

Determination of cadmium, chromium and lead in marine sediment slurry samples by electrothermal atomic absorption spectrometry using permanent modifiers

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Abstract

A procedure for the determination of cadmium, chromium, and lead in marine sediment slurries by electrothermal atomic absorption spectrometry is proposed. Slurry was prepared by mixing 10 mg of ground sample with particle size smaller than 50 μm completed to the weight of 1.0 g with a 3% nitric acid and 10% hydrogen peroxide solution. The slurry was maintained homogeneous with an aquarium air pump. For cadmium, the best results were obtained using iridium permanent with optimum pyrolysis and atomization temperatures of 400 and 1300 $^{\circ}\text{C}$, respectively, a characteristic mass, m_o (1% absorption), of 2.3 pg (recommended 1 pg). Without modifier use, zirconium, ruthenium, and rhodium m_o were 3.4, 4.1, 4.6, and 4.8 pg, respectively. For chromium, the most sensitive condition was obtained with zirconium permanent with optimum pyrolysis and atomization temperatures of 1500 and 2500 $^{\circ}\text{C}$, m_o of 6.6 pg (recommended 5.5 pg); and without modifier use, rhodium, iridium, and ruthenium m_o were 5.3, 8.8, 8.8, and 8.9 pg, respectively. For lead, the best modifier was also zirconium, m_o of 8.3 pg for the optimum pyrolysis and atomization temperatures of 600 and 1400 $^{\circ}\text{C}$, respectively, (recommended m_o of 9.0 pg). For iridium, ruthenium, without modifier, and rhodium, m_o were 14.7, 15.5, 16.5, and 16.5 pg, respectively. For all the modifiers selected in each case, the peaks were symmetrical with r^2 higher than 0.99. Being analyzed ($n = 10$), two marine sediment reference materials (PACS-2 and MESS-2 from NRCC), the determined values, $\mu\text{g l}^{-1}$, and certified values in brackets, were 2.17 ± 0.05 (2.11 ± 0.15) and 0.25 ± 0.03 (0.24 ± 0.01) for cadmium in PACS-2 and MESS-2, respectively. For chromium in PACS-2 and MESS-2 the values were 94.7 ± 5.6 (90.7 ± 4.6) and 102.3 ± 10.7 (106 ± 8), respectively. Finally, for lead in PACS-2 and MESS-2, the results obtained were 184 ± 7 (183 ± 8) and of 25.2 ± 0.40 (21.9 ± 1.2), respectively. For cadmium and lead in both samples and chromium in PACS-2, calibration was accomplished with aqueous calibration curves. For chromium in MESS-2, only with the standard addition technique results were in agreement with the certified ones. The limits of detection ($k = 3$, $n = 10$) obtained with the diluents were 0.1, 3.4, and 3.6 $\mu\text{g l}^{-1}$ for cadmium, chromium, and lead, respectively.

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1. Introduction

Usually, sediments are solubilized using alkaline fusion or acid digestion before trace element determination. However, these procedure is time consuming, requires relatively high amounts of reagents, and can contaminate the sample solution [1]. In addition, the loss of volatile elements such as

As, Cd, and Pb can occur during sample preparation if the conditions are not properly controlled. In contrast, the use of slurries in electrothermal atomic absorption spectrometry (ET AAS) is a well-established methodology whose advantages have been recently reviewed [2]. The direct analysis of solids as slurries offers advantages over more conventional sample preparation procedures. Among these advantages are the shorter sample preparation time, reduced sample contamination risk, increased sensitivity (less dilution), lower analyte loss through volatilization prior to analysis, and the

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possibility of selective analysis of micro-amounts of solids [3–12].

In addition, the analysis of slurries combines the advantages of solid and liquid sampling, allowing dilution, the use of the same devices available for liquid sampling [13], and calibration with aqueous solutions [14].

An important requirement of the preparation of suspensions is that these should be maintained homogeneous during autosampling collection. Several devices have been proposed for this end. Ultrasonic or magnetic agitation [5,6,13,15–17], use of introduction of argon [18] and of air with aid by a peristaltic pump [19] have been used with good results.

The employment of permanent modifiers has shown to be a promising alternative for metal determinations by ET AAS, besides ETV ICP-MS. In many cases the modifier assures the thermal stability of the analyte [20–23], prolongs the lifetime of the graphite tube [6,23], and acts as a catalyst, destroying either thoroughly or partially complexes matrixes such as urine, blood serum, blood, among others [24–27], avoiding in this way the previous digestion of the sample and in many cases making aqueous calibration possible.

In the present study, we propose procedures to determine cadmium, chromium, and lead in sediments such as slurries, using iridium, rhodium, ruthenium and zirconium as permanent modifiers and without modifier. Optimization of parameters was carried out using the PACS-2 marine sediment reference material, and the method developed was then applied to the analysis of other sediment reference materials.

2. Experimental

2.1. Instrumentation

A GBC model 906 AA atomic absorption spectrometer (Vic., Australia), equipped with deuterium-arc background correction, a GF 3000 (GBC) electrothermal atomizer, and an autosampler PAL-300 (GBC) were used. Pyrolytic graphite tubes without platform were obtained from the same manufacturer. Measurements were carried out using hollow cathode lamps operating in the experimental conditions given in Table 1. Argon was used as the inert gas with a flow rate of 250 ml min⁻¹ in all stages, except during atomization, when the flow was stopped. Background-corrected integrated absorbance was used as the analytical signal. The hollow cathode lamps were from GBC for Cd operating in specified

conditions. Cr and Pb hollow cathode lamps from Photron (Narren Warren, Australia) were used.

2.2. Reagents

The following reagents were used:

- Nitric acid: Supra Pure, 65% (Merck, Darmstadt, Germany).
- Copper, lead, and cadmium standard solutions: GFS Chemicals, Multielement standard, Columbus, OH (Nos. 1842 and 1845); working solution ranges 10–50 µg l⁻¹ (Cu and Pb) and 1–5 µg l⁻¹ (Cd), in 0.2% (v/v) nitric acid.
- Iridium standard solution: Fluka (No. 58195), 1 mol l⁻¹ in hydrochloric acid.
- Ruthenium standard solution: Aldrich (No. 84033), 1 mol l⁻¹ in hydrochloric acid.
- Zirconium standard solution: Fluka (No. 65741), 1 mol l⁻¹ in hydrochloric acid.
- Rhodium standard solution: Fluka (No. 83722), 1 mol l⁻¹ in hydrochloric acid.
- Water: All solutions were prepared with de-ionized water with a specific resistivity of 18 Ωm cm, which was obtained by filtering distilled water through a Milli-Q (Elga Maxima) purifier twice immediately before use.

The treatment of the graphite tubes with the permanent modifiers was described in details in previous studies [6,27].

2.3. Materials

As exhaustive cleaning is very important to eliminate the possibility of metal contamination, all glassware and polyethylene materials were washed with detergent solutions and rinsed abundantly with water, maintained in nitric acid bath with 50% (v/v) for a period not inferior to 1 h and later rinsed several times with de-ionized water. The blank levels obtained were low.

2.4. Certified samples

The method was validated with two reference materials, namely, marine sediments, MESS-2 and PACS-2 from the National Research Council of Canada (NRCC).

2.5. Procedure

The sediment samples were weighed (~10 mg), added with a 3% nitric acid and 10% hydrogen peroxide optimized solution. This suspension was maintained homogeneous by air bubbling with an aquarium pump. MESS-2 samples were used to obtain the pyrolysis and atomization temperature curves for cadmium and lead. For cadmium, the volume was completed to 1 ml while for lead the final volume was 3 ml. For chromium, the PACS-2 sample was used and the volume was completed to 30 ml to obtain absorption values lower than 1.0.

Table 1
Instrumental parameters and operational conditions for the determination of metals in sediment slurries by ET AAS

Parameter	Cd	Cr	Pb
Wavelengths (nm)	228.8	357.9	283.3
Slit (nm)	0.5	0.2	0.5
Current (mA)	3.0	6.0	5.0
Time constant	0.5	0.5	0.2

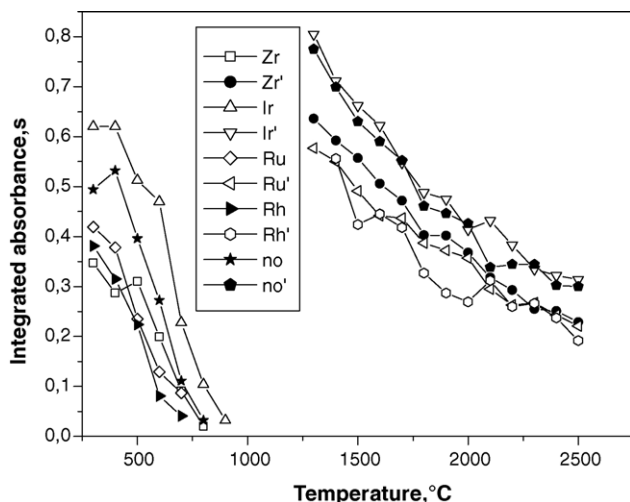


Fig. 1. Pyrolysis and atomization temperature curves for 0.4 ng of cadmium in sediment slurry sample.

3. Results and discussion

3.1. Pyrolysis and atomization temperature curves

3.1.1. Cadmium

The optimal drying temperature and holding time used in the drying step were studied, being the optimal values 300 °C with holding and ramp times of 4 and 20 s. Fig. 1 presents the pyrolysis and atomization temperature curves for cadmium in the MESS-2 sample prepared as described in Section 2.5. As can be observed, with the use of iridium as a modifier, the best pyrolysis and atomization temperatures were 400 and 1600 °C with characteristic mass, m_o , of 2.2 pg (manufacturer recommendation of 1.0 pg for aqueous solutions). For the other modifiers, the best pyrolysis and atomization temperatures were 400 and 1900 °C (m_o 3.4 pg) without modifier; 300 and 1500 °C (m_o 4.1 pg) for zirconium; 300 and 1600 °C (m_o 4.8 pg) for rhodium, and 300 and 1600 °C (m_o 4.6 pg) for ruthenium.

The graphite furnace temperature program presented in Table 2 was determined based on the pyrolysis and atomization temperature curves. For urine samples, comparisons of the determination of lead without modifier, with the mixture of Pd + Mg in solution (universal modifier), Ir and Ru (500 µg

Table 2
Temperature programs for the determination of cadmium, chromium, and lead in sediment slurry sample using iridium as a permanent modifier

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow (mL min ⁻¹)
1	90	3.0	2.0	250
2	140	20.0	4.0	250
3	400 ^a , 1500 ^b , 600 ^c	1.0	2.0	250
4 ^d	1300 ^a , 2500 ^b , 1400 ^c	0.0	2.0	0.0
5	2600	2.0	2.0	250

^a Cd.

^b Cr.

^c Pb.

^d Reading at this step.

of each) as permanent modifiers were investigated as shown in Figure 3.

It is interesting to observe that for all the modifiers tested, the sensitivity decreased with the increase in atomization temperature. The absorbance values obtained for cadmium without modifier use and with permanent iridium were quite close, however the absorption pulse observed for the metal without modifier use was irregular and badly formed. Using iridium permanent, the absorption pulse was symmetrical with fully corrected background. In spite of the low thermal stability observed for all the modifiers, with the optimized iridium value (400 °C), the background absorption is low and fully corrected. The low atomization temperature contributes to raise the graphite tube lifetime. In experiments made with the sediment dissolved in water, the background was very high and consecutive absorption pulses for the same solution showed a very poor precision. This suggests that nitric acid and hydrogen peroxide act together with the modifier in the destruction of the matrix, which is reflected in the low background absorption value observed.

3.1.2. Chromium

For the preparation of the slurry for the study of chromium, 10 mg of sample PACS-2 was weighed and completed to 15 ml with diluents. This slurry was homogenized manually and transferred to autosampler cups. Homogenization was continued by aeration with an aquarium pump. Fig. 2 shows the results obtained. In spite of the condition without modifier being the most sensitive one, the absorption pulse does not return to the base line. The condition that presented the best defined peak was the one with permanent zirconium, which showed a very symmetrical peak. In this case, the optimum pyrolysis and atomization temperatures were 1500 and 2500 °C with an m_o of 6.6 pg (manufacturer recommendation of 5.5 pg for aqueous solutions without modifier). For the other modifiers, the best pyrolysis and atomization temperatures 1300 and 2500 °C (m_o 5.3 pg) without modifier, 1500 and 2500 °C (m_o 8.8 pg) for iridium, 700 and 2500 °C

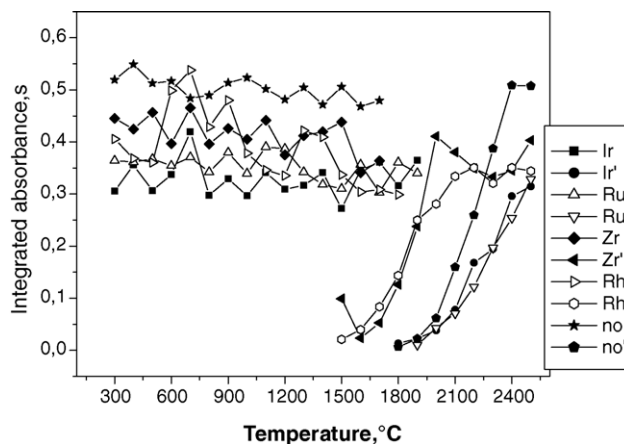


Fig. 2. Pyrolysis and atomization temperature curves for 0.6 ng of chromium in sediment slurry sample.

Table 3

Analytical figures of merit in the determination of some metals as sediment slurries using permanent modifiers

Analyte	Modifier	m_0 (pg)	LOD ($\mu\text{g l}^{-1}$)	RSD, $n = 10$	r^2	Calibration range ($\mu\text{g l}^{-1}$)
Cd	Ir	2.3	0.1	<3	0.996	1–10
Cr	Zr	6.6	3.4	<3	0.997	5–60
Pb	Zr	8.3	3.6	<3	0.997	10–400

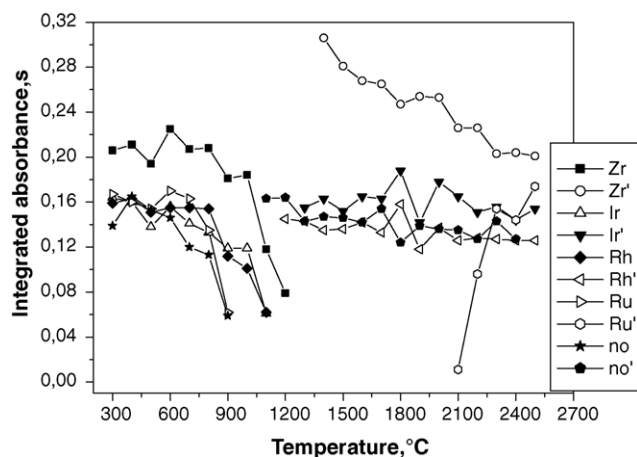


Fig. 3. Pyrolysis and atomization temperature curves for 1.7 ng of lead in sediment slurry sample.

(m_0 8.8 pg) for rhodium, and 1100 and 2500 °C (m_0 8.9 pg) for ruthenium.

3.1.3. Lead

The pyrolysis and atomization temperature curves for lead were obtained with MESS-2 sediment in agreement with item 2.5. For all the modifiers studied, the absorption pulse for Pb sediment slurry for permanent zirconium is symmetrical returning to the base line in an interval smaller than 2 s. The best pyrolysis and atomization temperatures were 600 and 1400 °C with a m_0 of 8.3 pg (recommended 9.0 pg). For iridium, the best pyrolysis and atomization temperatures were 600 and 1800 °C with an m_0 of 14.7 pg; without modifier, the best temperatures were 400 and 1600 °C with an m_0 of 15.5 pg; for rhodium, the best temperatures were 600 and 1800 °C with an m_0 of 16.5, and for ruthenium the optimum temperatures were 600 and 2400 °C with an m_0 of 16.5 pg.

3.2. Analytical figures of merit

The furnace temperature program presented in Table 2 was obtained based on the pyrolysis and of atomization temperature curves of each analyte and after optimizing drying to eliminate the solvent without sputtering and after cleaning to avoid matrix effects. The analytical figures of merit for all analytes studied are presented in Table 3. In this way, calibration with 1% nitric acid was used, as already mentioned, with a calibration range of 0.5–10.0 $\mu\text{g l}^{-1}$ for cadmium and 0.5–50 $\mu\text{g l}^{-1}$ for chromium and lead. The correlation coefficient of the linear regression for the calibration curves for all analytes were higher than 0.99, with typical slopes of 0.062 s

Table 4

Determined values ($\mu\text{g l}^{-1}$) for two certified sediments as slurry using permanent modifiers

Analyte	PACS-2		MESS-2	
	Certified	Determined	Certified	Determined
Cd	2.11 ± 0.15	2.17 ± 0.05	0.24 ± 0.01	0.25 ^a ± 0.01
Cr	184 ± 7	183 ± 8	25.2 ± 0.4	21.9 ± 1.2
Pb	90.7 ± 4.6	94.7 ± 5.6	106 ± 8	103 ± 7

^a Preconcentrated 10 times directly in the graphite furnace.

($\mu\text{g l}^{-1}$)⁻¹ for cadmium; 0.011 for chromium, and 8.060 s ($\mu\text{g l}^{-1}$)⁻¹ for lead. The limits of detection were defined as the ratio of three times the standard deviation often measurements of the blank (3%, v/v in nitric acid and 10%, v/v in hydrogen peroxide). As shown in Table 4, most of the concentration values obtained are within a 95% confidence interval of certified values, demonstrating the accuracy of the methodologies proposed. The precision values of the certified materials were also good, from 2.3 to 6.8 (Table 4).

4. Conclusions

The use of slurries prepared in 3% nitric acid and in 10% hydrogen peroxide, allied with the used of an aquarium pump to maintain the slurry homogeneous, showed that the methodology is good for the determination of cadmium, chromium, lead, and sea sediments. Of all the permanent modifiers studied, iridium was the most appropriate (good sensitivity and well-formed peak) for cadmium, while zirconium was the best choice to determinate chromium and lead. The limits of detection were compatible to determine sediments in the form of slurries by ET AAS. Probably, the same sample preparation and permanent modifiers can be applied to other metals in sediment slurry samples after temperature optimisation.

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