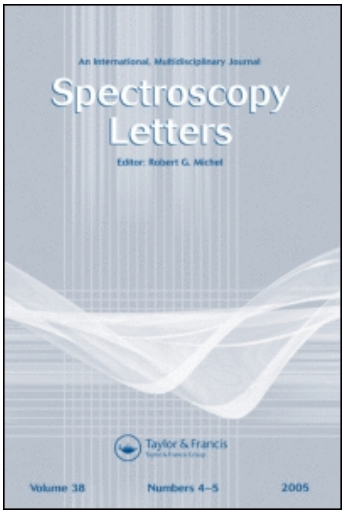

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Ultrasonic Extraction-Ozonation Sequential Sample Treatment for the Determination of Arsenic in Environmental Certified Reference Materials by Hydride Generation-Atomic Fluorescence Spectrometry

Carmen Fernández-Costas[a]; Isela Lavilla[a]; Carlos Bendicho[a]
[a] Departamento de Química Analítica y Alimentaria, Area de Química Analítica, Facultad de Química, Universidad de Vigo, Vigo, Spain

To cite this Article Fernández-Costas, Carmen , Lavilla, Isela and Bendicho, Carlos(2006) 'Ultrasonic Extraction-Ozonation Sequential Sample Treatment for the Determination of Arsenic in Environmental Certified Reference Materials by Hydride Generation-Atomic Fluorescence Spectrometry', Spectroscopy Letters, 39: 6, 713 — 725
To link to this Article: DOI: 10.1080/00387010600934717
URL: http://dx.doi.org/10.1080/00387010600934717

Spectroscopy Letters, 39: 713–725, 2006

ISSN 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010600934717

Ultrasonic Extraction–Ozonation Sequential Sample Treatment for the Determination of Arsenic in Environmental Certified Reference Materials by Hydride Generation–Atomic Fluorescence Spectrometry

Carmen Fernández-Costas, Isela Lavilla, and Carlos Bendicho

Departamento de Química Analítica y Alimentaria, Area de Química Analítica, Facultad de Química, Universidad de Vigo, Vigo, Spain

Abstract: A sample pretreatment method based on ultrasound-assisted extraction followed by ozonation is developed for sensitive determination of total As in biological and environmental certified reference materials and an unknown plant sample (*Acacia dealbata*) by flow injection and continuous-flow hydride generation–atomic fluorescence spectrometry. The method is meant to minimize the use of corrosive and oxidizing acids for sample decomposition and common errors in trace analysis. Problems derived from introduction of sonicated extracts in continuous flow and flow injection manifolds in combination with an atomic fluorescence detector, such as excessive foaming and flame instability, are addressed. The following certified reference materials (CRMs) were employed for method assessment: BCR CRM 482 lichen; BCR CRM 60 and 61 aquatic plants; BCR CRM 279 sea lettuce; NIST 1633b fly ash; BCR 320 river sediment; RTC CRM 024-050 soil. Effect of variables such as extraction time, ultrasound amplitude, concentration of extractant acid,

Received 25 March 2006, Accepted 31 July 2006

The authors were invited to contribute this paper to a special issue of the journal entitled "Spectroscopy and Automation". This special issue was organized by Miguel de la Guardia, Professor of Analytical Chemistry at Valencia University, Spain.

Address correspondence to Carlos Bendicho, Departamento de Química Analítica y Alimentaria, Area de Química Analítica, Facultad de Química, Universidad de Vigo, Campus As Lagoas-Marcosende s/n, 36310 Vigo, Spain. Fax: +34-986-812556; E-mail: bendicho@uvigo.es

sample mass, drying mode, and particle size was investigated. Leaves of *Acacia dealbata* were also employed for method development. Limits of detection ranged from 0.03 to 0.15 μg/g As depending on the sample. Between-batch precision values ranged from 2% to 11%. Sample throughput was 40 hr^{-1} with flow injection.

Keywords: Arsenic, arsine generation, atomic fluorescence spectrometry, flow injection, fly ash, ozonation, plant, sediment, soil, ultrasonic extraction

INTRODUCTION

At present, hydride generation in combination with an atomic detector is a well-established technique for As determination in a huge variety of samples on a routine basis.[1] For efficient arsine generation, matrix decomposition by an intensive treatment using dry or wet oxidation is required. Nitric acid, which is usually present in the acid digests, strongly interferes with arsine generation and the prereduction of the As(V) formed upon oxidizing conditions to As(III).[2] This prereduction is recommended for maximum sensitivity.[3] Ultrasonic extraction has emerged as a promising technique to simplify sample pretreatment in trace element analysis.[4] Trace metals and metalloids can be efficiently extracted from the solid under mild conditions (i.e., room temperature, normal pressure) using low reagent consumption, usually a diluted acid.[5] This, in turn, brings about some benefits concerning production of laboratory wastes, which are drastically decreased with ultrasonic extraction procedures. More importantly, possible errors in trace analysis caused by volatilization or sample contamination are diminished. Several applications of ultrasound-assisted extraction have been reported for As determination in biological and environmental samples by electrothermal atomic absorption spectrometry.[6,7]

Hydride generation (HG) allows circumvention of many limitations inherent to sample introduction into the atomic detector, but efficient arsine generation requires the breakdown of organic As species that are nonreactive toward sodium borohydride and elimination of organic matrix. These shortcomings are mainly evident when extracts obtained upon sonication instead of digests derived from wet oxidation or dry ashing procedures are employed as the analytical sample. In past years, novel strategies for sample pretreatment in the hydride generation technique have been addressed to the use of ozone as a single oxidizing agent (ozonation)[8] or in combination with ultrasound (sonozonation).[9] In these applications, hydride generation-atomic absorption spectrometry (AAS) and hydride generation-electrothermal-atomic absorption spectrometry (ETAAS) following *in situ* trapping have been reported for determination of As in a variety of biological and environmental samples. Atomic fluorescence spectrometry (AFS) has become very popular during past years as an extremely sensitive technique for determination of toxic elements that form volatile covalent hydrides.

This technique displays better detection limits for hydride-forming elements (As, Sb, Se . . .), less spectral and matrix interferences, and wider linear dynamic range than AAS.[10] AFS is competitive with inductively coupled plasma–mass spectrometry (ICP-MS) in detection capability, having lower purchase price and operating costs, which makes it more attractive for routine analysis.[11] In addition, serious polyatomic interferences arise in ICP-MS (e.g., $^{75}ArCl^{+}$ interferes with mono-isotopic $^{75}As^{+}$), which can be solved with collision cell ICP-MS instruments.[10] Accordingly, HCl (i.e., a nonoxidant acid commonly recommended for ultrasonic extraction) should not be employed for detection by ICP-MS unless sophisticated instruments are employed.

So far, application of HG-AFS has been limited to determination of total As using complete sample dissolution by an acid digestion procedure.[12–14] Nevertheless, no work has been reported concerning less intensive sample pretreatment methods based on the use of ultrasound. In this work, As extraction from a variety of certified reference materials (plant, soil, fly ash, sediment) using probe sonication and determination by continuous flow (CF) and flow injection (FI)-HG-AFS is performed. The enhanced sensitivity of atomic fluorescence as compared with, for example, atomic absorption, makes it possible to omit prereduction of As(V) to As(III) prior to arsine generation. Influence of extraction parameters including treatment time and ultrasound amplitude as well as other factors such as the effect of sample drying and particle size on extraction are addressed.

MATERIALS AND METHODS

Instrumentation

An Excalibur (PS Analytical, Kent, UK) model atomic fluorescence detector (AFD) equipped with an integrated continuous hydride generation system and an As-boosted hollow cathode lamp (Photron, Victoria, Australia) was employed. Arsine generation was carried out using a chemifold, a gas–liquid separator made of glass and two peristaltic pumps. Argon was used as carrier gas in the gas–liquid separator. The gas was dried by means of a hygroscopic membrane drying tube (Perma Pure Products, Farmingdale, USA) before entering the flame. Nitrogen was used as the drying gas at a flow rate of 2.5 L/min. Optimal instrumental parameters are shown in Table 1. Flow injection operation was carried out by using a Chemiert model C12 eight-port external volume sample injector (Valco instruments Co., Houston, TX, USA) incorporating a 500 μL capacity loop. A four-channel peristaltic pump (Ismatec, Zurich, Switzerland) was employed for introducing extracts into the sampling loop. The complete system is depicted in Fig. 1. A 100-W, 20-kHz VC-100 ultrasonic processor (Sonics and Materials, Danbury, CT, USA) equipped with a 6-mm titanium microtip was used for solid–liquid extraction

Table 1. Instrument parameters (flow injection and continuous flow)

Atomic fluorescence detector	
Wavelength (nm)	193.7
Bandpass (nm)	0.5
Primary current (mA)	27.5
Boost current (mA)	35
Range	100
Continuous hydride generation	
[$NaBH_4$] (%) (m/v)	0.7
[HCl] (%) (v/v)	30
N_2 flow rate (L/min)	2.5
Ar flow rate (L/min)	0.3
$NaBH_4$ flow rate (mL/min)	4
HCl flow rate (mL/min)	8
Signal adquisition	
Delay (s)	10
Analysis (s)	20
Memory (s)	50

of As. A centrifuge (model 2–16; Sigma, Germany) was used for fast separation of the supernatant from the solid residue. Ozone was generated from air with a Sogatec model D3-E generator (ozone generation rate of 200 mg/h) (Ourense, Spain). A CEM microwave oven, model MDS-2000 (Matthews, NC, USA) was used for digestion of *Acacia dealbata* samples. The CEM system is equipped with a pressure monitoring option and allowed to operate at a power of up to 630 ± 50 W (100% full power). The following drying devices and conditions were used: a Telstar Model Cryodos-50 Lyophilizer

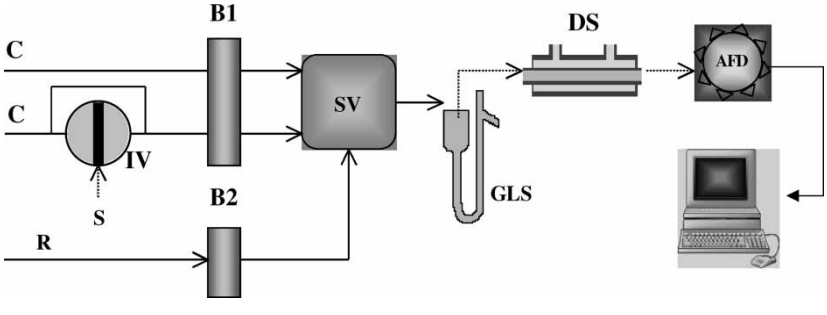

Figure 1. Schematic diagram showing the flow injection–atomic fluorescence spectrometry system. B1, B2, peristaltic pumps; SV, selection valve; IV, injection valve; DS, drying system; GLS, gas–liquid separator; AFD, atomic fluorescence detector; C, carrier; R, reducing agent.

(Tarrasa, Spain); freeze-drying was performed at ca. −50°C temperature and a pressure in the range 0.058–0.076 mB. A domestic microwave oven (Samsung) operated at 100 W power. A Selecta oven-heater (Barcelona, Spain) operated at 50°C. Air drying was carried out inside a laminar flow hood (Telstar, micro-H, Tarrasa, Spain). Drying times with each method were as follows: oven drying, 48 hr; microwave drying, 4 hr; freeze-drying, 36 hr; air drying, 15 days. Sieves made of nylon with mesh sizes of <50, <100, and <200 μm were used.

Reagents

All chemicals were of analytical reagent grade. Deionized water from a Milli-Q water purifier (Millipore, Molsheim, France) was used throughout. Arsenic standard solutions (1000 μg/mL) were made from $Na_2HAsO_4 \cdot 7H_2O$ (Panreac, Barcelona, Spain). Diluted working standards for calibration were made from the As(V) stock standard solution. $(CH_3)_2HAsO_2$] (DMA; Riedel-de Haën, Seelze, Germany) and $CH_3AsO(ONa)_2$ $6H_2O$ (MMA; Carlo Erba, Italy) and As_2O_3 (Merck, Germany) were also employed for evaluation of the ozonation treatment. For hydride generation, 0.7% (w/v) sodium tetrahydroborate (III) (Merck) and 30% (v/v) hydrochloric acid (Merck) solutions were used. The $NaBH_4$ solution was daily prepared by diluting the appropriate amount of $NaBH_4$ powder in an 0.4% (w/v) NaOH (Carlo Erba) solution and filtered before use.

Samples

The following certified reference materials (CRMs) certified in total As concentration were used for evaluation of the proposed procedure: BCR 482 (Lichen), BCR 279 (Sea lettuce), BCR 60 (*Lagarosiphon major*), BCR 61 (*Platihypnidium riparoides*), BCR 320 (river sediment) from the Community Bureau of Reference (Brussels, Belgium); NIST 1633b (coal fly ash) from the National Institute of Standards and Technology (Gaithersburg, MD, USA); RTC 024-050 (soil) from the R.T. Corporation (Laramie, Wyoming, USA).

Leaves from *Acacia dealbata* were collected in Vigo town and used as target sample so as to study the influence of particle size and drying operation on As extraction. Several trees were selected in order to obtain a representative sample. The height of sampling was about 1.5 m. Leaves were collected with plastic gloves and introduced into decontaminated plastic bottles. Once in the laboratory, leaves were subjected to a soft cleaning procedure to eliminate soil-dust contamination and minimize arsenic leaching from plant tissue. Leaves were washed with a chloroform–water (1:1) solution for 10 s, rinsed three times with deionized water, and dried. This procedure proved useful for sample pretreatment in the

determination of Cd and Pb in leaves of *Platanus occidentalis* and *Pinus sylvestris*.[15] For studying the influence of drying mode on the extracted As content, the four drying systems mentioned above were used (i.e., freeze-drying, microwave drying, oven drying, and air drying). Once dried, leaves were ground with a mixer mill equipped with agate balls for 5 min. Sample separation into different particle size fractions was carried out by sieving. Three fractions were chosen for analysis: $Ø < 50$ μm, $100 < Ø < 200$ μm, and $Ø > 200$ μm. Samples were stored in a dessicator until analysis.

Analytical Procedures

Ultrasonic Extraction

Ultrasonic extraction was performed in polyethylene tubes (50-mL capacity) inserted in an ice bath so that the temperature did not exceed 25°C during the ultrasonic treatment. A 10–100 g portion of sample was placed in the polyethylene tube and 20 mL of 30% (v/v) HCl was added. Sonication was performed for 3 min at 80% amplitude, and then it was centrifuged for 15 min at 7500 rpm. The supernatant was filtered through 0.45-μm supported membrane filters in order to get a particle-free extract that can be incorporated into the sample loop without any risk of clogging. Ozone was introduced through a PTFE capillary into the extract for 40 min (*warning*: ozonation must be performed in a fume cupboard). Excess ozone remaining after treatment was purged from the extract by ultrasonic degassing (3-min probe sonication).

Microwave Digestion

The following general procedure was employed for digestion of *Acacia dealbata* samples: a portion of 400 mg was weighed into PTFE advanced digestion vessels, the digestion acids were added [5 mL of 65 %w/w HNO_3 and 0.5 mL of 48% (w/w) HF] and then the reactor was closed and heated under a preselected program (two stages of 1min at 40 and 80 psi, respectively, and a final stage at 120 psi for 5 min; the power used was 300 W). The contents of each vessel were heated to dryness and dissolved with 1 mL of HCl; the solution was quantitatively transferred into a 25-mL volumetric flask and made up to volume with 30% (v/v) HCl. Blanks were treated in the same way.

RESULTS AND DISCUSSION

Optimization of the Ultrasound-Assisted Extraction of As

Application of ultrasound irradiation for metal extraction has shown that sonication time (i.e., time for which a suspension of the finely powdered

material is subjected to ultrasound irradiation), ultrasound amplitude, and acidity of the extractant are the most significant variables.[5,9] However, other features such as the effect of the drying operation and particle size have scarcely been addressed and should also be investigated. Previous work carried out by this group on As extraction from several matrices using HG-AAS as the measurement technique has indicated the need for HCl as extractant at a concentration higher than 25% (v/v).[9] Prereduction of As(V) to As(III) for maximum sensitivity after ultrasonic extraction was hampered by the presence of coextracted matrix. AFS should overcome the lack of sufficient detection power of AAS for samples containing low As contents, hence avoiding the prereduction step. To tackle the direct introduction of extracts obtained upon sonication in the HG-AFS technique, several shortcomings have to be overcome. Atomization conditions and stability of the hydrogen diffusion flame are critically dependent on parameters governing the hydride generation reaction. For instance, extracts obtained from some plants caused foaming in the gas–liquid separator and the flame took off very often. Two strategies were followed to overcome these drawbacks, namely, the use of flow–injection instead of continuous flow (i.e., the hydride generation system originally provided for hydride generation in the PSA instrument), and the elimination of organic matter from extracts using ozonation. The effect of the HCl concentration in the sample solution on the atomic fluorescence signal of As was studied. Although a slightly higher peak height of the flow injection signal is observed for the 1% (v/v) HCl solution, less tailing signals are reached on increasing HCl concentration. A 30% (v/v) HCl solution was chosen as the extractant medium,

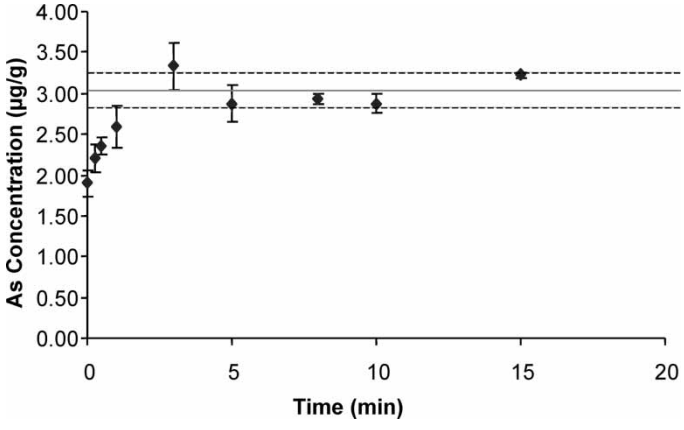

Figure 2. Influence of the sonication time on the As extraction from CRM BCR 279 sea lettuce. The certified concentration and uncertainty interval for this material is shown. Extraction conditions: 40 mg sample mass; 20 mL volume; 50% ultrasound amplitude; 30% (v/v) HCl concentration as extractant.

which is the concentration employed in the carrier as well. Figure 2 shows the effect of the sonication time on As extraction efficiency from BCR CRM 279 sea lettuce, which was employed as target sample for optimization. Extraction efficiency values were close to 100% for a sonication time longer than 3 min using a 50% sonication amplitude. This short time is in agreement with the time required for efficient extraction of other elements using the same ultrasonic processor.[4] Figure 3 shows the effect of sonication amplitude on As extraction efficiency from the same CRM as above. A sonication amplitude higher than 50% was found as optimal for efficient extraction. Experiments addressed to investigate the effect of the sample mass showed that a mass in the range 10–100 mg was suitable to achieve complete extraction of As.

Influence of Particle Size

Usually, small particles facilitate the extraction of the sought analyte from the solid into the liquid medium as a result of the increased contact surface. To study the effect of particle size on extractability of As, *Acacia dealbata* leaves were employed. The As content of this sample was $0.93 \pm 0.12\ \mu g/g$ $(n = 5)$ as measured by HG-AFS after microwave-assisted digestion. The effect of particle size was studied with *Acacia dealbata* samples sieved to have three ranges of particle size: $Ø < 50\ \mu m$, $100 < Ø < 200\ \mu m$, and $Ø > 200\ \mu m$. Although an acceptable extraction efficiency is observed for the fraction with particle size between 100 and 200 μm, a particle size less than 50 μm is recommended. The latter particle size was also found as optimum for extraction of Mn, Mg, and Zn for plant tissue.[16]

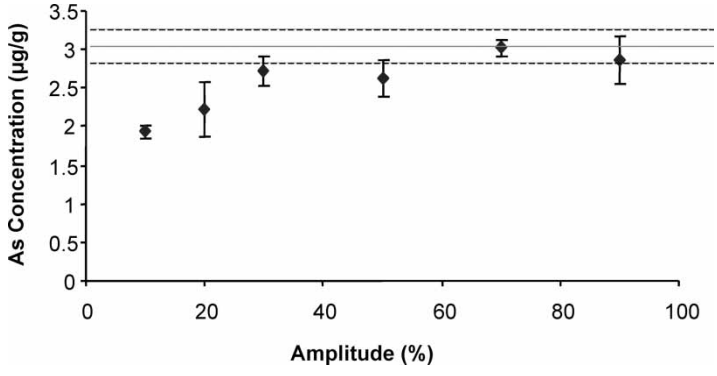

Figure 3. Influence of the ultrasound amplitude (%) on the As extraction from CRM BCR sea lettuce. The certified concentration and uncertainty interval for this material is shown. Extraction conditions: 40 mg sample mass; 20 mL volume; 3 min sonication time; 30% (v/v) HCl concentration as extractant.

Influence of the Drying Operation

The influence of the drying operation has been scarcely considered in ultrasonic extraction procedures. Extraction of Se from slurried seafood samples subjected to ultrasonic mixing has shown that the lowest efficiency was obtained with freeze-drying, other procedures providing similar results.[17] This was attributed to the nondenaturing character of freeze-drying as compared with other drying modes such as oven drying and microwave drying. On the other hand, ultrasonic extraction of easily mobilizable arsenic from river sediment was facilitated with air drying (using a laminar flow hood) and freeze-drying. Nevertheless, oven drying and microwave drying caused a significant decrease in the extractability of several elements (not only As).[18] The influence of the drying mode on As extraction from *Acacia dealbata* samples was established using oven drying, microwave drying, air drying, and lyophilization. Similar As extraction efficiencies are reached with the four drying modes attempted.

Influence of Ozonation

Direct introduction of extracts obtained upon sonication of biological matrices caused several problems in the flow injection or continuous flow system. Excessive foaming took place in the reaction of the sample with $NaBH_4$. This effect, which was mainly observed with terrestrial plants such as lichen and *Acacia dealbata*, caused the hydrogen diffusion flame to blow out. The addition of an antifoaming agent such as silicone was unsuccessful. In order to avoid the use of oxidant acids so that the matrix can be removed, ozone has proved a useful alternative. Ozone is a strong oxidizing agent (redox potential in acid medium: $+2.075$ V) that can oxidize organic matter to carbon dioxide. An increase in the oxidation of organic matter by ozone can be achieved by simultaneously applying ultrasound. Ozonation combined with sonication of powdered biological samples suspended in HCl medium caused organic matrix decomposition (i.e., conversion of proteins and other macromolecular constituents into small molecules) but no carbon dioxide was formed due to the presence of radical scavengers. Total carbon measurement of organic extracts subjected to ozonation did not significantly change in comparison with non-ozonated extracts.[9] Figure 4 shows the influence of the ozonation time on As extraction efficiency. As can be observed, ozone causes the As extraction efficiency to improve. The optimum ozonation time was 40 min. Removal of the excess ozone remaining in the solution was necessary in order to avoid the consumption of sodium borohydride by this oxidizing agent. Therefore, degassing of the solution by ultrasound irradiation was needed after ozonation using a 3-min sonication time at 60% amplitude of the probe vibration. For extracts subjected to ozonation, foaming drastically decreased and no flame instability was observed.

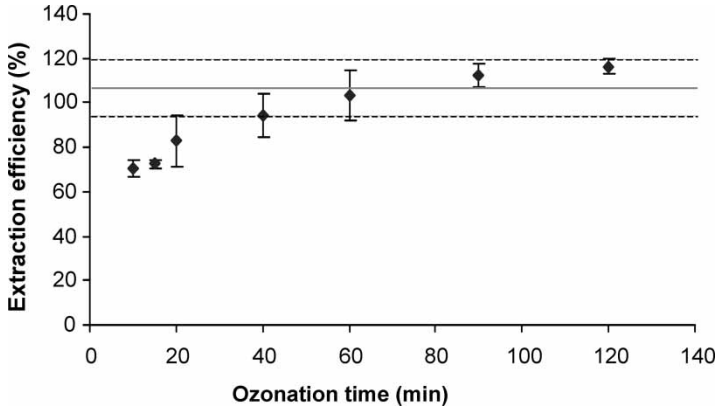

Figure 4. Influence of the ozonation time on the As extraction efficiency from *Acacia dealbata*. Extraction efficiency is expressed as the ratio between the As concentration found with ultrasonic extraction–ozonation and that found with microwave-assisted digestion in percentage.

Analytical Characteristics

The calibration curves using range 100 in the atomic fluorescence detector (1–10 ng/mL As) were the following:

Flow injection mode: $FI = 12.234\ [As] - 1.14$ ($R^2 = 0.9978$)
Continuous flow mode: $FI = 29.331\ [As] - 3.395$ ($R^2 = 0.991$)

FI is fluorescence intensity expressed as arbitrary units, and [As] is As concentration expressed as ng/mL. The detection limit (3 σ criterion) was 0.15 ng/mL (FI) and 0.18 (CF), and the quantification limit (10 σ criterion) was 0.5 ng/mL (FI) and 0.6 ng/mL (CF). Precision study was performed with extracts from CRM BCR 279 sea lettuce. Repeatability measured from a 5 ng/mL As(V) solution and expressed as relative standard deviation was 3.1%.

Analytical Results

A recovery study was also made so as to check whether typical As species present in biological samples were efficiently converted into As(V) upon treatment. An extract obtained from BCR 279 sea lettuce spiked with As(V), As(III), DMA, and MMA was subjected to sonication and subsequent ozonation. Efficiency conversions of these species into As(V) ranged from 93% to 108%, thereby showing the ability of the proposed sample pretreatment to break down those species.

Analytical results for determination of As in certified reference materials of plant tissue, coal fly ash, sediment, and soil are shown in Table 2. Three different extractions from each CRM were measured in quintuplicate. Detection limits of As in the solid materials (dry weight) ranged from 0.03 to 0.15 μg/g As. Between-batch precision values ranged from 2% to 11%.

Average As concentrations found and certified values were statistically compared (*t*-test) as to whether they significantly differed. As can be observed, no significant differences occurred for lichen, sea lettuce, coal fly ash, sediment, and the aquatic plant (BCR 61). Significant differences were observed for the soil and the aquatic plant (BCR 60). The latter plant material was provided with an indicative value. For the soil, there is an overlapping of the uncertainty intervals of the certified and found value meaning an acceptable agreement between both values. As extracted could be measured with ozonation by CF- or FI-HG-AFS. Ozonation and FI-HG-AAS was needed for the determination of As in plant extracts obtained from BCR CRM 482 (lichen) and *Acacia dealbata*.

CONCLUSIONS

Ultrasound-assisted extraction combined with ozonation provides remarkable improvements in the sample pretreatment for determination of As in environmental samples such as plant tissue, soil, sediment, and fly ash by HG-AFS. Corrosive and oxidant acids are unnecessary, and matrix decomposition can be performed at room temperature and normal pressure. A nonoxidant acid such as hydrochloric acid can replace the use of concentrated nitric acid, which is mandatory for efficient organic matrix removal in wet oxidation

Table 2. Analytical results for determination of As in certified reference materials (CRMs)

CRM	Certified value (μg/g)[a]	Found value (μg/g)[b]
BCR CRM 482 (lichen)	0.85 ± 0.07	0.80 ± 0.08
BCR CRM 279 (sea lettuce)	3.09 ± 0.20	2.76 ± 0.16
RTC 024-050 (soil)	3.42 ± 1.14	2.35 ± 0.18
NIST CRM 1633b (fly ash)	136.2 ± 2.6	135 ± 3
BCR CRM 320 (river sediment)	76.7 ± 3.4	87 ± 10
BCR CRM 61 (aquatic plant)[c]	7	8.6 ± 0.8
BCR CRM 60 (aquatic plant)[c]	8	11.1 ± 0.9

[a]Average value ± confidence interval (p = 0.05).
[b]Average value ± standard deviation (n = 3).
[c]Indicative value.

procedures. Besides, nitric acid is a strong interference in the arsine generation methods, and hence, the evaporation step usually recommended to eliminate this acid is not needed. When this sample pretreatment method is employed in conjunction with AFS for detection, the last prereduction step typically carried out to transform As(V) into As(III) for maximum sensitivity can be omitted.

ACKNOWLEDGMENT

Financial support from the Galician government (Xunta de Galicia) (project PGIDIT05PXIB31401PR) is gratefully acknowledged.

REFERENCES

1. Sturgeon, R. E.; Guo, X.; Mester, Z. Chemical vapor generation: are further advances yet possible? *Anal. Bioanal. Chem.* **2005**, *382*, 881–883.
2. Flores, E. M. D.; da Silva, L. L. C.; Barin, J. S.; Saidelles, A. P. F.; Zanella, R.; Dressler, V. L.; Paniz, J. N. G. Minimization of volatile nitrogen oxides inter ference in the determination of arsenic by hydride generation atomic absorption spectrometry. *Spectrochim. Acta B* **2001**, *56*, 1883–1891.
3. Jutta, F.; Krachler, M.; Shotyk, W. Determination of arsenic in peat samples using HG-AFS and l-cysteine as pre-reductant. *J. Anal. At. Spectrom.* **2006**, *21*, 204–207.
4. Ashley, K.; Andrews, R. N.; Cavazos, L.; Demange, M. Ultrasonic extraction as a sample preparation technique for elemental analysis by atomic spectrometry. *J. Anal. At. Spectrom.* **2001**, *16*, 1147–1153.
5. Bendicho, C.; Lavilla, I. Applications of ultrasound-assisted metal extractions. In *Encylopaedia of Separation Science*; Academic Press: London, 2000; pp. 4421–4426.
6. Väisänen, A.; Suontamo, R. 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. Anal. At. Spectrom.* **2002**, *17*, 739–742.
7. Santos, C.; Alava, 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. Anal. At. Spectrom.* **2000**, *15*, 987–994.
8. Matusiewicz, H.; Mroczkowska, M. G. Hydride generation from slurry samples after ultrasonication and ozonation for the direct determination of trace amounts of As(III) and total inorganic arsenic by their in situ trapping followed by graphite furnace atomic absorption spectrometry. *J. Anal. At. Spectrom.* **2003**, *18*, 751–761.
9. Capelo, J. L.; Lavilla, I.; Bendicho, C. Ultrasonic extraction followed by sonolysis-ozonolysis as a sample pretreatment method for determination of reactive arsenic toward sodium tetrahydroborate by flow injection-hydride generation-AAS. *Anal. Chem.* **2001**, *73*, 3732–3736.

10. Chen, B.; Krachler, M.; González, Z. I.; Shotyk, W. Improved determination of As in environmental and geological specimens using HG-AFS. *J. Anal. At. Spectrom.* **2005**, *20*, 95–102.
11. Francesconi, K. A.; Kuehnelt, D. Determination of As species: a critical review of methods and applications. 2000–2003. *Analyst* **2004**, *129*, 373–395.
12. Hanwen, S.; Zhanfeng, L.; Wenjuan, W.; Liqing, L.; Hongmei, S. Simultaneous determination of arsenic and selenium in biological samples by HG-AFS. *Anal. Bioanal. Chem.* **2005**, *382*, 1060–1065.
13. Zhong-Xi, L.; Yue-an, G. Simultaneous determination of trace arsenic, antimony, bismuth and selenium in biological samples by hydride generation-four-channel atomic fluorescence spectrometry. *Talanta* **2005**, *65*, 1318–1325.
14. Wei, L.; Gupta, P.; Hernández, R.; Farhat, F. Determination of ultratrace selenium and arsenic at parts-per-trillion levels in environmental and biological samples by atomic fluorescence spectrometry with flow injection-hydride generation technique. F. *Microchem. J.* **1999**, *62*, 83–98.
15. Amoedo, L.; Capelo, J. L.; Lavilla, I.; Bendicho, C. Evaluation of *Platanus occidentalis* and *Pinus sylvestris* as bioindicators for lead and cadmium by slurry sampling-electrothermal atomic absorption spectrometry. *J. AOAC Int.* **2002**, *85*, 212–218.
16. Filgueiras, A. V.; Capelo, J. L.; Lavilla, I.; Bendicho, C. Comparison of ultrasound-assisted extraction and microwave-assisted digestion for determination of Mg, Mn, and Zn in plant samples by flame-atomic absorption spectrometry. *Talanta* **2000**, *53*, 433–441.
17. Méndez, H.; Alava, F.; Lavilla, I.; Bendicho, C. Determination of Se in marine biological tissues by transverse heated electrothermal atomic absorption spectrometry with longitudinal Zeeman background correction and automated ultrasonic slurry sampling. *J. AOAC Int.* **2001**, *84*, 1921–1926.
18. Huerga, A.; Lavilla, I.; Bendicho, C. Speciation of the immediately mobilisable As(III), As(V), DMA, and MMA in River sediments by high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry following ultrasonic-extraction. *Anal. Chim. Acta* **2005**, *534*, 121–128.