Determination of arsenic in sediment and soil slurries by electrothermal atomic absorption spectrometry using W–Rh permanent modifier

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A simple method is described for the determination of As in sediments and soils by electrothermal atomic absorption spectrometry (ETAAS). The procedure combines slurry sampling ETAAS with a 250 μg W + 200 μg Rh permanent chemical modifier. Slurries were sonicated for 20 s before being delivered to the previously W–Rh treated platform. The detection limit for 0.50% m/v slurries was 0.4 µg g⁻¹. The RSD for 783 consecutive measurements of 20 µl of 0.50% m/v soil-5 slurry was 3.8%. In order to verify the accuracy and precision of the proposed method, five sediment and two soil certified reference materials were analysed and the results obtained were in agreement with the certified values.

Introduction

Recently, W–Rh permanent chemical modifiers have been successfully employed in electrothermal atomic absorption spectrometry (ETAAS) for the determination of Cd and Pb in aqueous solutions,1 biological materials and sediment digests,2,3 biological materials and sediment slurries.4,5 Several advantages over the conventional modifiers were reported,1,4 such as diminution of the time consumed for sample dispensing, leading to simpler and faster heating programmes for ETAAS;1,6 lowering modifier blanks owing to elimination of volatile impurities during graphite treatment, with better detection limits; longer signal term stability, reducing the number of recalibrations during routine analysis; and substantial improvement in the tube lifetime.1–6 Lowering analytical costs.2,6

Although permanent chemical modifiers provide attractive advantages, they have rarely been applied to the analysis of real samples by ETAAS, with successful determinations of a few elements such as Cd,1,3,4,6,7 Pb1,2,5,8 Ag,7,8 Sn,9 As,7 Bi7 and Sb7. However, just Cd and Pb were investigated in depth with permanent modifiers, for their determination in different sample matrices employing sample digests5,8 or slurry sampling ETAAS.2,4,6 In this context, there is a need for a more detailed investigation of permanent chemical modifiers applied to the analysis of real samples by ETAAS.

With respect to slurry sampling and ETAAS, a large number of investigations dealing with the analysis of biological tissues,9–13 and inorganic materials2,6,14–20 have demonstrated the analytical benefits of simplifying sample preparation procedures and for avoiding some inconveniences inherent to wet and dry ashing decomposition procedures. Introduction of slurry samples combines the advantages of direct solid sampling (shortening the sample preparation time; reducing risk of sample contamination; reducing risks of analyte losses through volatilisation prior to analysis and/or associated with retention by insoluble residues) and liquid sampling (sampling dispensing by using an autosampler; calibration carried out with aqueous reference solutions).2,4,6,9–20

The aim of this paper is to show the use of W–Rh permanent modifier for the determination of As in sediments and soils by slurry sampling ETAAS. The main advantages expected when employing the W–Rh modifier, when compared with the conventional Pd + Mg(NO₃)₂ modifier, such as improvements in the measurement precision, better sample throughput and much longer tube lifetime, are demonstrated.

Experimental

Apparatus

A Perkin-Elmer Model (Überlingen, Germany) 4100ZL atomic absorption spectrometer with a longitudinal Zeeman effect background correction system furnished with a transversely heated graphite atomiser (THGA), an AS-71 autosampler and a USS-100 controller for the Vibracell VC 50 ultrasonic processor with a titanium probe (Sonics and Materials, Danbury, CT, USA) were used. The standard Perkin-Elmer THGA (Part No. B050-4033) with integrated platforms was used, either without any previous treatment (referred to as the pyrolytic carbon platform), or after pre-treatment first with W and then with Rh (referred to as the W–Rh treated platform).1

All measurements were based on integrated absorbance and performed at 193.7 nm (spectral bandpass 0.7 nm) by using a Perkin-Elmer EDL II electrodeless discharge lamp system.

The graphite platform with the W–Rh permanent chemical modifier was prepared automatically by using the facilities provided by the original software for the autosampler and graphite furnace, then 250 µg of W and 200 µg of Rh were thermally and sequentially deposited in the integrated platform as described elsewhere.1

The furnace programme for the direct determination of arsenic in soil and sediment slurries is shown in Table 1. All measurements were made with at least five replicates and were based on integrated absorbance. Argon (AGA, Campinas, Brazil) was used as protective gas throughout.

Reagents, materials and solutions

High purity de-ionised water (resistivity 18.2 MΩ cm) obtained with a Milli-Q water purification system (Millipore, Bedford,
MA, USA) was used throughout. Analytical reagent grade HNO₃ and HCl (Merck, Rio de Janeiro, Brazil) were distilled in quartz sub-boiling stills (Kühner, Rosenheim, Germany).

All solutions were stored in high density polypropylene bottles. Plastic bottles, autosampler cups and glassware materials were cleaned by soaking in 10% v/v HNO₃ for 24 h and rinsing five times with Milli-Q water and dried and stored in a class 100 laminar flow hood.

Slurries were prepared in 0.04% v/v Triton X-100 (Amer-shaw, Searle, Arlington Heights, VA, USA) containing 0.5% v/v HNO₃.

The washing water used to clean the sampling capillary was replaced with a solution containing 0.1% v/v HNO₃ + 0.01% v/v Triton X-100 to avoid clogging of the autosampler pipe, thus improving dispensing of the slurry on to the platform.

The tungsten and rhodium solutions for graphite surface treatment have been described elsewhere.

The conventional chemical modifier (added at each firing), used for analyte staining with untreated pyrolytic carbon platforms, was 0.05% m/v Pd + 0.03% m/v Mg(NO₃)₂, which were prepared from 10.0 g l⁻¹ Pd (Suprapur, Merck, Darmstadt, Germany) and 10.0 g l⁻¹ Mg(NO₃)₂ solution (Suprapur, Merck).

A 1000 mg l⁻¹ As(m) stock standard solution was prepared by dissoluntion of As₂O₃ (Johnson Matthey, Royston, UK) in dilute HCl. Analytical reference solutions were prepared in the range 10.0–200.0 μg l⁻¹ As by suitable serial dilution of stock standard solutions in 0.5% v/v HNO₃. The calibration was checked periodically after each 25 measurements with 50.00 μg ml⁻¹ of As solution.

Samples

Ordinary sediment samples were collected from a lake located in Sáo Mateus do Sul, Parana State, Brazil. Sediments were collected with an acid-washed plastic scoop and returned to the laboratory in polyethylene bags. The sediment was oven-dried at 60 °C and large aggregates were broken up. Stones and large shell fragments were discarded and the material that passed through a 2 mm mesh nylon sieve was retained for analysis.

The following reference materials were used for checking the accuracy of the proposed method: Buffalo River (SRM 2704) and Lake Sediment (SL-1), from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA); River Sediment (CRM 320) from the Community Bureau of Reference (BCR, Brussels, Belgium); Pond Sediment (NIES 2) from the National Institute for Environmental Studies (NIES, Ibaraki, Japan); and Soil-5 and Soil-7 from International Atomic Energy Agency (IAEA, Vienna, Austria).

Samples of ordinary river sediments and reference materials were ground in a ball-mill (Marconi, Piracicaba, Brazil) for 30 min, obtaining samples with diameter < 30 μm which was further determined by scanning electron microscopy (SEM). Before grinding a new sample, the ball-mill was first cleaned with a brush to remove most of the material, then it was cleaned with a stream of synthetic air (AGA) for 2–3 min. Arsenic contamination was not observed for the reference materials during this procedure. In order to estimate the sample diameter, three ground samples were chosen for the SEM measurements. As the densities of all the samples employed did not differ greatly, a grinding time of 30 min was sufficient to obtain samples with diameter < 30 μm.

Slurry preparation

Slurries were prepared by accurately weighing 0.1–0.5 g of the sample in 50 ml glass calibrated flasks and diluting to the mark with 0.04% Triton X-100 containing 0.5% v/v HNO₃. The resulting slurry was homogenised in an ultrasonic bath (Thornton, Vinhedo, Brazil) for 10 min in order to break up particle agglomerates. Under sonication, slurries were transferred into acid-cleaned polypropylene autosampler cups. All operations were carried out in a clean bench. For each sample, five slurries were prepared and all measurements were carried out with at least five replicates.

Prior to pipetting, the slurry was homogenised by sonication at about 10 W for 20 s. In order to avoid possible sedimentation errors, the autosampler capillary was immersed 10 mm below the surface of the slurry. Then, 20 μl of slurry were taken up and delivered into the atomiser. For untreated platforms, 10 μl of chemical modifier were subsequently deposited on the atomiser.

The heating programme in Table 1 was employed throughout. Calibration was performed by using aqueous reference solutions.

Wet digestion

For comparative purposes, a microwave assisted wet decomposition was performed. Sediments were decomposed (n = 5) in an Anton Paar PDM microwave oven according to the following procedure: 0.2 g of sample was accurately weighed in a PFA decomposition vessel, then 1.5 ml of HNO₃, 0.5 ml of HCl and 1.5 ml of HF were subsequently added to the vessel. The bomb was placed inside the microwave oven and decomposition was carried out at 550–700 W for 10–15 min. After cooling, the bomb cap was removed and the open vessel was placed on a hot-plate. In order to eliminate the excess of HF, 1 ml of H₂SO₄ (Suprapur, Merck) was added to the bomb and the sample was boiled nearly to dryness and subsequently transferred to 50–100 ml volumetric flasks, adjusting the final acidity with 0.5% v/v HNO₃.

The resulting solutions were analysed by ETAAS by delivering 20.0 μl of decomposed sample materials into the atomiser and using appropriate conditions of the heating programme in Table 1. When the conventional modifier was employed, 10.0 μl of its solution were subsequently delivered into the atomiser, after delivering the sample solution, and the heating programmes in Table 1 were also employed.

Determination of sampling efficiency

An empty THGA tube was initially weighed and then 40–100 consecutive pipettings of 20 μl of slurry and drying steps were performed with a series of slurries of several concentrations. The mass difference between the tube containing the dry sample and the empty tube divided by the theoretical sampled mass gives the sampling efficiency. This procedure was performed at least three times for each slurry concentration.

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### Table 1 Heating programme for the determination of As in sediment and soil slurries (injection temperature: 100 °C)

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature/°C</th>
<th>Run/s</th>
<th>Hold/s</th>
<th>Ar flow rate/ ( \text{ml min}^{-1} )</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>130</td>
<td>2</td>
<td>20,30ab</td>
<td>250</td>
</tr>
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<td>2</td>
<td>180</td>
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<td>20,30ab</td>
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</tr>
<tr>
<td>3</td>
<td>1200a, 1300b</td>
<td>10</td>
<td>15</td>
<td>250</td>
</tr>
<tr>
<td>4</td>
<td>2100b,2200b</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2300b</td>
<td>1</td>
<td>4</td>
<td>250</td>
</tr>
</tbody>
</table>

\( a \) Permanent modifier 250 μg of W + 200 μg of Rh. \( b \) Conventional modifier 5 μg of Pd + 3 μg of Mg(NO₃)₂.
Results and Discussion

Permanent chemical modifier

As reported earlier, a suitable coverage of the THGA platform with the permanent modifier was accomplished by delivering 50 µl aliquots of the modifier solutions, which spread throughout the platform during the graphite surface treatment. A better performance of the permanent modifier was obtained with 250 µg of W deposited on the graphite platform. Higher W masses were tried, but double and broader peaks were observed for As, requiring a high atomisation temperature to avoid memory effects.

Several W–Rh graphite platform treatments using different masses of rhodium were performed for arsenic determination in 2 ng of As(III) delivered as an aqueous solution and 20 µl of the 0.5% m/v Pond Sediment slurry (As content 1.2 ± 0.2 ng). Higher recoveries for the aqueous solution, and slurry sample were obtained with the following sequence: aqueous solution, 250 µg W + 200 µg Rh (100%) > 250 µg W + 250 µg Rh (94%) > 250 µg W + 150 µg Rh (93%) > 250 µg W + 300 µg Rh (90%) > 250 µg W + 100 µg Rh (87%) > 250 µg W + 50 µg Rh (83%) > 250 µg W (34%); and slurry sample, 250 µg W + 200 µg Rh (100%) > 250 µg W + 150 µg Rh (92%) > 250 µg W + 250 µg Rh (87%) > 250 µg W + 100 µg Rh (85%) > 250 µg W + 50 µg Rh (71%) > 250 µg W + 300 µg Rh (69%) > 250 µg W (66%).

Pyrolysis curves for 2 ng of As(III) and for 20 µl of the 0.5% m/v Pond Sediment slurry (As content 1.2 ± 0.2 ng) with and without W–Rh permanent chemical modifier are shown in Fig. 1. As can be seen, arsenic present in the sediment slurry is stabilised up to 1300 °C with and without modifier. This is an indication that arsenic was probably stabilised in the sediment matrix, most probably by occlusion in the sample particles, as observed earlier by Bendicho and Loos-Vollebregt. It should be noted that in aqueous solutions without modifier the As signal decreases abruptly. It was also observed that maximum attainable pyrolysis temperature for arsenic in aqueous solution was 1200 °C when using the 250 µg of W + 200 µg of Rh permanent modifier.

Although the stabilisation of arsenic sediment and soil slurries can be attained without the use of chemical modifiers, under those conditions, the arsenic recovery in Pond Sediment slurry was only 80%. In addition, when no modifier was used the relative standard deviation (RSD) for 10 measurements was > 10.0% for all samples analysed, whereas, when the W–Rh permanent modifier and 5 µg of Pd + 3 µg of Mg(NO₃)₂ were employed the RSD was < 3.5% and quantitative recovery was observed. For this reason, 250 µg of W + 200 µg of Rh was chosen as the permanent modifier throughout this work. In order to compare the results, the recommended Pd + Mg(NO₃)₂ conventional modifier was employed.

Fig. 2 shows the absorbance signals for 1.2 ng of As(III) in aqueous solution and in 20 µl of 0.5% m/v Pond Sediment slurry (As content 1.2 ± 0.2 ng) using the W–Rh permanent modifier. Small differences in the peak profiles obtained for As in aqueous solution and in the slurry are observed, which could suggest that the atomic precursors from slurry and aqueous medium would be the same, but a more suitable experimental design would be recommended for explaining a possible modification mechanism for As. Then, future studies and reflections must be made for a better understanding of the action of the W–Rh permanent modifier. Anyway, it is clear that its use for the determination of arsenic in sediment and soil slurries by ETAAS diminished the thermal behaviour differences between slurry and aqueous solutions, allowing the use of aqueous standards for calibration.

Slurry optimisation

The choice of the particle size depends on the density of the material and the analyte homogeneity. The higher the density of the material, the smaller should be its particles. In order to limit sampling errors, it was established that at least 50 particles should be introduced into the atomiser when 20 µl of slurry are sampled. In this work, the estimated number of particles varied from 1300 to 6700 for sediment and 1500 to 7400 for soil, on dispensing 20 µl of slurry containing 0.2–1.0% m/v (40–200 µg) of sample into the atomiser. In the calculations the particle was considered to be spherical (diameter 30 µm) and the average densities of sediments and soils, determined as recommended, were 2.1 and 1.9 g cm⁻³, respectively. The large number of particles introduced should give a low sampling error.

Notwithstanding, although the number of particles introduced into the atomiser in sediment and soil slurries was reasonably higher than 50 for 0.05 and 0.1% m/v slurries, i.e., from 337 to 675 for sediment and 373 to 745 for soil, the precision of measurements (n = 10) was impaired (RSD > 10%), which indicates that sample was not so homogeneous for masses < 50 mg (final volume 50 ml). On the other hand, for slurries containing up to 1.5% m/v there was a linear relationship between integrated absorbance and amount of sample introduced into the atomiser. For slurry concentrations > 2.0% m/v (> 400 µg of sample) the RSD for the measurements was > 5% (n = 10). In this case, the introduction of large amounts of inorganic sample into the graphite tube contributes to the build-up of inorganic residue on the atomiser surface, as already observed. Taking into account the mean arsenic peak profiles with W–Rh permanent modifier, A, 1.2 ng of As(III) in aqueous solution; B, 20 µl of 0.5% m/v Pond Sediment slurry (As content 1.2 ± 0.2 ng).
contents in the samples and the precision, it was decided to work with sediment and soil slurries within the 0.2–1.0% m/v range.

Another variable taken into account to avoid sedimentation errors was the sampling depth. The slurry was pipetted 10 mm below the sample surface, as recommended. Under these conditions, the sampling efficiency varied from 97.1 ± 2 to 104.2 ± 1% (n = 3) for slurries ranging from 0.2 to 1.0% m/v when the samples were sonicated for 20 s before sampling. When the ultrasonic probe was turned off, the sampling efficiencies were very low, varying from 54.3 ± 2 to 58.7 ± 4% for a 0.2 and 1.5% m/v slurry, respectively. As expected, agitation of the slurry prior to pipetting avoids settlement of the particles and also breaks up sample agglomeration, allowing the sampling errors to be minimised.

**Analytical characteristics**

Calibrations were carried out against aqueous reference solutions, with a linear range extending up to 200 µg l⁻¹ As. The characteristic masses obtained for the analytes employing the W–Rh permanent modifier, based on integrated absorbance, were 39 ± 1 pg As employing standard THGA tubes. The uncertainties were based on 10 average results obtained on different days with different atomisers.

Detection limits, calculated from 20 consecutive measurements of the blank solutions according to IUPAC, for a 0.5% m/v sediment and soil was 0.4 µg g⁻¹ As, employing the W–Rh permanent modifier.

It is important to point out that each platform treatment lasted for about 250–300 analytical firings when working with sediment and soil slurries. As already described, W–Rh permanent modifier increases tube lifetimes by up to 100% when compared with untreated pyrolytic carbon platforms for a permanent modifier increases tube lifetimes by up to 100% estimated. The treatment remained stable for approximately

**Analysis of samples**

Five sediment certified reference materials, two soil certified reference materials and two ordinary sediment samples were analysed (n = 5) by the slurry method employing the proposed W–Rh permanent modifier and 5 µg of Pd + 3 µg of Mg(NO₃)₂ (Table 2). For comparison purposes, the samples were also digested and arsenic contents were determined in the digests employing Pd + Mg(NO₃)₂ modifier. In all cases the calibration was run against aqueous reference solutions.

The analyte contents obtained with the different methods were in agreement with the certified values (Table 2). The results are presented as average ± confidence interval (at 95% confidence level, tstudent = 2.776).

The performance and accuracy of the method employing W–Rh platform treatment with different coatings and tubes for arsenic determination in the chosen samples are better than those obtained with the conventional modifier. It should be pointed out that the standard deviations of the results for all samples using 250 µg of W + 200 µg of Rh as permanent modifier were always lower than those with the conventional modifier for slurry and digested samples.

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**Table 2** Arsenic determination in sediment and soil samples by ETAAS (n = 5). Permanent modifier, 250 µg of W + 200 µg of Rh; conventional modifier, 5 µg of Pd + 3 µg of Mg(NO₃)₂. Heating programme as specified in Table 1. Confidence interval at 95% confidence level (tstudent = 2.776)

<table>
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<th>Sample</th>
<th>Certified value</th>
<th>Slurry</th>
<th>Digest</th>
<th>W-Rh</th>
<th>Pd + Mg</th>
<th>W-Rh</th>
<th>Pd + Mg</th>
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<tbody>
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<td>Pond Sediment NIES 2</td>
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*Confidence interval: 12.5–14.2 µg g⁻¹.
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References