



Magnetic ferrite particles combined with electrothermal atomic absorption spectrometry for the speciation of low concentrations of arsenic

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ABSTRACT

Freshly in situ prepared ferrite particles were used for the micro-solid phase extraction of arsenic species. When the separation was carried out at pH 8, inorganic arsenic (As(III) + As(V)) and monomethylarsonic acid (MMA) were retained in the magnetic material. A second aliquot was treated with 2,3 dimercapto propanol, leading to the retention of As(V) + MMA, while a third aliquot was first treated with sodium thiosulphate, in which case only inorganic arsenic passed to the solid phase. In all cases, the solid residue collected by a magnet was suspended in a dilute nitric acid solution containing Triton X-100 and introduced into the electrothermal atomizer to obtain the analytical signal of arsenic. The use of palladium as a chemical modifier allowed calibration to be carried out with aqueous standards. The detection limit was $0.02 \mu\text{g L}^{-1}$ arsenic for a 10 mL sample volume. The procedure was applied to waters and herbal infusions, and its reliability was evaluated by analyzing eleven certified reference materials for which speciation data are provided.

1. Introduction

The interest in determining arsenic in foods, waters and environmental samples is clear due to both the ubiquitous presence of the element and the toxicity inherent to its compounds [1,2]. However, the task is not easy, since the element has a complicated chemistry with a variety of species. Thus, in addition to arsenite and arseniate, organic compounds such as monomethylarsonic (MMA), dimethylarsinic acids and arsenobetaine (AsB), among other less relevant species, also occur in agricultural, marine and other biological samples [3]. If, instead of determining the total amount of arsenic present, speciation or fractionation is required, the difficulty involved in the determination increases since the total amount of the element, which is usually very low, is distributed among the above mentioned compounds [4]. This means that, in practice, after careful sample preparation in order not to alter the proportion of the species present, some type of chromatographic separation, together with a very sensitive analytical technique such as inductively coupled plasma mass spectrometry (ICP-MS), has to be used [5–7]. While this is a good way to tackle the problem it is without its own difficulties, and an ICP-MS instrument is not always available in a low or medium-size laboratory. By contrast, electrothermal atomic absorption spectrometry (ETAAS) is commonly present in most laboratories and, indeed, is frequently underused. A serious drawback of

ETAAS measurements is the discontinuous way of operation that hinders any combination with column-based chromatography, but it does present the advantage of high sensitivity together with the need for low volumes of liquid samples. Consequently, interest has arisen in recent years into combining ETAAS with modern microextraction techniques [8–10], since the high preconcentration achieved results in reliable and sensitive ETAAS procedures whose performance is comparable or even better than ICP-MS based techniques.

A variety of procedures involving dispersive liquid-liquid or solid-liquid microextraction processes has been devised for the purpose of determining low arsenic concentrations [11]. An interesting alternative to conventional microextraction processes, which usually require a density-based separation, is the use of magnetic particles [12]. In such a case, the separation of phases after the microextraction stage is carried out by means of a magnet, obviating the need for a centrifugation step. This is the way followed herein taking advantage of the excellent adsorptive properties of ferrite nanoparticles towards arsenic species [10,13,14]. To the best of our knowledge, the analytical procedures for arsenic speciation involving magnetic materials are scarce, and only involve inorganic arsenic. This manuscript presents the results of our investigation with freshly prepared ferrite nanoparticles, which resulted in a new, reliable and highly sensitive way for the non-chromatographic speciation of As(III), As(V) and MMA.

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Table 1
Instrumental parameters and furnace heating program.

Parameter	Value		
EDL Lamp current, mA	300		
Wavelength, nm	193.7		
Slit, nm	0.7		
Atomizer	Platform		
Injected sample volume, μL	20		
Chemical modifier	1 μg Pd		
Sample volume, mL	10		
Slurry volume, μL	100		
Suspension media	1% v/v HNO_3 with 1% w/v Triton X-100		
Furnace program			
Stage	Temperature, $^\circ\text{C}$	Ramp, s	Hold, s
1: Dry	110	1	20
2: Dry	130	5	30
3: Ash	1200	10	30
4: Atomization ^a	2200	0	5
5: Clean	2500	1	3

^a Reading stage. The inner gas flow was stopped.

2. Experimental

2.1. Apparatus

All the atomic absorption measurements were carried out with a Perkin-Elmer model 800 spectrometer (Waltham, MA) equipped with a transversely heated graphite atomizer, Zeeman-effect background correction device and autosampler (model AS-800). Pyrolytic graphite platforms inserted into pyrolytically coated tubes were obtained from the same manufacturer. Argon flowing at 250 mL min^{-1} was the inert gas. An electrodeless discharge lamp (EDL, PerkinElmer) operated at 300 mA was used as the radiation source. The instrumental parameters are summarized in Table 1.

The hydride generation atomic fluorescence spectrometric (HGAFS) measurements were carried out with a Millennium Excalibur spectrometer (PS Analytical, Orpington, UK) operating in continuous flow mode, the analytical signal being obtained at 193.7 nm. Argon was used as the carrier. A solution containing 3.5 mol L^{-1} hydrochloric acid, 1% (m/v) potassium iodide and 0.2% (m/v) ascorbic acid was pumped at 9.0 mL min^{-1} and a reducing solution containing 0.6% (m/v) sodium tetrahydroborate stabilized with sodium hydroxide (0.075 mol L^{-1}) was run at 4.5 mL min^{-1} .

Permanent magnets ($50 \times 15 \times 15 \text{ mm}$ blocks weighing 86 g and with a strength of 33 kg) composed of Nd-Fe-B were supplied by Supermagnete (Gottmadingen, Germany). For comparison purposes, complete digestion of the samples was carried out with a Multiwave 3000 microwave digestion system (Anton Paar, Austria). A 50 W ultrasound bath (ATU, Valencia, Spain) was used for the ultrasonic treatment. The studies of the particle size and zeta potential were carried out using a Malvern Zetasizer nano zsp instrument (Malvern, UK).

2.2. Reagent and samples

Pure water ($18 \text{ M}\Omega \text{ cm}$ resistivity) obtained with a Millipore system (Millipore, Bedford, MA) was used exclusively. All glassware was washed with 10% (v/v) nitric acid and then rinsed with water before use. The inorganic arsenic standard solutions ($1000 \mu\text{g mL}^{-1}$) were prepared from NaAsO_2 and Na_2HAsO_4 (Fluka, Buchs, Switzerland) and stored in PTFE bottles at $4 \text{ }^\circ\text{C}$. The dimethylarsinic acid ($(\text{CH}_3)_2\text{As(O)OH}$, DMA, Sigma, St. Louis, MO, USA) and sodium monomethylarsonate ($\text{CH}_3\text{AsO}(\text{ONa})_2 \cdot 6\text{H}_2\text{O}$, MA, Carlo Erba, Milan, Italy) solutions, containing $1000 \mu\text{g mL}^{-1}$ arsenic, were prepared in water and stored in the same way. Diluted solutions were prepared daily. An arsenobetaine (AB) standard solution (certified content of

$1031 \pm 6 \mu\text{g g}^{-1}$) was obtained from the Institute for Reference Materials and Measurements (IRMM). Moreover, 2,3-dimercapto-1-propanol (BAL) and sodium thiosulfate from Sigma were also used. The rest of the chemicals used were obtained from Fluka or Sigma.

A seawater sample was obtained from near the shore, close to a harbour in south-eastern Spain. Four bottled water samples were purchased from a supermarket, and tap water was collected from the main supply of the University of Murcia. Eight samples of herbs, prepared in bags for making infusions (four of tea, two of chamomile, one of linden and another of thyme), were purchased from a local supermarket.

Eleven standard reference materials were used to assess the reliability of the results. Seven of them were waters, namely NIST 1640a (trace elements in natural water), NASS-6 (seawater reference material for trace metals), SPS-SW2 Batch 125 (reference material for measurement of elements in surface waters), ERM-CA011b (hard drinking water), TMRAIN-04 (simulated rain sample), TM-23.4 (trace element fortified sample) and TM-25.4 (low level fortified sample), and the others were solid materials, namely DORM-4 (fish protein), NCS DC73351 (tea), NIST 1572 (citrus leaves) and NIST 1566a (oyster tissue). These materials were provided by the National Institute of Standards and Technology (NIST), National Research Council Canada, Spectrapure Standards, European Reference Materials and Environment Canada (TM materials), China National Analysis Center for Iron and Steel, and National Institute of Standards and Technology.

The four reference materials obtained as solids were mineralized following the EPA 3502 procedure. For this, nitric acid, hydrochloric acid and hydrogen peroxide were added to 0.3 g of sample, and the mixture was digested in a microwave oven for 30 min at $260 \text{ }^\circ\text{C}$ in order to attain total mineralization of the arsenobetaine to As(V) [15,16].

2.3. Procedures

2.3.1. Obtention of ferrite nanoparticles

To 10 mL of pure water placed in a 15-mL test tube, 100 μL of a 0.2 mol L^{-1} Fe(II) solution and 100 μL of a 0.1 mol L^{-1} Fe(III) solution were added. The tube was placed in a water-bath at $80 \text{ }^\circ\text{C}$ for 1 min (the solution took on a slight yellow colour) and then 20 μL of concentrated ammonia solution were incorporated. The mixture was shaken briefly and then placed in an ultrasound-bath at $80 \text{ }^\circ\text{C}$ for 4 min. The dark particle ferrites obtained were collected by the magnet, and the supernatant was discarded. As shown in the Supplementary material (Fig. S1), the study of the particle size indicated most of the particles were in the 50–100 nm range and they were negatively charged in the 4–9 pH range (Fig. S2). These particles, FNPs, were then used for the following procedures.

2.3.2. Determination of total arsenic (As(III) + As(V) + MMA)

A small amount of sodium hydrogen carbonate was first added to 10 mL of the sample and the resulting solution, with a pH close to 8, was then added to the tube containing the freshly prepared FNPs obtained as indicated in 2.3.1. After shaking for 1.5–2 min, the solid particles were collected with the aid of the magnet. The supernatant was discarded and the solid washed twice with 2 mL pure water, the washing liquid being discarded. After drying with a smooth stream of purified air, the solid was suspended in 100 μL of a solution containing 1% v/v of concentrated nitric acid and 1% m/v Triton X-100. Ultrasounds were applied for 10 min and 20 μL aliquots were injected into the electrothermal atomizer. The heating program given in Table 1 was run and the signal due to arsenic obtained. Calibration was carried out by means of aqueous standard solutions of arsenic.

2.3.3. Determination of As(V) + MMA

The sample (10 mL) was brought to pH 4 by adding a diluted nitric acid solution. Next, 25 μL of a 1 mol L^{-1} BAL solution was added, and the solution was left to stand for 15 min. Then the solution was added to the tube containing the ferrite particles obtained as indicated in

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