjac flour	α-amylase	50°C, pH 6.5	ETAAS	8.0 h	181
As, Cd, Cr, Cu, Mn		Trypsina	37°C, buffer 0.1 M/0.1 M PDHP/PHP[a], pH 9.0 (As, Cd, Cu), pH 6.0 (Cr, Mn)	ICP-OES	24 h	174
Cr, Ni, Pb	Mussels	Pancreatin	37°C, buffer 0.1 M/0.1 M PDHP/PHP, pH 9.0 (Ni), pH 6.0 (Cr, Pb)		24 h	
Cu, Cr, Mn, Pb, Zn		Pepsin	37°C, 0.2 M NaCl, pH 1.0 (with HCl)		6.0 h	
As, Zn	Seaweed	Pepsin	37°C, 1.0%(m/v) NaCl, pH 1.0 (with HCl)	ICP-OES	6.0 h	182
As, Cd, Cr, Cu, Mn, Ni, Pb	Mussels	Trypsin[b]	37°C, buffer 0.2 M/0.2 M PDHP/PHP, pH 8.0	ICP-OES	30 min	183
As, Cd, Cr, Mn, Ni, Pb		Pancreatin[b]	37°C, buffer 0.5 M/0.5 M PDHP/PHP, pH 8.0			
Cu, Cr, Mn, Ni, Pb, Zn		Pepsin[b]	37°C, 1.0%(m/v) NaCl, pH 1.0 (with HCl)			
As, Cd, Cu, Fe, Mn, Ni, Pb, Zn	Seaweed	Pepsin[b]	37°C, 1.0%(m/v) NaCl, pH 1.0 (with HCl)	ICP-OES	30 min	182
As, Cd, Co, Cu, Hg, Li, Mn, Pb, Se, Sr, Zn	Biological materials	Pepsin[c]	50°C, 1500 psi, 3 PLE cycles, Milli-Q water, pH 1.0 (with HCl)	ICP-OES	6.0 min	10
Selenomethionine	Selenized yeast	Protease/ lipase/ driselase[d]	60 W, 37°C, 2 cycles	HPLC-ICP-MS	30 min	11

[a]PDHP/PHP, potassium dihydrogen phosphate/potassium hydrogen phosphate.
[b]Ultrasound bath assisted enzymatic hydrolysis.
[c]Pressurized enzymatic hydrolysis.
[d]Microwave assisted enzymatic hydrolysis.

recoveries for all elements investigated offers advantages over time-consuming and contaminant wet digestion methods, commonly required to destroy the quartz filter. Recently, Maurí-Aucejo et al. have also applied chelating agent–based PLE to extract Cd and Zn from plants.[168]

Other PLE methods involved the use of diluted carboxylic acids as extracting solutions, such as

Downloaded At: 02:47 30 January 2011

formic acid to leach several trace elements from biological materials (CRMs from marine origin),[169] or diluted acetic acid to treat marine sediment and soil samples,[170] human hair,[171] and seaweed.[172] The concentration of formic acid or acetic acid and the extraction temperature were found to be the most statistically significant PLE factors affecting the leaching process for CRMs of marine origin and marine sediments and soils.[169,170] However, for biological samples such as human hair and seaweed, the sample mass to dispersing support mass ratio was the most important parameter. Quantitative recoveries for several trace elements (As, Ca, Cd, Co, Cr, K, Li, Mg, Mn, Na, Ni, Pb, Sr, and Zn) were obtained when analyzing seafood, human hair, and seaweed samples[169,171,172] but only As, Cd, Cr, Ni, and Pb were quantitatively released from marine sediments and soils.[170] This fact could be explained taking into account that these elements are mainly bonded to an organic fraction of the sediments and soils rather than silicate and iron fractions. Nevertheless, lack of accuracy has been reported by the authors for Al and Cu extractions from all materials.[169–172]

ENZYMATIC HYDROLYSIS METHODS

Enzymatic hydrolysis or enzymic hydrolysis is a group of procedures that digests biological samples under mild conditions, avoiding the use of polluting or toxic reagents and being, therefore, environmentally friendly procedures. The enzymatic hydrolysis consists of hydrolyzing biomolecules by breaking down certain bonds of these biomolecules at certain environmental conditions (pH, temperature, and ionic strength).[173] After hydrolysis, the analyte (metal or organometallic specie) is released from the solid biological matrix and it can be finally measured. Enzymes, mainly proteolytic enzymes (proteases), such as pronase E, pepsin, pancreatin, and trypsin, or lipase and amylase, must be carefully selected in base of the nature of sample (high protein, fat, or carbohydrate content). In some cases, a mixture of different enzymes can be used simultaneously but this approach is not always possible because the optimum pH value for a certain enzyme cannot be same for the other one (i.e., pepsin normally operates at pH around 2 while lipase or amylase work at a pH around 7).[174]

The first work involving the use of enzymes to extract metals was carried out in 1981 by Carpenter,[175] who used subtilisin Carlsberg proteolytic enzyme for hydrolyzing human liver and kidney tissues (Table 5). Soon, other authors used the high potential of enzymes for organometallic speciation studies mainly because of the mild temperature and pH conditions inherent to enzymatic hydrolysis, which guarantees the integrity of organometallic species during extraction. Therefore, several enzymatic hydrolysis procedures mainly for arsenic, selenium, and tin speciation were developed, as it can be seen in recent reviews.[9,176]

Concerning total metal contents, since the pioneer work by Carpenter,[175] Abou-Shakra et al. used pronase E to assess total selenium in blood serum.[177] This enzyme was also used for treating mussel soft tissue and human hair in order to release Ag, As, Cd, Cu, Fe, Mg, Pb, and Zn.[44,178] Results showed that only As, Cd, and Cu were quantitatively extracted from mussel soft tissue, being these elements mainly associated to proteins hydrolysable by pronase E.[178] Other enzymes such as lipase, cellulose, and Protease Type XIV were also used for releasing Se from biological materials (animal and botanical CRMs) prior to a slurry sampling-ETAAS method.[179,180] A similar approach has recently been developed by Chen et al.[181] for treating konjac flour (a gel-forming edible dietary fiber) with α-amylase to determine Cd and Pb by slurry sampling–ETAAS.

Different proteases, such as pepsin, pancreatin, and trypsin, and α-amylase and lipase, were used to treat mussel soft tissue[174] (Table 5). As, Cd, Cu, Cr, and Mn were quantitatively extracted from mussel soft tissue by using trypsin, while Cu, Cr, Mn, Pb, and Zn were recovered when using pepsin.[174] The pancreatin-based enzymatic hydrolysis only gave good accuracy for Cr, Ni, and Pb.[174] The systematic evaluation of parameters affecting the enzymatic hydrolysis process showed that temperature, pH, and ionic strength were the most significant variables when hydrolyzing mussel soft tissue. Pepsin, trypsin, and α-amylase were also used to treat seaweed samples.[182] In this case, quantitative recoveries were obtained for As and Zn using pepsin, while non-quantitative recoveries were obtained for all elements investigated when using trypsin and α-amylase.[182] Due to the high salts content in the samples (dried edible seaweed), the high ionic

Downloaded At: 02:47 30 January 2011

strength in enzyme/sample mixture controlled the enzymatic hydrolysis process and other variables such as pH and temperature were less significant than when treating mussel soft tissues.[174,182]

Ultrasounds/Microwave/Pressurized–Assisted Enzymatic Hydrolysis

The main drawback of enzymatic hydrolysis procedures is the long time required to complete the hydrolysis process, around 5–16 hr to assess Se in blood serum and trace metals in mussels,[9] within 12–24 hr when using Protease Type XIV,[180,181] or between 6 and 24 hr for the use of pepsin, pancreatin, and trypsin for hydrolyzing mussels[174] and seaweed samples.[182] In order to speed up the enzymatic hydrolysis process, ultrasounds have been proposed for both total element determination and speciation studies.[9] The reduction on the enzymatic hydrolysis time when using ultrasounds can be attributed to cell membrane disruptions by the action of ultrasounds and the direct cytosolic content attack by enzymes.[183] By this way, enzymatic hydrolysis time can be reduced from hours to minutes, around 30 min when using ultrasound water bath[182,183] or even 1 to 2 min when using ultrasounds probes.[184] Pressurization has also been used to disrupt cell membranes before enzymatic digestion of biological materials (seafood CRMs, fatty tissue CRMs, and plant CRMs).[10] The pretreatment time for the pressurized enzymatic hydrolysis procedure can be shortened to 6 min (3 PLE cycles of 2 min each one at 50°C and 1500 psi) for the use of pepsin or pancreatin.[10] Recently, microwave energy has also been used to accelerate the enzymatic hydrolysis of protein-bound selenium. A focused microwave oven (60 W) and a two-step enzymatic hydrolysis with protease/lipase/driselase were used to reduce the enzymatic digestion to 30 min.[11]

CONCLUSION

The development of solid sample pretreatments for atomic spectrometry analysis involving the avoidance of corrosive reagents and the use of safe operating conditions is an active research field in modern analytical chemistry. Slurry sampling technique is still the most appealing methodology because it allows the successful introduction and analysis of inorganic materials in most of the current atomic spectrometric techniques. Other approaches such as acid leaching using diluted acids or certain reagents under ultrasound, microwave, or pressurization conditions have been found useful to assess most of the trace essential and toxic elements in biological samples. However, most of the procedures fail when analyzing inorganic samples for which some trace elements are associated to the silica fraction, or even for biological samples when determining trace elements such as Al. Therefore, efforts must be made in order to increase the analyte releasing from inorganic matrices using diluted reagents and even to improve the developed methods for extracting certain elements such as Al and Fe. Enzymatic hydrolysis procedures have also been adequate for many applications and this group of methods is promising for total element determination and speciation, especially when being assisted (ultrasounds, microwave, or pressurization) in order to speed up the whole process.

REFERENCES

1. Anastas, P. T.; Breen, J. J. Design for the environment and green chemistry: The heart and soul of industrial ecology. *J. Cleaner Production* **1997**, *5*, 97–102.
2. Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: Oxford, UK, 2000.
3. Anastas, P. T. Green chemistry and the role of analytical methodology development. *Critical Rev. in Analytical Chem.* **1999**, *29*, 167–175.
4. Namieśnik, J. Green analytical chemistry—Some Remarks. *J. Separation Sci.* **2001**, *24*, 151–153.
5. He, Y.; Tang, L.; Wu, X.; Hou, X. D.; Lee, Y.-I. Spectroscopy: The best way toward green analytical chemistry? *Appl. Spectroscopy Rev.* **2007**, *42*, 119–138.
6. Koel, M.; Kalijurand, M. Application of the principles of green chemistry in analytical chemistry. *Pure and Appl. Chem.* **2006**, *78*, 1993–2002.
7. Armenta, S.; Garrigues, S.; de la Guardia, M. Green analytical chemistry. *Trends in Analytical Chem.* **2008**, *27*, 497–511.
8. Brady, D. V.; Montalvo, J. G.; Glowacki, G.; Pisciotta, A. Direct determination of zinc in sea-bottom sediments by carbon tube atomic absorption spectrometry. *Analytica Chimica Acta* **1974**, *70*, 448–452.
9. Bermejo, P.; Capelo, J. L.; Mota, A.; Madrid, Y.; Cámara, C. Enzymatic digestion and ultrasonication: A powerful combination in analytical chemistry. *Trends in Analytical Chem.* **2004**, *23*, 654–663.
10. Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P.; Moreda-Piñeiro, J.; Alonso-Rodríguez, E.; Muniategui-Lorenzo, S.; López-Mahía, P.; Prada-Rodríguez, D. Feasibility of pressurization to speed up enzymatic hydrolysis of biological materials for multielement determinations. *Analytical Chem.* **2007**, *79*, 1797–1805.
11. Peachey, E.; McCarthy, N.; Goenaga-Infante, H. Acceleration of enzymatic hydrolysis of protein-bound selenium by focused microwave energy. *J. Analytical Atomic Spectrometry* **2008**, *23*, 487–492.
12. Bendicho, C.; de Loos-Vollebregt, M. T. C. Solid sampling in electrothermal atomic absorption spectrometry using commercial

Downloaded At: 02:47 30 January 2011

atomizers. A review. *J. Analytical Atomic Spectrometry* **1991**, *8*, 353–374.
13. Kürfust, V. *Solid Sample Analysis*; Springer: Berlin, Germany, 1998.
14. Cal-Prieto, M. J.; Felipe-Sotelo, M.; Carlosena, A.; Andrade, J. M.; López-Mahía, P.; Muniategui, S.; Prada, D. Slurry sampling for direct analysis of solid materials by electrothermal atomic absorption spectrometry (ETAAS). A literature review from 1990 to 2000. *Talanta* **2002**, *56*, 1–51.
15. Vale, M. G. R.; Oleszczuk, N.; dos Santos, W. N. L. Current status of direct solid sampling for electrothermal atomic absorption spectrometry. A critical review of the development between 1995 and 2005. *Applied Spectroscopy Rev.* **2006**, *41*, 377–400.
16. Carnrick, G. R.; Daley, G.; Fotinopoulos, A. Design and use of a new automated ultrasonic slurry sampler for graphite-furnace atomic absorption. *Atomic Spectroscopy* **1989**, *10*, 170–174.
17. Majidi, V.; Holcombe, J. A. Error analysis for sampling of slurries: Sedimentation errors. *Spectrochimica Acta Part B* **1990**, *45*, 753–761.
18. Miller-Ihli, N. J. Ultrasonic slurry sampling graphite furnace atomic absorption spectrometry: Analytical considerations for analysis of high density glass material. *Spectrochimica Acta Part B* **1997**, *52*, 431–436.
19. Bermejo-Barrera, P.; Verdura-Constenla, E. M.; Moreda-Piñeiro, A.; Bermejo-Barrera, A. Rapid acid leaching and slurry sampling procedures for the determination of methylmercury and total mercury in human hair by electrothermal atomic absorption spectrometry. *Analytica Chimica Acta* **1999**, *398*, 263–272.
20. Bermejo-Barrera, P.; Barciela-Alonso, M. C.; Moreda-Piñeiro, J.; González-Sixto, C.; Bermejo-Barrera, A. Determination of trace metals (As, Cd, Hg, Pb, and Sn) in marine sediment slurry samples by electrothermal atomic absorption spectrometry using palladium as a chemical modifier. *Spectrochimica Acta Part B* **1996**, *51*, 1235–1244.
21. Almeida-Pereira, L.; Amorim, I.; Borba da Silva, J. B. Determination of cadmium, chromium and lead in marine sediment slurry samples by electrothermal atomic absorption spectrometry using permanent modifiers. *Talanta* **2006**, *68*, 771–775.
22. Cal-Prieto, M. J.; Carlosena, A.; Andrade, J. M.; Muniategui, S.; López-Mahía, P.; Fernández, E.; Prada, D. Development of an analytical scheme for the direct determination of antimony in geological materials by automated ultrasonic slurry sampling-ETAAS. *J. Analytical Atomic Spectrometry* **1999**, *14*, 703–710.
23. Miller-Ihli, N. J. Influence of slurry preparation on the accuracy of ultrasonic slurry electrothermal atomic absorption spectrometry. *J. Analytical Atomic Spectrometry* **1994**, *9*, 1129–1134.
24. Alves, F. L.; Cadore, S.; Jardim, W. F.; Arruda, M. A. Z. River sediment analysis by slurry sampling faas: Determination of copper, zinc and lead. *J. Brazilian Chem. Soc.* **2001**, *12*, 799–803.
25. da Silva, E. G. P.; do N. Santos, A. C.; Costa, A. C. S.; da N. Fortunato, D. M.; José, N. M.; Korn, M. G. A.; dos Santos, W. N. L.; Ferreira, S. L. C. Determination of manganese and zinc in powdered chocolate samples by slurry sampling using sequential multi-element flame atomic absorption spectrometry. *Microchemical J.* **2006**, *82*, 159–162.
26. Ferreira, H. S.; dos Santos, W. N. L.; Fiuza, R. P.; Nobrega, J. A.; Ferreira, S. L. C. Determination of zinc and copper in human hair by slurry sampling employing sequential multi-element flame atomic absorption spectrometry. *Microchemical J.* **2007**, *87* (2), 128–131.
27. Alonso, R.; Río, S.; Fernández, E. Comparison of slurry sampling and microwave-assisted digestion for calcium, magnesium, iron, copper and zinc determination in fish tissue samples by flame atomic absoprtion spectrometry. *Talanta* **2007**, *72*, 60–65.
28. Ebdon, L.; Foulkes, M.; Sutton, K. Slurry nebulizations in plasmas. *J. Analytical Atomic Spectrometry* **1997**, *12*, 213–229.
29. Santos, M. C.; Nóbrega, J. A. Slurry nebulization in plasmas for analysis of inorganic materials. *Applied Spectroscopy Rev.* **2006**, *41*, 427–448.
30. Cernohorsky, T.; Krejcova, A.; Pouzar, M.; Vavrusova, L. Elemental analysis of flour-based ready-oven foods by slurry sampling inductively coupled plasma optical emission spectrometry. *Food Chem.* **2008**, *106*, 1246–1252.
31. Krejcova, A.; Kahoun, D.; Cernohorsky, T.; Pouzar, M. Determination of macro and trace element in multivitamins preparations by inductively coupled plasma optical emission spectrometry with slurry sample introduction. *Food Chem.* **2006**, *98*, 171–178.
32. Baralkiewicz, D.; Kanecka-Hanc, A.; Gramowska, H. ICP slurry introduction for simple and rapid determination of Pb, Mg and Ca in plant roots. *Central European J. Chem.* **2007**, *5*, 1148–1157.
33. Zachariadis, G. A.; Valianou, L. I. Evaluation and comparison of two combinations of pneumatic nebulizers and spray chambers for direct slurry aspiration and multielement analysis of infant milk powders by axial-viewing inductively coupled plasma atomic emission spectrometry. *Applied Spectroscopy* **2008**, *62*, 716–720.
34. Xiang, G.; Jiang, Z.; He, M.; Hu, B. Direct determination of trace rare earth elements in ancient porcelain samples with slurry sampling electrothermal vaporization inductively coupled plasma mass spectrometry. *Spectrochimica Acta Part B* **2005**, *60*, 132–1348.
35. Matusiewicz, H. Chemical vapour generation with slurry sampling: A review of atomic absorption applications. *Applied Spectroscopy Rev.* **2003**, *3*, 263–294.
36. Moreda-Piñeiro, J.; López-Mahía, P.; Muniategui-Lorenzo, S.; Fernández-Fernández, E.; Prada-Rodríguez, D. Tin determination in marine sediment, soil, coal fly ash and coal slurried samples by hydride generation-electrothermal atomic absorption spectrometry. *Analytica Chimica Acta* **2002**, *461*, 261–271.
37. Moreda-Piñeiro, J.; López-Mahía, P.; Muniategui-Lorenzo, S.; Fernández-Fernández, E.; Prada-Rodríguez, D. Determination of As, Bi and Se in acidified slurries of marine sediment, soil and coal samples by hydride generation electrothermal atomic absorption spectrometry. *J. Analytical Atomic Spectrometry* **2002**, *17*, 721–726.
38. Cava-Montesinos, P.; Cervera, M. L.; Pastor, A.; de la Guardia, M. Determination of As, Sb, Se, Te and Bi in milk by slurry sampling hydride generation atomic fluorescence spectrometry. *Talanta* **2004**, *62*, 175–184.
39. Torres, D. P.; Vieira, M. A.; Ribeiro, A. S.; Curtius, A. J. Slurry sampling for arsenic determination in sediments by hydride generation atomic absorption spectrometry. *J. Brazilian Chem. Soc.* **2007**, *18*, 728–732.
40. Vieira, M. A.; Ribeiro, A. S.; Curtius, A. J. Determination of As, Ge, Hg, Pb, Sb, Se and Sn in coal slurries by CVG-ETV-ICP-MS. *Microchemical J.* **2006**, *82*, 127–136.
41. dos Santos, E. D.; Herrmann, A. B.; Vieira, M. A.; Frescura, V.; Curtius, A. J. Evaluation of slurry preparation procedures for the determination of mercury by axial view inductively coupled plasma optical emission spectrometry using on-line cold vapour generation. *Spectrochimica Acta Part B* **2005**, *60*, 659–665.
42. Moreda-Piñeiro, J.; Moscoso-Pérez, C.; López-Mahía, P.; Muniategui-Lorenzo, S.; Fernández-Fernández, E.; Prada-Rodríguez, D. Use of aqueous slurries of coal fly ash samples for the direct determination of As, Sb and Se by hydride generation-atomic fluorescence spectrometry. *Atomic Spectroscopy* **2006**, *27*, 19–25.
43. Moreda-Piñeiro, J.; Moscoso-Pérez, C.; Piñeiro-Iglesias, M.; López-Mahía, P.; Muniategui-Lorenzo, S.; Fernández-Fernández, E.; Prada-Rodríguez, D. Aqueous and acidified slurry sampling approaches in the As, Sb and Sn determination of urban dust samples by GH-ETAAS. *Atomic Spectroscopy* **2007**, *28*, 137–143.
44. Bermejo-Barrera, P.; Moreda-Piñeiro, A.; Bermejo-Barrera, A. Sample pre-treatment methods for the trace elements determination in seafood products by atomic absorption spectrometry. *Talanta* **2002**, *57*, 969–984.
45. Lorentzen, E. M. L.; Kingston, H. M. Comparison of microwave-assisted and conventional leaching using EPA method 3050B. *Analytical Chem.* **1996**, *68*, 4316–4320.

Downloaded At: 02:47 30 January 2011

46. Westöö, G. Determination of methylmercury salts in various kinds of biological material. *Acta Chemica Scandinavia* **1968**, *22*, 2277–2280.
47. Ebdon, L.; Fisher, A. In *Encyclopedia of Analytical Chemistry*; Meyers, A. R., Ed.; Wiley and Sons: New York, USA, 2002; 3064–3084.
48. Gleyzes, C.; Tellier, S.; Astruc, M. Fractionation studies of trace elements in contaminated soils and sediments: A review of sequential extraction procedures. *Trends in Analytical Chem.* **2002**, *21*, 451–467.
49. Puchyr, R. F.; Shapiro, R. Determination of trace elements in foods by HCl-HNO_3 leaching and flame atomic absorption spectroscopy. *J. Association Official Analytical Chem.* **1986**, *69*, 868–870.
50. Torstensen, T. K. D.; Johnsen, K.; Lund, W. Fractionation of metals in thermomechanical pulp by selective leaching and inductively-coupled plasma mass spectrometry. *The Science of the Total Environment* **1998**, *220*, 11–18.
51. Vidal, M. T.; Pascual-Martí, M. C.; Salvador, A.; Llabata, C. Determination of essential metals in complete diet feed by flow injection and flame atomic absorption spectrometry. *Microchemical J.* **2002**, *72*, 221–228.
52. Luque-García, J. L.; Luque de Castro, M. D. Ultrasound: A powerful tool for leaching. *Trends in Analytical Chem.* **2003**, *22*, 41–46.
53. Santos Júnior, D.; Krug, F. J.; de Godoy Pereira, M.; Korn, M. Currents on ultrasound-assisted extraction for sample preparation and spectroscopic analytes determination. *Applied Spectrosccopy Rev.* **2006**, *41*, 305–321.
54. Capelo, J. L.; Maduro, C.; Viena, C. Discussion of parameters associated with the ultrasonic solid-liquid extraction for elemental analysis (total content) by electrothermal atomic absorption spectrometry. An overview. *Ultrasounds Sonochemistry* **2005**, *12*, 225–232.
55. Mason, T. J.; Lorimer, J. P. *Applied sonochemistry: Uses of Power Ultrasounds in Chemistry and Processing*; Wiley-VCH: Weinheim, Germany, 2002.
56. Capelo, J. L.; Mota, A. M. Ultrasonication for analytical chemistry. *Current Analytical Chem.* **2005**, *1*, 193–201.
57. Santos, H. M.; Capelo, J. L. Trends in ultrasonic-based equipment for analytical sample treatment. *Talanta* **2007**, *73*, 795–802.
58. Chmilenko, F. A.; Baklanov, A. N. Atomic absorption determination of toxic and biologically active trace elements in dairy products using ultrasound for acceleration of mineralization. *Zhurnal Analitike Khimistry* **1992**, *47*, 1322–1327.
59. Nakamura, Y.; Etoh, T.; Noto, Y.; Murai, Y. Determination of wear metals in lubricating oils by inductively coupled plasma emission spectrometry. *Bunseki Kagaku* **1985**, *34*, T85–T88.
60. Sánchez, J.; García, R.; Millán, E. Ultrasonic bath digestion procedures for analysis for heavy metals in several reference materials. *Analusis* **1994**, *22*, 222–225.
61. Sánchez, J.; Millán, M. E. Use of ultrasound in digestion of biological reference materials for determination of heavy metals. *Química Analítica* (Barcelona, Spain) **1992**, *11*, 3–10.
62. Kumina, D. M.; Gribovskaya, I. F.; Karyakin, A. V. Method for extraction of elements from plants into solution using ultrasound. *Zhurnal Analitike Khimistry* **1985**, *40*, 1184–1187.
63. Matejovic, Y.; Durackova, A. Comparison of microwave digestion, wet and dry mineralization, and solubilization of plant sample for determination of calcium, magnesium, potassium, phosphorus, sodium, iron, zinc, copper, and manganese. *Communications in Soil Science and Plant Analysis* **1994**, *25*, 1277–1288.
64. Dyg, S.; Anglov, T.; Christensen, J. M. Preparation of filters loaded with welding dust. A homogeneity and stability study of hexavalent chromium. *Analytica Chimica Acta* **1994**, *286*, 273–282.
65. Mierzwa, J.; Adeloju, S. B.; Dhindsa, H. S. Ultrasound accelerated solid-liquid extraction for the determination of selenium in biological samples by electrothermal atomization atomic absorption spectrometry. *Analytical Sciences* **1997**, *13*, 189–193.
66. Liva, M.; Muñoz-Olivas, R.; Cámara, C. Determination of Cd in sonicate slurries and leachates of biological and environmental materials by FI-CV-AAS. *Talanta* **2000**, *51*, 381–387.
67. Nascentes, C. C.; Korn, M.; Arruda, M. A. Z. A fast ultrasound-assisted extraction of Ca, Mg, Mn and Zn from vegetables. *Microchemical J.* **2001**, *69*, 37–43.
68. Aleixo, P. C.; Júnior, D. S.; Tomazelli, A. C.; Rufino, I. A.; Berndt, H.; Krug, F. J. Cadmium and lead determination in foods by beam injection flame furnace atomic absorption spectrometry after ultrasound-assisted sample preparation. *Analytica Chimica Acta* **2004**, *512*, 329–337.
69. El Azouzi, H.; Cervera, M. L.; de la Guardia, M. Multi-elemental analysis of mussel samples by atomic absorption spectrometry after room temperature sonication. *J. Analytical Atomic Spectrometry* **1998**, *13*, 533–538.
70. Minami, H.; Honjyo, T.; Atsuya, I. A new solid-liquid extraction sampling technique for direct determination of trace elements in biological materials by graphite furnace atomic absorption spectrometry. *Spectrochimica Acta Part B* **1996**, *51*, 211–220.
71. Bermejo-Barrera, P.; Muñiz-Naveiro, O.; Moreda-Piñeiro, A.; Bermejo-Barrera, A. The multivariate optimization of ultrasonic bath-induced acid leaching for the determination of trace elements in seafood products by atomic absorption spectrometry. *Analytica Chimica Acta* **2001**, *439*, 211–227.
72. Bermejo-Barrera, P.; Muñiz-Naveiro, O.; Moreda-Piñeiro, A.; Bermejo-Barrera, A. Experimental designs in the optimization of ultrasonic bath acid leaching procedures for the determination of trace elements in human hair samples by atomic absorption spectrometry. *Forensic Sciences* **2000**, *107*, 105–120.
73. Bermejo-Barrera, P.; Moreda-Piñeiro, A.; Bermejo-Barrera, A. Factorial designs for Cd, Cr, Hg, Pb and Se ultrasound-assisted acid leaching from human hair followed by atomic absorption spectrometric determination. *J. Analytical Atomic Spectrometry* **2000**, *15*, 121–130.
74. Melo, M. H. A.; Costa, A. C. S.; Nóbrega, J. A.; Ferreira, S. L. C. The use of water soluble tertiary amine reagent for solubilization and metal determination in fish muscle tissue. *J. Brazilian Chem. Soc.* **2005**, *16*, 69–73.
75. Ladra-Ramos, N.; Domínguez-González, R.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. Determination of major and trace elements in edible seaweed by AAS after ultrasound-assisted acid leaching. *Atomic Spectroscopy* **2005**, *26*, 59–67.
76. Domínguez-González, R.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. Application of ultrasound-assisted acid leaching procedure for major and trace elements determination in edible seaweed by inductively coupled plasma-optical emission spectrometry. *Talanta* **2005**, *66*, 937–942.
77. Muñoz, O.; Vélez, D.; Montoro, R. Optimization of the solubilization, extraction and determination of inorganic arsenic [As(III) + As(V)] in seafood products by acid digestion, solvent extraction and hydride generation atomic absorption spectrometry. *Analyst* **1999**, *124*, 601–607.
78. Muñiz-Naveiro, O.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. AAS determination of total arsenic and total inorganic arsenic in seaweed after high-temperature ultrasound-assisted extraction. *Atomic Spectroscopy* **2004**, *25*, 79–87.
79. Borkowska-Burnecka, J.; Wisz, J.; Zyrnicki, W. Applicability of ultrasonic leaching by diluted acids for determination of total metal contents in plant materials. *Chemia Analityczna* (Warsaw) **2003**, *48*, 115–126.
80. Álvarez, J.; Marcó, L. M.; Arroyo, J.; Greaves, E. D.; Rivas, R. Determination of calcium, potassium, manganese, iron, copper and zinc levels in representative samples of two onion cultivars using total reflection X-ray fluorescence and ultrasound extraction procedure. *Spectrochimica Acta Part B* **2003**, *58*, 2183–2189.
81. Borkowska-Burnecka, J.; Jankowiak, U.; Zyrnicki, W.; Wilk, K. A. Effect of surfactant addition on ultrasonic leaching of trace elements from plant samples in inductively coupled plasma-atomic emission spectrometry. *Spectrochimica Acta Part B* **2004**, *59*, 585–590.

Downloaded At: 02:47 30 January 2011

82. Río Segade, S.; Diéguez Albor, M. C.; Fernández Gómez, E.; Falqué López, E. A fractional factorial design applied to the optimization of microwave- and ultrasound-assisted acid leaching methods for heavy metals determination in sludge by flame atomic absorption spectrometry. *International J. Environmental Analytical Chem.* **2003**, *83*, 343–356.
83. Moreda-Piñeiro, A.; Bermejo-Barrera, P.; Bermejo-Barrera, A. Chemometric investigation of systematic error in the analysis of biological materials by flame and electrothermal atomic absorption spectrometry. *Analytica Chimica Acta* **2006**, *560*, 143–152.
84. Manutsewee, N.; Aeungmaitrepirom, W.; Varanusupakul, P.; Imyim, A. Determination of Cd, Cu and Zn in fish and mussel by AAS after ultrasound-assisted acid leaching extraction. *Food Chem.* **2007**, *101*, 817–824.
85. Brisbin, J. A.; Caruso, J. A. Comparison of extraction procedures for the determination of arsenic and other elements in lobster tissue by inductively coupled plasma mass spectrometry. *Analyst* **2002**, *127*, 921–929.
86. Ashley, K.; Andrews, R. N.; Cavazos, L.; Demange, M. Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry. *J. Analytical Atomic Spectrometry* **2001**, *16*, 1147–1153.
87. Väisänen, A.; Suontamo, R. J. Comparison of ultrasound-assisted extraction, microwave-assisted acid leaching and reflux for the determination of arsenic, cadmium and copper in contaminated soil samples by electrothermal atomic absorption spectrometry. *J Analytical Atomic Spectrometry* **2002**, *17*, 739–742.
88. Collasiol, A.; Pozebon, D.; Maia, S. M. Ultrasound assisted mercury extraction from soil and sediment. *Analytica Chimica Acta* **2004**, *518*, 157–164.
89. Brunori, C.; Ipolyi, I.; Macaluso, L.; Morabito, R. Evaluation of an ultrasonic digestion procedure for total metal determination in sediment reference materials. *Analytica Chimica Acta* **2004**, *510*, 101–107.
90. Guengoer, H.; Elik, A. Comparison of ultrasound-assisted leaching with conventional and acid bomb digestion for determination of metals in sediment samples. *Microchem. J.* **2007**, *86*, 65–70.
91. López-García, I.; Campillo, N.; Arnau-Jeréz, I.; Hernández-Córdoba, M. Electrothermal atomic absorption spectrometric determination of germanium in soils using ultrasound-assisted leaching. *Analytica Chimica Acta* **2005**, *531*, 125–129.
92. Rao, S. V.; Venkateswarlu, G.; Dash, K.; Dhavile, S. M.; Chaurasia, S. C.; Arunnachalam, J. Ultrasound-assisted acid extraction of trace impurities from quartz samples followed by ICP-OES analysis. *Atomic Spectroscopy* **2004**, *25*, 251–256.
93. Capelo, J. L.; Lavilla, I.; Bendicho, C. Ultrasound-assisted extraction of cadmium from slurried biological samples for electrothermal atomic absorption spectrometry. *J. Analytical Atomic Spectrometry* **1998**, *13*, 1285–1290.
94. Lavilla, I.; Capelo, J. L.; Bendicho, C. Determination of cadmium and lead in mussels by electrothermal atomic absorption spectrometry using an ultrasound-assisted extraction method optimized by factorial design. *Fresenius' J. Analytical Chem.* **1999**, *363*, 283–288.
95. Maduro, C.; Vale, G.; Alves, S.; Galesio, M.; da Silva, M. D. R. G.; Fernández, C.; Catarino, S.; Rivas, M. G.; Mota, A. M.; Capelo, J. L. Determination of Cd and Pb in biological reference materials by electrothermal atomic absorption spectrometry: A comparison of three ultrasonic-based sample treatment procedures. *Talanta* **2006**, *68*, 1156–1161.
96. Lima, E. C.; Barbosa, F.; Drug, F. J.; Silva, M. M.; Vale, M. G. R. Comparison of ultrasound-assisted extraction, slurry sampling and microwave-assisted digestion for cadmium, copper and lead determination in biological and sediment samples by electrothermal atomic absorption spectrometry. J. *Analytical Atomic Spectrometry* **2000**, *15*, 995–1000.
97. Amoedo, L.; Capelo, J. L.; Lavilla, I.; Bendicho, C. Ultrasound-assisted extraction of lead from solid samples: A new perspective on the slurry-based sample preparation methods for electrothermal atomic absorption spectrometry. *J. Analytical Atomic Spectrometry* **1999**, *14*, 1221–1226.
98. Capelo, J. L.; Filgueiras, A. V.; Lavilla, I.; Bendicho, C. Solid-liquid extraction of copper from slurried samples using high intensity probe sonication for electrothermal atomic absorption spectrometry. *Talanta* **1999**, *50*, 905–911.
99. Santos, F. C.; Álava-Moreno, F.; Lavilla, I.; Bendicho, C. Total as in seafood as determined by transverse heated electrothermal atomic absorption spectrometry-longitudinal zeeman background correction: An evaluation of automated ultrasonic slurry sampling, ultrasound-assisted extraction and microwave-assisted digestion methods. *J. Analytical Atomic Spectrometry* **2000**, *15*, 987–994.
100. Lavilla, I.; Vilas, P.; Bendicho, C. Fast determination of Arsenic, selenium, nickel and vanadium in fish and shellfish by electrothermal atomic absorption spectrometry following ultrasound-assisted extraction. *Food Chemistry* **2007**, *106*, 403–409.
101. Lavilla, I.; Vilas, P.; Millos, J.; Bendicho, C. Development of an ultrasound-assisted extraction method for biomonitoring of vanadium and nickel in the coastal environment under the influence of the prestige fuel spill (North East Atlantic Ocean). *Analytical Chimica Acta* **2006**, *577*, 119–125.
102. Méndez, H.; Álava, F.; Lavilla, I.; Bendicho, C. Ultrasonic extraction combined with fast furnace analysis as an improved methodology for total selenium determination in seafood by electrothermal-atomic absorption spectrometry. *Analytica Chimica Acta* **2002**, *452*, 217–222.
103. Lavilla, I.; Mosquera, A.; Millos, J.; Cameselle, J.; Bendicho, C. Ultrasound-assisted extraction technique for establishing selenium contents in breast cancer biopsies by zeeman-electrothermal atomic absorption spectrometry using multi-injection. *Analytica Chimica Acta* **2006**, *566*, 29–36.
104. Río-Segade, S.; Bendicho, C. Ultrasound-assisted extraction for mercury speciation by the flow injection-cold vapor technique. *J. Analytical Atomic Spectrometry* **1999**, *14*, 263–268.
105. Lavilla, I.; Pérez-Cid, B.; Bendicho, C. Leaching of heavy metals from an aquatic plant (Lagarosiphon major) used as environmental biomonitor by ultrasonic extraction. *International J. Environmental Analytical Chem.* **1998**, *72*, 47–57.
106. Filgueiras, A. V.; Capelo, J. L.; Lavilla, I.; Bendicho, C. Comparison of ultrasound-assisted extraction and microwave-assisted digestion for determination of magnesium, manganese and zinc in plant samples by flame atomic absorption spectrometry. *Talanta* **2000**, *53*, 433–441.
107. García-Rey, R. M.; Quiles-Zafra, R.; Luque de Castro, M. D. New methods for acceleration of metal sample preparation prior to determination of the metal content by atomic absorption spectrometry. *Analytical and Bioanalytical Chem.* **2003**, *377*, 316–321.
108. Filgueiras, A. V.; Lavilla, I.; Bendicho, C. Ultrasound-assisted solubilization of trace and minor metals from plant tissue using ethylenediaminetetraacetic acid in alkaline medium. *Fresenius' J. Analytical Chem.* **2001**, *369*, 451–456.
109. Balarama Krishna, M. V.; Ranjit, M.; Karunasagar, D.; Arunachalam, J. A rapid ultrasound-assisted thiourea extraction method for the determination of inorganic and methyl mercury in biological and environmental samples by CVAAS. *Talanta* **2005**, *67*, 70–80.
110. Chen, D.; Lázaro, F.; Luque de Castro, M. D.; Valcárcel, M. Direct spectrophotometric determination of total boron in soils with ultrasonic leaching in automatic flow systems. *Analytical Chimica Acta* **1989**, *226*, 221–227.
111. Lázaro, F.; Luque de Castro, M. D.; Valcárcel, M. Direct introduction of solid samples into continuous-flow systems by use of ultrasonic irradiation. *Analytica Chimica Acta* **1991**, *242*, 283–289.
112. Herrera, M. C.; Luque de Castro, M. D. Dynamic approach based on iiterative change of the flow direction for microwave-assisted leaching of cadmium and lead from plant prior to GF-AAS. *J. Analytical Atomic Spectrometry* **2002**, *17*, 1530–1533.
113. Shiowatana, J.; Tantidanai, N.; Nookabkaew, S.; Nacapricha, D. A novel continuous-flow sequential extraction procedure for metal speciation in solids. *J. Environmental Quality* **2001**, *30*, 1195–1205.

Downloaded At: 02:47 30 January 2011

114. Moreno-Cid, A.; Yebra, M. C. Flow injection determination of copper in mussels by flame atomic absorption spectrometry after on-line continuous ultrasound-assisted extraction. *Spectrochimica Acta Part B* **2002**, *57*, 967–974.
115. Priego-Capote, F.; Luque de Castro, M. D. Dynamic ultrasound-assisted leaching of essential macro and micronutrient metal elements from animal feeds prior to flame atomic absorption spectrometry. *Analytical and Bioanalytical Chem.* **2004**, *378*, 1376–1381.
116. Moreno-Cid, A.; Yebra, M. C. Continuous ultrasound-assisted extraction coupled to a flow injection-flame atomic absorption spectrometric system for calcium determination in seafood samples. *Analytical and Bioanalytical Chem.* **2004**, *379*, 77–82.
117. Yebra, M. C.; Moreno-Cid, A.; Cespón, R. M.; Cancela, S. Flame AAS determination of total chromium in mussel samples using a continuous ultrasound-assisted extraction system connected to an on-line flow injection manifold. *Atomic Spectroscopy* **2003**, *24*, 31–36.
118. Yebra, M. C.; Moreno-Cid, A.; Cancela, S. Flow injection determination of copper and iron in seafoods by a continuous ultrasound-assisted extraction system coupled to FAAS. *International J. Environmental Analytical Chem.* **2005**, *85*, 315–323.
119. Yebra, M. C.; Moreno-Cid, A. Continuous ultrasound-assisted extraction of iron from mussel samples coupled to a flow injection-atomic spectrometric system. *J. Analytical Atomic Spectrometry* **2002**, *17*, 1425–1428.
120. Yebra, M. C.; Moreno-Cid, A. On-line determination of manganese in solid seafood samples by flame atomic absorption spectrometry. *Analytica Chimica Acta* **2003**, *477*, 149–155.
121. Moreno-Cid, A.; Yebra, M. C.; Cancela, S.; Cespón, R. M. Flow injection on-line ultrasound-assisted extraction of iron in meat samples coupled to a flame atomic absorption spectrometric system. *Analytical and Bioanalytical Chem.* **2003**, *377*, 730–734.
122. Yebra-Biurrun, M. C.; Moreno-Cid, A.; Cancela-Pérez, S. Fast on-line ultrasound-assisted extraction coupled to a flow injection-atomic absorption spectrometric system for zinc determination in meat samples. *Talanta* **2005**, *63*, 691–695.
123. Cespón-Romero, R. M.; Yebra-Biurrun, M. C. Flow injection determination of lead and cadmium in hair samples from workers exposed to welding fumes. *Analytica Chimica Acta* **2007**, *600*, 221–225.
124. Yebra-Biurrun, M. C.; Cespón-Romero, R. M. Fast ultrasound-assisted extraction of copper, iron, manganese and zinc from human hair samples prior to flow injection flame atomic absorption spectrometric detection. *Analytical and Bioanalytical Chem.* **2007**, *388*, 711–716.
125. Yebra-Biurrun, M. C.; Cancela-Pérez, S.; Moreno-Cid-Barinaga, A. Coupling continuous ultrasound-assisted extraction, preconcentration and flame atomic absorption spectrometric detection for the determination of cadmium and lead in mussel samples. *Analytica Chimica Acta* **2005**, *533*, 51–56.
126. Yebra, M. C.; Cancela, S.; Moreno-Cid, A. Continuous ultrasound-assisted extraction of cadmium from vegetable samples with on-line preconcentration coupled to a flow injection-flame atomic spectrometric system. *International J. Environmental Analytical Chem.* **2005**, *85*, 305–313.
127. Cancela, S.; Yebra, M. C. Flow injection setermination of Cd in meat samples using a continuous lixiviation/preconcentration system coupled to a flame AAS. *Atomic Spectroscopy* **2005**, *26*, 110–116.
128. Yebra, M. C.; Cancela, S. Continuous ultrasound-assisted extraction of cadmium from legumes and dried fruit samples coupled with on-line preconcentration-flame atomic absorption spectrometry. *Analytical and Bioanalytical Chem.* **2005**, *382*, 1093–1098.
129. Cancela, S.; Yebra, M. C. Flow-injection flame atomic absorption spectrometric determination of trace amounts of cadmium in solid and semisolid milk products coupling a continuous ultrasound-assisted extraction system with the online preconcentration on a chelating aminomethylphosphoric acid resin. *J. AOAC International* **2006**, *89*, 185–191.
130. Yebra, M. C.; Cancela, S.; Cespón, R. M. Automatic determination of nickel in foods by flame atomic absorption spectrometry. *Food Chem.* **2008**, *108*, 774–778.
131. Yebra-Biurrun, M. C.; Cancela-Pérez, S. Continuous approach for ultrasound-assisted acid extraction-minicolumn preconcentration of chromium and cobalt from seafood samples prior to flame atomic absorption spectrometry. *Analytical Sciences* **2007**, *23*, 993–996.
132. Cespón-Romero, R. M.; Yebra-Biurrun, M. C. Determination of trace amounts of zinc in welding fumes by flow-injection flame atomic absorption spectrometry. *Spectroscopy Letters* **2006**, *39*, 727–735.
133. Cespón-Romero, R. M.; Yebra-Biurrun, M. C. Application of factorial designs for optimisation of on-line determination of cadmium, lead and nickel in welding fumes by atomic absorption spectrometry. *International J. Environmental Analytical Chem.* **2008**, *88*, 539–547.
134. Yebra, M. C.; Cespón, R. M. Determination of hexavalent chromium in welding fumes by flow injection flame atomic absorption apectrometry after dynamic alkaline ultrasound-assisted extraction/anion exchange preconcentration. *Atomic Spectroscopy* **2008**, *29*, 27–31.
135. Zlotorzynski, A. The application of microwave radiation to analytical and environmental chemistry. *Critical Reviews in Analytical Chem.* **1995**, *25*, 43–76.
136. Jin, Q.; Liang, F.; Zhang, H.; Zhao, L.; Huan, Y.; Song, D. Application of microwave techniques in analytical chemistry. *Trends in Analytical Chem.* **1999**, *18*, 479–484.
137. Abu-Samra, A.; Morris, J. S.; Koirtyohann, S. R. Wet ashing of some biological samples in a microwave oven. *Analytical Chem.* **1975**, *47*, 1475–1477.
138. Agazzi, A.; Pirola, C. Fundamentals, methods and future trends of environmental microwave sample preparation. *Microchemical J.* **2000**, *67*, 337–341.
139. Srogi, K. A review: Application of microwave techniques for environmental analytical chemistry. *Analytical Letters* **2006**, *39*, 1261–1288.
140. Zhou, C. Y.; Wong, M. K.; Koh, L. L. Microwave-assisted dilute acid extraction of trace metals from biological samples for atomic absorption spectrometric determination. *J. Analytical Atomic Spectrometry* **1996**, *11*, 585–590.
141. Bermejo-Barrera, P.; Moreda-Piñeiro, A.; Muñiz-Naveiro, O.; Gómez-Fernández, A. M. J.; Bermejo-Barrera, A. Optimization of a microwave-pseudo-digestion procedure by experimental designs for the determination of trace elements in seafood products by atomic absorption spectrometry. *Spectrochimica Acta Part B* **2000**, *55*, 1351–1371.
142. Borkowska-Burnecka, J. Microwave assisted extraction for trace element analysis of plant materials by ICP-AES. *Fresenius' J. Analytical Chem.* **2000**, *358*, 633–637.
143. Seco-Gesto, E. V.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. Multi-element determination in raft mussels by fast microwave-assisted acid leaching and inductively coupled plasma-optical emission spectrometry. *Talanta* **2007**, *72*, 1178–1185.
144. Serafimovxki, I.; Karadjova, I. B.; Stafilov, T.; Tsalev, D. L. Determination of total arsenic and toxicologically relevant arsenic species in fish by using electrothermal and hydride generation atomic absorption spectrometry. *Microchemical J.* **2006**, *83*, 55–60.
145. Soriano, S.; Pereira Netto, A. D.; Cassella, R. J. Multivariate optimization of a microwave-assisted leaching procedure using dilute acid solutions for faas determination of cu, fe, mn, and zn in multivitamin/multimineral supplements. *Analytical and Bioanalytical Chem.* **2007**, *387*, 1113–1120.
146. Costa, L. M.; Gouveia, S. T.; Nóbrega, J. A. Comparison of heating extraction procedures for Al, Ca, Mg and Mn in tea samples. *Analytical Sci.* **2002**, *18*, 313–318.
147. Fernández-Pérez, V.; García-Ayuso, L. E.; Luque de Castro, M. D. Focused microwave Soxhlet device for rapid extraction of mercury,

Downloaded At: 02:47 30 January 2011

arsenic and selenium from coal prior to atomic fluorescence detection. *Analyst* **2000**, *125*, 317–322.
148. Fisher, J. A.; Scarlett, M. J.; Stott, A. D. Accelerated solvent extraction: An evaluation for screening of soils for selected U.S. EPA semivolatile organic priority pollutants. *Environmental Sci. Technol.* **1997**, *31*, 1120–1127.
149. Giergielewicz-Mozajska, H.; Dabrowski, L.; Namiesnik, J. Accelerated solvent extraction (ASE) in the analysis of environmental solid samples–Some aspects of theory and practice. *Critical Reviews in Analytical Chem.* **2001**, *31*, 149–165.
150. Carabias-Martínez, R.; Rodríguez-Gonzalo, E.; Revilla-Ruiz, P.; Hernández-Méndez, J. Pressurized lliquid extraction in the analysis of food and biological samples. *J Chromatography A* **2005**, *1089*, 1–17.
151. Kronholm, J.; Hartonen, K.; Riekkola, M.-L. Analytical extractions with water at elevated temperatures and pressures. *Trends in Analytical Chem.* **2007**, *26*, 396–412.
152. Alonso-Rodríguez, E.; Moreda-Piñeiro, J.; López-Mahía, P.; Prada-Rodríguez, D.; Fernández-Fernández, E.; Muniategui-Lorenzo, S.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. Pressurized liquid extraction of organometals and its feasibility for total metal extraction. *Trends in Analytical Chem.* **2006**, *25*, 511–519.
153. Rico Varadé, C. M.; Luque de Castro, M. D. Determination of selenium in solid samples by continuous subcritical water extraction, flow injection derivatisation and atomic fluorescence detection. *J. Analytical Atomic Spectrometry* **1998**, *13*, 787–791.
154. Fernández-Pérez, V.; Jiménez-Carmona, M. M.; Luque de Castro, M. D. Continuous extraction with acidified subcritical water of arsenic, selenium and mercury from coal prior to on-line derivatisation-atomic fluorescence detection. *J. Analytical Atomic Spectrometry* **1999**, *14*, 1761–1765.
155. Jiménez-Carmona, M. M.; Fernández-Pérez, V.; Gualda-Bueno, M. J.; Cabanás-Espejo, J. M.; Luque de Castro, M. D. Acidified subcritical water extraction of major ash-forming elements from coal. *Analytica Chimica Acta* **1999**, *395*, 113–118.
156. Salvador, F.; Merchán, M. D. USA Patent 5,400,642, 1995.
157. Morales-Muñoz, S.; Luque-García, J. L.; Luque de Castro, M. D. Acidified pressurized hot water for the continuous extraction of cadmium and lead from plant materials prior to ETAAS. *Spectrochimica Acta Part B* **2003**, *58*, 159–165.
158. Fernández-Pérez, V.; Jiménez-Carmona, M. M.; Luque de Castro, M. D. Continuous liquid–liquid extraction using modified subcritical water for the demetalisation of used industrial oils. *Analytica Chimica Acta* **2001**, *433*, 47–52.
159. Morales-Muñoz, S.; Luque-García, J. L.; Luque de Castro, M. D. Demetalization of oils resulting from recycled tires by liquid–liquid extraction using modified superheated water. An environmentally friendly approach. *Talanta* **2004**, *63*, 391–396.
160. Morales-Muñoz, S.; Luque-García, J. L.; Luque de Castro, M. D. Pressurised liquid–liquid extraction. An approach to the removal of inorganic non-metal species from used industrial oils. *Chemosphere* **2004**, *56*, 943–947.
161. Morales-Riffo, J. J.; Richter, P. Rapid determination of inorganic elements in airborne particulate matter by using acidified subcritical-water extraction and inductively-coupled plasma–optical-emission spectrometry. *Analytical and Bioanalytical Chem.* **2004**, *380*, 129–134.
162. Tavakoli, O.; Yoshida, H. Effective recovery of harmful metal ions from squid wastes using subcritical and supercritical water treatments. *Environmental Sci. Technol.* **2005**, *39*, 2357–2363.
163. Webb, B. L.; Hanks, D. H.; Jolley, V. D. A pressurized hot water extraction method for boron. *Communication on Soil Science and Plant Analysis* **2002**, *33*, 31–39.
164. Zougagh, M.; Valcárcel, M.; Ríos, A. Supercritical fluid extraction: A critical review of its analytical usefulness. *Trends in Analytical Chem.* **2004**, *23*, 399–405.
165. Heltai, G.; Percsich, K.; Halász, G.; Jung, K.; Fekete, I. Estimation of ecotoxicological potential of contaminated sediments based on a sequential extraction procedure with supercritical CO_2 and subcritical H_2O solvents. *Microchemical J.* **2005**, *79*, 231–237.
166. Wanekaya, A. K.; Myung, S.; Sadik, O. A. Pressure assisted chelating extraction: A novel technique for digesting metals in solid matrices. *Analyst* **2002**, *127*, 1272–1276.
167. Alonso-Rodríguez, E.; Moreda-Piñeiro, J.; López-Mahía, P.; Muniategui-Lorenzo, S.; Prada-Rodríguez, D.; Moreda-Piñeiro, A.; Bermejo-Barrera, P. Use of chelating solvent-based pressurized liquid extraction combined with inductively coupled plasma-optical emission spectrometry for trace element determination in atmospheric particulate matter. *J. Analytical Atomic Spectrometry* **2007**, *22*, 1089–1096.
168. Maurí-Aucejo, A. R.; Arnandis-Chover, T.; Marín-Sáez, R.; Llobat-Estellés, M. Application of pressurized fluid extraction to determine cadmium and zinc in plants. *Analytica Chimica Acta* **2007**, *581*, 78–82.
169. Moreda-Piñeiro, J.; Alonso-Rodríguez, E.; López-Mahía, P.; Muniategui-Lorenzo, S.; Fernández-Fernández, E.; Prada-Rodríguez, D.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. Pressurized liquid extraction as a novel sample pre-treatment for trace element leaching from biological material. *Analytica Chimica Acta* **2006**, *572*, 172–179.
170. Moreda-Piñeiro, J.; Alonso-Rodríguez, E.; López-Mahía, P.; Muniategui-Lorenzo, S.; Prada-Rodríguez, D.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P. As, Cd, Cr, Ni and Pb pressurized liquid extraction with acetic acid from marine sediment and soil samples. *Spectrochimica Acta Part B* **2006**, *61*, 1304–1309.
171. Moreda-Piñeiro, J.; Alonso-Rodríguez, E.; López-Mahía, P.; Muniategui-Lorenzo, S.; Prada-Rodríguez, D.; Moreda-Piñeiro, A.; Bermejo-Barrera, P. Determination of major and trace elements in human scalp hair by pressurized-liquid extraction with acetic acid and inductively coupled plasma-optical emission spectrometry. *Analytical and Bioanalytical Chem.* **2007**, *388*, 441–449.
172. Moreda-Piñeiro, J.; Alonso-Rodríguez, E.; López-Mahía, P.; Muniategui-Lorenzo, S.; Prada-Rodríguez, D.; Moreda-Piñeiro, A.; Bermejo-Barrera, P. Development of a new sample pre-treatment procedures based on pressurized liquid extraction for the determination of metals in edible seaweed. *Analytica Chimica Acta* **2007**, *598*, 95–102.
173. Holme, D. J.; Peck, H. *Analytical Biochemistry,* 2nd ed.; Wiley & Sons: New York, 1994.
174. Peña-Farfal, C.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P.; Pinochet-Cancino, H.; de Gregori-Henríquez, I. Use of enzymatic hydrolysis for the multi-element determination in mussel soft tissue by inductively coupled plasma-atomic absorption spectrometry. *Talanta* **2004**, *64*, 671–681.
175. Carpenter, R. C. The determination of cadmium, copper, lead and thallium in human liver and kidney tissue by flame atomic absorption spectrometry after enzymatic digestion. *Analytica Chimica Acta* **1981**, *125*, 209–213.
176. Vale, G.; Rial-Otero, R.; Mota, A.; Fonseca, L.; Capelo, J. L. Ultrasonic-Assisted Enzymatic Digestion (USAED) for total elemental determination and elemental speciation: A tutorial. *Talanta* **2008**, *75*, 872–884.
177. Abou-Shakra, F. R.; Rayman, M. P.; Ward, N. I.; Hotton, V.; Bastian, G. Enzymatic digestion for the determination of trace elements in blood serum by inductively coupled plasma mass spectrometry. *J. Analytical Atomic Spectrometry* **1997**, *12*, 429–433.
178. Bermejo-Barrera, P.; Fernández-Nocelo, S.; Moreda-Piñeiro, A.; Bermejo-Barrera, A. Usefulness of enzymatic hydrolysis procedures based on the use of pronase e as sample pre-treatment for multi-element determination in biological materials. *J. Analytical Atomic Spectrometry* **1999**, *14*, 1893–1900.
179. Tan, Y.; Marshall, W. D. Enzymic digestion–high-pressure homogenization prior to slurry introduction electrothermal atomic absorption spectrometry for the determination of selenium in plant and animal tissues. *Analyst* **1997**, *122*, 13–18.
180. Chen, X.; Marshall, W. D. Enzymatic digestion-high-pressure homogenization prior to slurry introduction graphite furnace atomic

Downloaded At: 02:47 30 January 2011

absorption spectrometry for selenium determination in plant and animal tissues. *J. Agricultural and Food Chem.* **1999**, *47*, 3727–3732.
181. Chen, H.; Hu, W.; Li, S. Q.; Wang, M. Direct determination of Cd and Pb in gel forming konjac samples by enzymatic hydrolysis assisted slurry sampling graphite furnace atomic absorption spectrometry. *Mikrochimica Acta* **2008**, *162*, 133–139.
182. Peña-Farfal, C.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P.; Pinochet-Cancino, H.; de Gregori-Henríquez, I. Speeding up enzymatic hydrolysis procedures for the multi-element determination in edible seaweed. *Analytica Chimica Acta* **2005**, *548*, 183–191.
183. Peña-Farfal, C.; Moreda-Piñeiro, A.; Bermejo-Barrera, A.; Bermejo-Barrera, P.; Pinochet-Cancino, H.; de Gregori-Henríquez, I. Ultrasound bath-assisted enzymatic hydrolysis procedures as sample pretreatment for the multielement determination in mussels by inductively coupled plasma atomic absorption spectrometry. *Analytical Chem.* **2004**, *76*, 3541–3547.
184. Capelo, J. L.; Ximénez-Embún, P.; Madrid-Albarrán, Y.; Cámara, C. Enzymatic probe sonication: Enhancement of protease-catalyzed hydrolysis of selenium bound to proteins in yeast. *Analytical Chem.* **2004**, *76*, 233–237.

Downloaded At: 02:47 30 January 2011