Determination of Cadmium in Sediments and in Sewage Sludge by Slurry Sampling Electrothermal Atomic Absorption Spectrometry Using Iridium as Permanent Modifier

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A procedure for the determination of Cd in sediment and sewage sludge as slurries by electrothermal atomic absorption spectrometry is proposed. The slurry, 1 mg mL⁻¹, was prepared by mixing sample ground to a particle size \( \leq 50 \mu m \) with 5% v/v nitric acid in an ultrasonic bath. The homogeneity of the slurries was assured by passing a constant flow of argon into the autosampler cup, just before transferring an aliquot to the graphite furnace. Two permanent modifiers deposited on the platform were tested: Ru and Ir. Modifiers in solution were also tested: Pd + Mg and phosphate, separately or plus Mg. The Ir-treated tube was adopted due to its good performance as modifier and also for practical reasons. About 80% of Cd is extracted to the water phase of the slurry. To test the accuracy of the method, three certified materials were analyzed: a marine sediment, a river sediment and a domestic sewage sludge. The concentrations obtained, using calibration against aqueous standards prepared in the same medium as the slurries, are in agreement with the certified values, at a confidence level of 95%, according to the Student-\( t \) test. The limit of detection (3\( \sigma \)) was 43 ng g⁻¹ in the solid sample and the relative standard deviation for the sediment MESS-2 was 2.3% (\( n = 10 \)).

Keywords: cadmium, slurry, ET AAS, modifier, sediment, sewage sludge

Introduction

Cadmium is a heavy metal, relatively rare and without known vital biological functions for human beings. However, it is quite toxic and its concentration in the environment, even if low, requires periodic control. Cadmium contamination of the environment is due to mining, the smelter industry, discard of products that contain cadmium, such as batteries, and sewage of domestic and industrial origin. A critical question in agriculture is the use of sewage sludge as fertilizers due to its increasing concentrations of toxic elements. In Europe, for example, the maximum allowed Cd concentration in sewage...
sludge for agricultural use is 20 mg kg$^{-1}$. Cadmium determination in sediments and in sewage sludge is becoming very important and necessary as a way to control its presence in the environment.

In general, the procedures for mineralization and dissolution of sediments and sewage are prone to sample contamination, besides being time consuming, even if assisted by microwaves. Direct solid analysis or slurry analysis are usually much faster and less subject to the risks of analyte contamination or losses. A review on direct solid, also including slurry analysis, was recently published by Kurfürst.$^4$ The procedure to prepare a slurry is usually also very simple and the obtained sensitivity is quite high, since less sample dilution can be employed. In addition, micro-quantities of solids, such as mineral inclusions, can be analyzed.$^5,6$ The determination of heavy metals in sediments and in sewage sludge as slurries or after acid dissolution$^3,7-10$ and the investigation of adequate modifiers for slurries,$^2,11$ demonstrate the continuing interest for rapid and precise methods for monitoring these metals in the environment.

The use of a chemical modifier$^{12}$ facilitates the separation of the matrix from the analyte during the pyrolysis step, by forming more stable compounds or phases with the analyte and, if possible, decreasing the thermal stability of the concomitants. Cadmium is a volatile element and the use of a chemical modifier, which allows a higher pyrolysis temperature is usually important for its determination by ETAAS. The chemical modifiers more frequently used for this analyte are phosphate, magnesium nitrate and the so-called universal modifier, a mixture of palladium and magnesium nitrates. These modifiers, in solutions, are added to the sample aliquot in the graphite tube each time the sample is introduced into the tube. An alternative is to use a tube treated with one or more refractory metals, called permanent modifiers. These modifiers can be purified in situ, by applying a furnace temperature program, leading to low blank signals.$^{13}$ In addition, they do not need to be pipetted into the tube each cycle, decreasing the analysis time and increasing the sample throughput. The reduced form of the platinum group metals (Pt, Ir, Ru, Rh etc.), mixed or not with another refractory metal (W, Zr etc.), are frequently used as permanent modifiers.$^{13,15}$

In this work, a simple and fast method for the routine determination of Cd in sediments and in sewage sludge is reported. The performances of two permanent modifiers, Ir and Ru, and of modifiers in solution, including a mixture of palladium and magnesium nitrates, are compared. After determining the optimized graphite furnace temperature conditions and the analyte extraction to the aqueous phase in the presence or not of hydrofluoric acid for different standing times of the slurry after its preparation, the accuracy is tested by the analysis of three certified reference materials.

**Experimental**

**Instrumentation**

A Perkin-Elmer (Norwalk, CT, USA) AAnalyst 100 atomic absorption spectrometer interfaced with a PC was used to carry out the measurements, using integrated absorbance for signal evaluation. The instrument was equipped with an HGA-800 graphite furnace and an AS-72 autosampler. Unspecific light absorption was corrected by continuum light source (deuterium lamp) background correction. Argon (99.996%, White Martins, São Paulo, Brazil) was used as purge gas. A hollow cathode lamp of Cd, used as a specific radiation source (wavelength of 228.8 nm and slit width of 0.7 nm), operating at 6 mA, was from Perkin-Elmer (Part No. 3050115). Commercial pyrolytic graphite coated tubes, Part No. B0091504 with L’vov platforms, Part No. 109 324 (all from Perkin-Elmer) were used as sample atomization reservoirs. Table 1 shows the optimized furnace temperature program for the Cd determination, using 20 µL of sample slurry or of the calibration solution plus 10 µL of the modifier, when applied in solution.

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature, °C</th>
<th>Ramp, s</th>
<th>Hold, s</th>
<th>Flow rate, mL min$^{-1}$</th>
<th>Read</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying</td>
<td>90</td>
<td>10</td>
<td>15</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Drying</td>
<td>130</td>
<td>15</td>
<td>15</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>700$^a$</td>
<td>1</td>
<td>30</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td>20</td>
<td>1</td>
<td>10</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Atomization</td>
<td>1500$^a$</td>
<td>0</td>
<td>5</td>
<td>0</td>
<td>X</td>
</tr>
<tr>
<td>Cleanout</td>
<td>2600$^b$</td>
<td>1</td>
<td>5</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Sewage Sludge: $T_p = 450$ °C and $T_A = 1300$ °C; $^b$Cleanout temperature when permanent modifier was used: 2200 °C.

**Reagents and samples**

Nitric acid (Carlo Erba, Milan, Italy, No. 408015) and hydrofluoric acid (Merck, Darmstadt, Germany, No. 334), used in slurry preparation, were further purified by sub-boiling distillation using, respectively, quartz and poly(tetrafluorethylene) sub-boiling stills, both from Kürner Analysentechnik, Rosenheim, Germany. The water was purified in a Milli-Q system (Millipore, Bedford, MA,
USA), yielding water with a resistivity of 18 MΩ cm. The calibration solutions were prepared from dilution of a standard stock solution, 1000 µg mL⁻¹, which was made from a high-purity, PLK20-Cd (CdO), Spex reagent (Edison, NJ, USA).

For the study of the modifiers, the following stock solutions were used: 10000 µg mL⁻¹ of Pd (Merck No. B634689 016 ) and 10000 µg mL⁻¹ of Mg (Merck No. B593213 431), both in 1 mol L⁻¹ HNO₃, 1000 µg mL⁻¹ of Ir and 1000 µg mL⁻¹ of Ru, both in 1 mol L⁻¹ HCl (Fluka, Buchs, Switzerland), and 24.2 g L⁻¹ of NH₄H₂PO₄, prepared from proper dissolution of the solid reagent from Merck, No. 101126 . The masses of the modifiers in solution, in the 10 µL volume that was pipetted into the tube, were: 15 µg Pd plus 10 µg Mg, 480 µg phosphate plus 20 µg Mg or 200 µg phosphate. The surface treatments with Ru or Ir, based on a previous work,¹³ were carried out by pipetting 40 µL of a 500 µg mL⁻¹ Ru solution or of a 500 µg mL⁻¹ Ir solution into the graphite tube, on the platform, and submitting the tube to the temperature program shown in Table 2. The entire procedure, that is, pipetting and heating, was repeated 25 times, in order to obtain a mass of permanent modifier in the tube of 500 µg. This temperature program also allowed the removal of contaminants from the modifiers, ensuring low blank values in the final analysis.¹³ The mass of the metal deposited in the platform is quite high to assure a permanent coating, since a higher mass of the metal results in higher particle sizes and, therefore, smaller losses due to vaporization.¹⁶ An increase in tube lifetime is also frequently observed, although no further investigation was performed in this work. This procedure has been used to treat tubes in previous works,¹³,¹⁷-¹⁹ with excellent results.

### Table 2. Temperature program for treating the graphite tube with Ru or Ir, as permanent modifier

<table>
<thead>
<tr>
<th>T / ºC</th>
<th>Ramp / s</th>
<th>Hold / s</th>
<th>Gas flow rate / mL min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>5</td>
<td>15</td>
<td>250</td>
</tr>
<tr>
<td>120</td>
<td>15</td>
<td>10</td>
<td>250</td>
</tr>
<tr>
<td>140</td>
<td>25</td>
<td>15</td>
<td>250</td>
</tr>
<tr>
<td>1000</td>
<td>0</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>2000</td>
<td>1</td>
<td>10</td>
<td>250</td>
</tr>
</tbody>
</table>

Three certified reference materials were analyzed: marine sediment MESS-2 (National Research Council of Canada, Ottawa, Canada), Buffalo River Sediment SRM 2704 (National Institute of Standards and Technology, NIST, Gaithersburg, MD, USA) and sewage sludge BCR 144R (Community Bureau of Reference, Brussels, Belgium).

### Slurry preparation

All samples were ground in an agate mortar and passed through a 50 µm polyester sieve. The slurries were prepared by mixing approximately 50 mg of the sample with 2.5 mL of nitric acid and 12 mL of water. After leaving the slurry in an ultrasonic bath for 30 min, the volume was made up to 50 mL with water. In this way, the solid concentration in the slurry was 1 mg mL⁻¹ in 5% v/v nitric acid. The slurry was left to stand for at least 12 h, and manually shaken just before it was poured into the autosampler cup, where it was homogenized by passing argon at a flow rate of 0.4 L min⁻¹ through the liquid just before transferring 20 µL of the slurry into the furnace.

### Results and Discussion

#### Modifiers

The pyrolysis and atomization temperature curves for slurries of the three certified materials are shown, respectively, in Figure 1 (marine sediment), in Figure 2 (river sediment) and in Figure 3 (sewage sludge), using the two permanent modifiers and Pd plus Mg in solution. For the sewage sludge, phosphate in solution was also evaluated as modifier. The first observation is that the thermal behavior of Cd, in the presence or not of the studied modifiers, is very dependent on the sample matrix. For the marine sediment (Figure 1), higher pyrolysis temperatures, up to around 900 °C, can be used in the presence of either the modifier in solution, Pd plus Mg, or the Ir-treated tube, although the sensitivity was slightly better with the Ir-treated tube. For the river sediment (Figure 2), the pyrolysis curves without a modifier or in the presence of the studied modifiers, are very similar.

![Figure 1. Pyrolysis and atomization curves for cadmium in marine sediment MESS-2 slurry (1 mg mL⁻¹ slurry in 5% v/v nitric acid). Atomization temperature for the pyrolysis curves: 1500 °C and pyrolysis temperature for the atomization curves: 700 °C.](image-url)
indicating that concomitants are acting as modifiers. The differences between the sediments of marine and river origins are evident, when Figures 1 and 2 are compared, especially when no modifier or a Ru-treated tube is used. Possibly, the chloride content in the marine sediment plays a role in these two situations, decreasing thermal stabilization. For the sewage sludge, Figure 3, the treated tubes almost did not improve the stabilization, with a maximum allowed pyrolysis temperature around 450 °C, the same as when no modifier is used. When phosphate or Pd plus Mg in solution are used, the maximum is around 1200 °C and when the phosphate is mixed with Mg, the maximum is at 1400 °C.

Table 3 shows the characteristic masses obtained using the different modifiers at different pyrolysis temperatures. The characteristic mass mentioned in the software of the spectrometer is 0.5 pg/0.0044 s. Different graphite tubes were used for the different modifiers, meaning that the data obtained are not directly comparable. However, higher sensitivities were obtained with the permanent modifiers and lower ones with phosphate, together or not with Mg, in solution.

Since the blanks were lower with the treated tubes and since the best overall performance was achieved with the Ir-treated tube, this one was adopted in this work, using a pyrolysis temperature of 700 °C and an atomization temperature of 1500 °C, except for the sewage sludge, for which the selected pyrolysis and atomization temperatures were 450 °C and 1300 °C, respectively.

Extract Analysis

The recoveries of the certified value in the aqueous phase of the MESS-2 slurry, using either 0.7 mol L⁻¹ (5% v/v) of nitric acid or 0.7 mol L⁻¹ nitric acid plus 0.3 mol L⁻¹ (or 1% v/v) hydrofluoric acid, for different standing times of the slurry are shown in Figure 4. The slurries were centrifuged after a certain standing time, and the aqueous phase was analyzed by ET AAS. When only nitric acid was used, the recoveries were around 80%, independent of the
standing time in the range studied. It is clear that the extraction was almost quantitative when the mixture of acids was used, and increased slightly with the standing time, indicating that some of the analyte is retained by the silica fraction (around 59% w/w for MESS-2). However, in order to simplify the procedure and reduce the risks of contamination, only nitric acid was used in the further experiments. A nitric acid medium is usually chosen for determinations by ET AAS, because this acid can be easily purified by sub-boiling distillation, allows an efficient extraction of the analyte to the water phase, stabilizes the analyte in solution and leads to less interference problems. The adopted nitric acid concentration of 5% v/v was based on a previous work. As will be shown, using this condition, the analytical results for the slurries were quite satisfactory.

Analytical characteristics and results

The detection limit (defined as three times the standard deviation of ten measurements of the blank divided by the slope of the calibration curve) in the solid was 43 ng g⁻¹, using the Ir-treated tube. The calibration was carried out with aqueous solutions containing the same concentration of nitric acid as in the slurry. The relative standard deviation for ten measurements of the MESS-2 slurry was 2.3%. The characteristic mass was already discussed.

The concentrations obtained for the three certified materials, shown in Table 4, agree very well with the certified values, according to the Student- test at a confidence level of 95%, indicating absence of interferences, even using calibration against aqueous standard solutions.

Table 4. Results for cadmium in certified reference materials, prepared as 1 mg mL⁻¹ slurries in 5% v/v HNO₃, using a Ir-treated tube as permanent modifier (n=5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Certified / (µg g⁻¹)</th>
<th>Determined / (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MESS-2</td>
<td>0.24 ± 0.01</td>
<td>0.24 ± 0.03</td>
</tr>
<tr>
<td>SRM 2704</td>
<td>3.24 ± 0.22</td>
<td>3.54 ± 0.13</td>
</tr>
<tr>
<td>BCR 144R</td>
<td>1.82 ± 0.10</td>
<td>1.87 ± 0.06</td>
</tr>
</tbody>
</table>

Conclusions

A simple, practical and efficient method is proposed for the determination of Cd in sediments and in sewage sludge by electrothermal atomization atomic absorption spectrometry, using Ir as a permanent modifier. The samples, after grinding to a particle size ≤ 50 µm, are analyzed as slurries prepared in a nitric acid solution. Calibration using aqueous solutions was effective for all the analyzed samples. About 80% of Cd migrates from the solid particles to the water phase of the slurry. The same method can probably be extended for the determination of other analytes in the same or in different samples.

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References


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