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Simultaneous determination of arsenic, cadmium, copper, chromium, nickel, lead and thallium in total digested sediment samples and available fractions by electrothermal atomization atomic absorption spectroscopy (ET AAS)

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ABSTRACT

This study describes the optimization and validation of a quick and simple method for the simultaneous determination of total content and available fractions of As, Cr, Cu, Ni, Pb and Tl in sediments by ET AAS, which has been proved to be useful for environmental research. The optimization was carried out using a 3^3 Box–Behnken factorial design which was applied to matrices of total digestion and to stages 1 and 2 of the modified BCR sequential extraction scheme for sediments in order to determine the appropriate atomization temperatures and masses for the chemical modifiers: $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$. The simultaneous determination of the elements in all matrices considered was performed, without the use of chemical modifiers at atomization temperatures of 1700 °C for Cd and Tl, and 2100 °C for As, Cu, Cr, Ni and Pb, using a standard calibration curve for calibration purposes. The characteristic masses and limits of detection obtained were 36.5, 1.8, 6.5, 28, 34, 46.5 and 48 μg and 0.11, 0.001, 0.022, 0.04, 0.2, 0.03 and 0.003 $\mu\text{g g}^{-1}$ for As, Cd, Cr, Cu, Ni, Pb and Tl, respectively. The analytical procedure was validated by analyzing three sediment certified reference materials (CRM NCS DC 73315 and LKSD-4 for total content and BCR 701 for available fractions). Good accuracy was obtained (tested statistically, $P=0.05$, and shown by the high recovery for each element in each matrix), except for total As in the matrix of total digestion, where losses of the analyte could be attributed to sample treatment with HNO_3 . The precision of the procedure was between 0.6% and 6%.

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1. Introduction

Metals are introduced into aquatic systems by the weathering and erosion of soils and rocks, volcanic eruptions and a large variety of human activities such as mining, the processing and use of metals and/or substances that contain metallic contaminants [1], agriculture and the disposal of waste waters [2]. Trace metals introduced into water bodies are converted as a part of the water-sediment system and their distribution is controlled by an assemblage of dynamic processes that involve physicochemical and equilibrium interactions [1]. The chemical analysis of sediments, including the identification, quantification and distribution of interconvertible species, provides valuable information for the evaluation of aquatic environments [3] that enables us to assess the environmental status of the sediments, identify the sources and routes by which metals have entered the system and even quantification of environmental risk. The widespread

contamination by heavy metals is of major concern because of their toxicity, persistence and bio-accumulative nature [4].

Measurements of the total content of metals in sediments do not provide precise information about the degree of environmental risk [1], since not all the chemical forms of a particular metal have the same environmental impact. Metals may be associated with different components of sediments and as a function of the strength of such associations, some fractions of metals may easily interact or not with other environmental compartments (water or biota). Thus, the analysis of metal fractions is vital for the characterization of environmental samples since it provides information about metal mobility and availability [5]. The treatment of sediments by means of a sequential extraction procedure (the use of different extractants with increasing extraction capacity) permits the isolation and identification of the fractions of a particular metal-containing matrix phase, such as, for example: an easily available water soluble and/or exchangeable fraction; a carbonate bound fraction, which could be available under acid conditions; manganese and iron oxides and moderately reducible oxides that contain metals that are easily or moderately reducible; and an organically bound fraction, which contains metals bound to straightforwardly extractable organic matter [5].

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Since the appearance of the first sequential extraction scheme proposed by Tessier et al., 1979 [6], several protocols for metal partitioning have been described using different extractants and conditions, which, together with the absence of certified reference samples, has made the comparison of the results of environmental investigations difficult. The development of the BCR sequential extraction scheme resulting from studies supported by the Commission of the European Community Bureau of Reference (BCR) however has helped to standardize different methodologies, thus permitting useful comparisons to be made [7]. Later studies have subsequently introduced changes that have improved the precision and repeatability of the procedure resulting in the modified BCR sequential extraction scheme [8], as well as contributing the first reference material for metal partitioning studies of environmental samples such as sediments [9,10] making this a widely used protocol. Currently, investigations aimed at reducing extraction times by means of ultrasonic baths and microwave digesters continue to be undertaken [11,12], as well as the employment of matrix solid-phase dispersion techniques (MSPD) to assist the extraction process [5].

Sediment matrices are complex and the concentrations of many heavy elements are found at trace levels. Among the most widely used techniques for sediment analysis that have provided satisfactory results, in terms of precision and accuracy are isotope dilution mass spectrometry (ID-ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-OES), X-ray fluorescence spectrometry, flame atomic absorption spectrometry (FAAS) and electrothermal atomic absorption spectrometry (ET AAS) [13]. The technique of ICP-MS is extensively used due to its high sensitivity, wide linear dynamic range and high capacity for multi-element and isotopic ratio measurement [14], ICP-OES is also often used for the analysis of major and minor elements [5,14–18], while FAAS is limited to the determination of major elements due to its poor detection levels [1,2,19–21].

ET AAS, despite its high sensitivity, is less commonly used than ICP-OES and ICP-MS for the analysis of sediments due to its limited capacity for multi-element analysis and narrow linear dynamic range. Studies using ET AAS for sediment analysis have been mainly aimed for determining total metal content [22–27]. Although, there have been some literatures that have reported improvements on the sensitivity and accuracy of metal determinations in sediment slurry [12,25–27], few studies have focused on identifying the available fractions of metals in sediments and their chemical fractionation [11,12,23,28–32], either using the BCR sequential extraction schemes or other similar procedures. Furthermore, differences on the non spectral interferences from the matrices, that could affect the atomization of analytes and hence their quantitative analysis, is an inconvenience to be considered when total content and the available fractions of metals in sediments are determined by ET AAS. Studies have shown that the matrices from the different stages of sequential extraction procedures can induce matrix interferences that affect the sensitivity of some elements [11,12].

Methods for simultaneous determination by ET AAS has been applied to different kinds of samples such as biological fluids [33–38], food stuff [39,40], metals and alloys [41,42], coal [43], environmental particulate [44], and water and geological materials [45]. Simultaneous determination using solid sampling and high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS-ET AAS) [46,47] has also been explored during the last decade. Up to our knowledge, simultaneous determination of the available fractions in sediments by ET AAS has not yet been performed.

The simultaneous determination in different matrices by ET AAS would considerably reduce analysis time. Finding the appropriate compromise conditions is, however, a challenge. The

application of experimental designs for the optimization of analytical conditions can significantly reduce the time spent on optimization and enable the detection of interactions between the variables under study, which is not possible using conventional univariate optimization methods [48]. Experimental designs are based on varying all factors simultaneously at a limited number of factor levels. Among the three-level, or response surface designs, the Box–Behnken design is one of the most important [48].

The aim of this investigation was to study the simultaneous determination of the total content and available fractions of As, Cd, Cr, Cu, Ni, Pb and Tl in sediments by ET AAS applying the conventional standard method for total sample digestion and metal partitioning, in order to propose a simple method useful for environmental research.

2. Materials and methods

2.1. Equipment

A Perkin Elmer atomic absorption spectrometer, model SIMAA 6000 (Bodenseewerk Perkin Elmer GmbH, Germany) with transverse heated electrothermal atomization and a longitudinal Zeeman-effect background correction system, applied inversely, was used. Samples were delivered with an AS-72 auto sampler and atomized with standard transverse-heated graphite atomizers (ST-THGA). Perkin Elmer electrode-less discharge lamps (EDLs) System 2[®] were used for As, Cd, Pb and Tl, Intensitron[®] hollow cathode lamps (HCL) for Ni and Lumina[®] hollow cathode lamps for Cr and Cu. Sediment sample digestion was carried out in a CEM MDS 2000 microwave digestion system.

2.2. Reagents

Nitric acid (65%, Merck KGaA, Darmstadt, Alemania), HF (48%, Ashland Reagent H-640, Covington, KY, USA) and H₃BO₃ (99.5%, Riedel-de Haën GmbH & Co. KG) were used for the total digestion of the sediments and glacial acetic acid (96%, Merck), hydroxylamine hydrochloride (98%, Scharlau Chemie SA, Barcelona, Spain) and ammonium acetate (97+% A.C.S. reagent, Sigma-Aldrich, St. Louis MO, USA) for the sequential extraction of the sediments. HNO₃ and HF were distilled three times in a Teflon distiller at sub-boiling temperatures. Aqueous solutions of the analytes were prepared from 1000 mg L⁻¹ uni-elemental stock solutions: As and Tl (Spex CertiPrep England), Cd and Cr (Merck), Ni and Pb (Riedel-de Haën) and Cu (Fluka Chemical, Sigma-Aldrich GmbH, USA). De-ionized water was used throughout the study (18 MΩ). The accuracy and precision of the methodology was evaluated throughout using the sediment certified reference materials LKSD-4 (Brammer Stanford Company INC, Houston, USA), CRM NCS DC 73315 and BCR 701 (Spex CertiPrep, England).

2.3. Experimental methodology

2.3.1. Sample digestion

Certified reference samples of sediments, CRM NCS DC 73315 and LKSD-4, were brought into solution by means of acid digestion assisted by a microwave digestion oven, following the standard procedure EPA 3052 [49], modified for the type of sediments under study. In each case, 5 mL of concentrated HNO₃, 2 mL of concentrated HF and 2 mL of water were added to 0.5 g of sediment in a Teflon vessel and digested in the microwave digestion oven by applying the heating program shown in Table 1. Finally, 20 mL of 5% w/v boric acid was added

Table 1
Microwave digestion program for the total digestion of the sediment samples.

Step	1	2	3	4
Power (%)	60	60	60	60
Pressure (psi)	100	130	160	170
T1 ¹ (min)	30	30	30	30
T2 ¹ (min)	15	10	5	5

¹T1: maximum time needed to reach the required pressure;
T2: time the sample remains at the required pressure.

and the solution brought to a final volume of 50 mL with de-ionized water.

2.3.2. Solutions of available fractions of metals in sediments

The certified reference material of sediments, BCR 701, was processed using the modified BCR sequential extraction scheme [8]. The extracts resulting from stages 1 and 2 of the procedure were then analyzed to determine: water soluble, interchangeable and carbonate-associated elements, and elements associated with manganese and iron oxyhydroxide, respectively.

For stage 1, 40 mL of CH₃COOH, 0.11 mol L⁻¹ were added to 1 g of sediment and the mixture left at room temperature for 16 h in a mechanical shaker. It was centrifuged and the supernatant filtered and brought to 45 mL. Stage 2 uses the residue from stage 1. The residue was washed with water, and 40 mL of NH₂OH.HCl, 0.5 mol L⁻¹ at pH 2 were added and the mixture left in a mechanical shaker for 16 h at room temperature. The mixture was then centrifuged, filtered and the supernatant brought to a final volume of 45 mL with de-ionized water. The supernatants from stages 1 and 2 were filtered (step not included in the modified BCR procedure) in order to remove any suspended particulate that could affect the accuracy and precision of analysis by ET AAS.

2.3.3. Optimization of simultaneous analysis by ET AAS

The optimization of the atomization temperature and mass of the chemical modifiers, Pd(NO₃)₂ and Mg(NO₃)₂, was carried out by applying the 3³ Box–Behnken factorial design [45]. The 3³ factorial design, consisted of 15 runs performed by triplicate in a random order, was applied to the different matrices under study: the solution of total digestion of sediments (STD), solutions resulting from stage 1 (SS1) and stage 2 (SS2) from the modified BCR sequential extraction procedure, and the standard aqueous solution (SAS). The measurement used for statistical analysis was the integrated absorbance. Data were processed using the Statgraphic Plus program Windows version 5.0. Statistically significant effects were calculated at a 95% confidence level ($P=0.05$).

Spectral overlap interferences present in the PE-SIMAA 6000 spectrometer (As–Cd, Tl–Pb and Cr–Ni) which are automatically detected by the PE-Simaachek software (incorporated into the spectrometer), can reduce the precision of the measurements, thus affecting the results of the experimental design. In order to avoid this, the elements were separated into two groups: Group 1; Ni, Pb and As, and Group 2; Cd, Tl, Cu and Cr. Table 2, shows the factors, levels and decoded values used in the 3³ Box–Behnken design for each group of elements.

The heating program for ET AAS consisted in a drying step at 110 °C for 30 s, a pyrolysis stage established at a low temperature (300 °C) due to differences in the volatility of the analytes and types of matrices considered, a cool step at 30 °C for 3 s and a cleaning step at 2550 °C for 2 s. Some authors have omitted the pyrolysis step for the atomization of Tl in order to avoid non-specific interferences from chlorides [50] and those due to the

Table 2
Factors, levels and decoded values in the Box–Behnken 3³ factorial design^a

Factors	Levels	Decoded values	
		Group 1	Group 2
A: Atomization temperature (°C)	–1	2100	1700
	0	2300	2000
	+1	2500	2300
B: Mass of Mg(NO ₃) ₂ (µg)	–1	0	0
	0	3	3
	+1	6	6
C: Mass of Pd(NO ₃) ₂ (µg)	–1	0	0
	0	5	5
	+1	10	10

^a Factorial design performed in 15 runs done by triplicate and in a random order. Group 1: As, Ni and Pb; Group 2: Cd, Cu, Cr and Tl.

presence of Pd and SO₂ [51,52], and others have used instead a “modified drying stage” [53]. The atomization temperature was optimized by factorial design, and the integration time for each analyte was established according to the results of preliminary assays (3, 8, 6, 8, 3 and 4 s for Cr, Cr, Cu, Ni, Pb and Tl, respectively). After data analysis, the elements were re-grouped according to the similarity of the optimum compromised conditions, determined by the factorial design.

2.3.4. Figures of merit

The analysis of all matrices was carried out under the optimum conditions for the simultaneous detection of each group of elements using a standard calibration curve. The figures of merit, characteristic mass, m_0 , and limit of detection, LOD , were determined ($m_0=0.0044/m$ and $LOD=3s/m$, where s is the standard deviation of ten readings of each matrix blank and m is the calibration sensitivity or slope). The accuracy ($P=0.05$) and precision (RSD) of the method were determined by triplicate analysis of the certified reference materials. The method recovery ($\%R_m=100 \times (C_{ob}/C_{cert})$, where C_{ob} and C_{cert} are the concentrations obtained and certified, respectively) and instrumental recovery ($\%R_i=100 \times (m_{obt}/m_{spk})$, where m_{obt} is the mass determined for the corresponding mass of the spike, m_{spk} , performed during the chemical analysis) were also calculated.

3. Results and discussion

3.1. Compromise conditions for simultaneous determination of the studied elements, by ET AAS

Figs. 1 and 2 show the Pareto charts representing the standardized values of the effects obtained from the analysis of the factorial design for elements groups 1 and 2, respectively. The sign (positive or negative) of the effects indicates how the analytical signal is modified when the factor is raised to a higher level. Thus, a positive or negative sign indicates that raising the factor level causes the integrated absorbance signal to increase or decrease, respectively.

Table 3 shows the decoded optimum values determined for the factors considered in this study, for which, the best integrated atomic absorption signals were obtained. Values in bold are those for which the effect was statistically significant ($P=0.05$). According to these results, the elements were re-grouped for the simultaneous analysis in the following way:

3.1.1. Cadmium and thallium

The optimum conditions for the simultaneous determination of these elements were an atomization temperature of 1700 °C

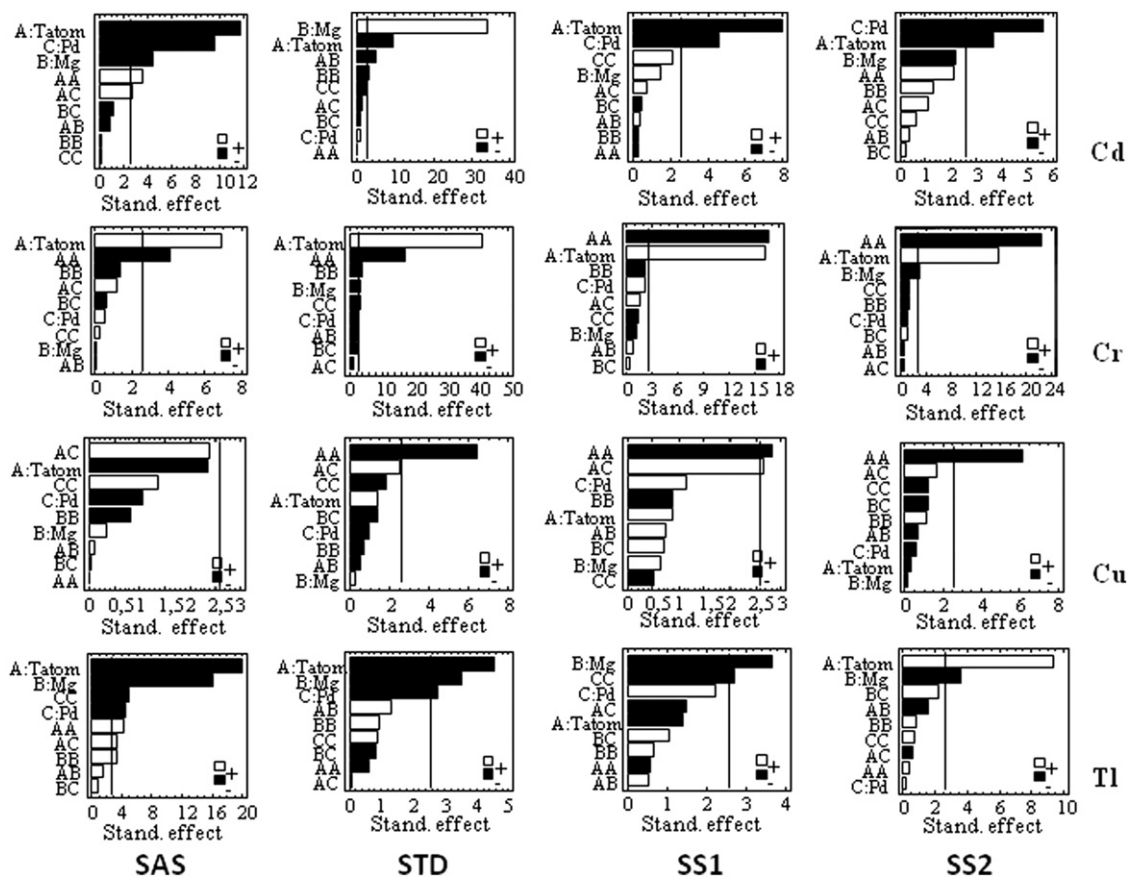


Fig. 1. Pareto charts for the Group 1 elements. Note: SAS: Standard aqueous solution; STD: Solution of total digestion of sediments; SS1: Sequential extraction solution stage 1; and SS2: Sequential extraction solution stage 2.

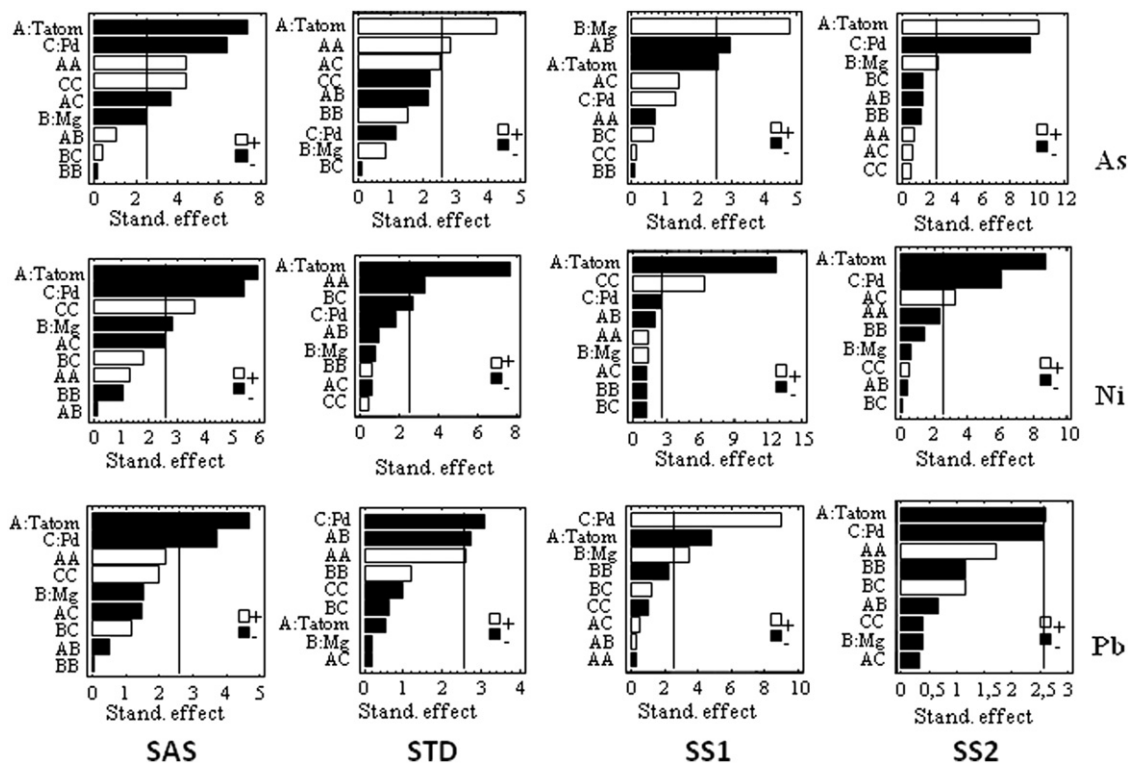


Fig. 2. Pareto charts for the Group 2 elements. Note: SAS: Standard aqueous solution; STD: Solution of total digestion of sediments; SS1: Sequential extraction solution stage 1; and SS2: Sequential extraction solution stage 2.

without the use of chemical modifiers. According to the results of the factorial design (Table 3 and Fig. 1), the atomic absorption signal of Tl, is affected negatively by the presence of $Mg(NO_3)_2$ in all solutions ($P=0.05$) and only produces significant improvement for Cd in the sediment total digested solution (STD). Similarly, the presence of $Pd(NO_3)_2$ does not significantly improve the signals of either Tl or Cd in any of the matrices, and has a significant negative effect on some of them (for Tl in SAS and STD solutions and for Cd in SAS, SS1 and SS2 solutions). Significant interactions between the effects of the chemical modifiers were not observed.

3.1.2. Arsenic, chromium, copper, nickel and lead

The results (Table 3) show that the compromise atomization temperature for the simultaneous determination of these elements falls between 2100–2300 °C. This, despite the fact that the sensitivity of As and its recovery from STD and SS2 may be affected since the optimum atomization temperature for these solutions is 2500 °C (according to the results of the factorial design). Regarding the element Cr, the second order effect associated with its atomization temperature (AA) was significant ($P=0.05$) and negative for all the solutions analyzed (Fig. 1). The optimum atomization temperature for this element was between 2000 and 2300 °C.

As regards the effects of the use of the chemical modifiers on this group of elements, the addition of $Pd(NO_3)_2$ modifier significantly

improved the Pb signal in the SS1 sample solution. In addition, it affected significantly and negatively the signal of most of the others elements (As, Ni and Pb in SAS and SS2 solutions) and showed a negative interaction with the atomization temperature (AC) for the majority of the elements in nearly all matrices considered, except for Ni in the SS2 solution (Figs. 1 and 2). By other hand, the effect of $Mg(NO_3)_2$ only had a significant and positive effect on As and Pb in SS1 solution, but had a significant negative effect on Ni in SAS solution and Cr in STD and SS1 solutions and a significant negative interaction on the atomization temperature (AB) that affected Pb in the STD solution (Figs. 1 and 2). For this group of elements, significant interaction between the effects of the chemical modifiers (BC) was only observed for Ni in the STD solution, and with a negative effect (Figs. 1 and 2). Thus, the chemical modifiers were not employed for Arsenic, Chromium, Copper, Nickel and Lead determination.

For the final selection of the compromise atomization temperatures, the certified material CRM NCS DC 73315 was analyzed using a standard calibration curve, at both atomization temperatures. The resulting characteristic masses (36, 10.6, 40 and 52 µg and 28, 6.5, 34 and 46.5 µg for Cu, Cr, Ni, Pb and at 2300 and 2100 °C, respectively). The accuracy of the method was better at 2100 °C than that at 2300 °C (recovery percentages between 65% and 85% and 89% and 104% at 2300 °C and 2100 °C, respectively). Thus, 2100 °C was selected as the compromise atomization

Table 3
Optimum values of the factors determined by the 3^3 factorial design^a.

Group 1		As			Ni			Pb					
Solutions		A	B	C	A	B	C	A	B	C			
SAS		2100	0	0	2100	0	0	2100	0	0			
STD		2500	0	7	2100	6	0	2100	6	0			
SS1		2100	6	10	2100	6	0	2100	5	10			
SS2		2500	5	0	2100	3	0	2100	2	0			
Group 2		Cd			Tl			Cu			Cr		
Solutions		A	B	C	A	B	C	A	B	C	A	B	C
SAS		1700	0	0	1700	0	1	2000	3	0	2200	2	3
STD		1700	6	6	1700	0	0	1700	4	3	2300	2	10
SS1		1700	6	0	1700	0	7	2200	6	10	2100	3	9
SS2		1700	0	0	2300	0	0	1900	6	1	2000	0	1

Values in bold for the effects that resulted significant ($P=0.05$).

Factors: A: Atomization temperature (°C); B: Mass of $Mg(NO_3)_2$ (µg); C: Mass of Pd (µg).

Solutions: SAS: Standard aqueous solution; STD: Solution of total digestion of sediments; and solutions from the modified BCR sequential extraction procedure⁸ stage 1: SS1, and stage 2: SS2.

^a Factorial design performed in 15 runs done by triplicate and in a random order.

Table 4
Characteristic mass and limits of detection in sediments by ET AAS^a.

	<i>m</i> o (µg)	SAS	LOD (µg g ⁻¹)	
			Obtained STD, SS1, SS2	Reported
As	36.5	0.11	0.03–0.07	0.044 ²⁵ ;
Cd	1.8	0.001	0.0005–0.001	0.05 ⁴⁵ ; 0.08 ²⁵ ; 0.043 ²⁶ ; 0.003 ²⁹ ; 0.05–0.14 ¹¹ ; 0.012–0.08 ³¹
Cr	6.5	0.022	0.008–0.028	0.02–0.35 ²⁷ ; 0.077–0.12 ²⁹
Cu	28	0.04	0.02–0.06	0.03–0.12 ²⁹
Ni	34	0.20	0.13–0.29	0.08–0.11 ²⁷ ; 0.001–0.003 ²⁹
Pb	46.5	0.03	0.04–0.10	0.06 ²⁵ ; 0.038–0.05 ²⁹ ; 0.0012–0.014 ³¹
Tl	48	0.003	0.003	

^a LOD determined for the blank solutions: SAS, Standard aqueous solution; STD, Solution of total digestion of sediments; and solutions SS1 and SS2 from de stage 1 and stage 2, respectively, of the modified BCR sequential extraction procedure [8].

temperature for the simultaneous atomization of As, Cr, Cu, Ni and Pb.

3.2. Figures of merit

The analysis was undertaken using a standard calibration curve without the use of chemical modifiers and compromise atomization temperatures at 1700 °C for the simultaneous determination of Cd and Tl and 2100 °C for As, Cr, Cu, Ni and Pb. Under these conditions, the figures of merit: characteristic mass, detection limit, as well as accuracy and precision of the analytical method were determined. The concentration intervals of the analytes in the standard calibration curve were 5–50, 0.5–2, 2–25, 10–120, 10–50, 2–50, 3–12 $\mu\text{g L}^{-1}$ for As, Cd, Cr, Cu, Ni, Pb and Tl, respectively, and the injection volume was 20 μL . Prior to the analysis, the matrices were diluted twenty times for STD and SS1 solutions, five times for Cr, Ni and Pb, fifty times for Cu and eighty times for Cd in the SS2 solution.

The values obtained for the characteristic mass (m_o) and the limit of detection (LOD) are shown in Table 4.

3.2.1. Characteristic mass

The m_o values obtained for the elements were comparable to, or less than those specified by the manufacturer of the instrument for the simultaneous analysis of the elements considered in this study (49, 1.8, 7, 20, 60 and 54 μg for As, Cd, Cr, Cu Pb and Tl, respectively) [54].

Regarding the analysis of sediments by other authors, a wide range of m_o values (0.4–1.5 μg) has been reported for Cd: 1.12–1.51 μg in matrices obtained from the modified BCR sequential extraction scheme with a standard calibration curve at an atomization temperature of 2200 °C without a pyrolysis step [11]; 0.6 μg in sediment slurry samples analyzed using a standard addition curve at a pyrolysis temperature of 700 °C using $\text{Mg}(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$ as modifier [25] and 0.4 μg using Ir as a modifier [26]; and 0.9 μg in water and geological materials by simultaneous analysis using a PE-SIMAA 6000 spectrometer operated at pyrolysis and atomization temperatures of 420 °C and 2200 °C and standard calibration curve, respectively, using the mixture of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ as modifier [45]. In this work an m_o value of 1.8 μg was obtained, which is comparable to that obtained by Filgueiras et al. [11] in matrices from the BCR procedure.

For the rest of the elements, few m_o values have been reported in the analysis of sediments, making comparisons difficult. Nevertheless, a wide range of values has been observed:

For Cr, Pazos-Capeãns et al. [12] obtained an m_o value of 3 μg during the analysis of matrices from the BCR procedure using pyrolysis and atomization temperatures of 1500 °C and 2400 °C, respectively; Felipe-Sotelo et al. [27] obtained a value of 4.1 μg during the analysis of slurry sampling of sediments; and Sen Gupta and Bouvier [45] obtained an m_o value of 13 μg during the simultaneous determination in water and geological materials at pyrolysis and atomization temperatures of 500 °C and 2400 °C, respectively. The m_o value of 6.5 μg obtained in this work (Table 4) falls within the range reported [12,27,45].

For Arsenic, P. Bermejo-Barrera et al. [25] reported an m_o value of 6.9 μg during the analysis of sediments slurry samples, using $\text{Mg}(\text{NO}_3)_2$ and $\text{Pd}(\text{NO}_3)_2$ as modifiers and pyrolysis and atomization temperatures of 1200 and 2300 °C, respectively; and Kopyśc et al. [55] have reported an m_o value of 36.1 μg during the analysis of aqueous solutions using Ir as chemical modifier and pyrolysis and atomization temperatures of 1500 and 2200 °C, respectively, in its simultaneous determination using a PE-SIMAA 6000 spectrometer. On the other hand, Man-Ching et al. [35] reported an

m_o value of 44.0 μg in its simultaneous determination in urine. In this study, an m_o value of 36.5 μg was obtained (Table 4) which is comparable to those obtained in the simultaneous determination [55,35].

For Ni, an m_o value of 14 μg has been reported by Felipe-Sotelo et al. [27] during the analysis of slurry sampling of sediments at pyrolysis and atomization temperatures of 1200 and 2600 °C; and a value of 65 μg was obtained during the simultaneous determination of Ni in water and geological samples at pyrolysis and atomization temperatures of 1500 and 2400 °C, respectively [45]. The m_o value of 34 μg obtained in this work (Table 4) falls within the range reported [27,45].

For Cu, an m_o value of 5 μg has been reported during its simultaneous determination in water and geological materials at pyrolysis and atomization temperatures of 800 and 2300 °C, respectively [45]; for Pb, it has been reported m_o values of 10 μg [25] in slurry sampling of sediments, and 13 μg during the simultaneous determination in water and geological materials at pyrolysis and atomization temperatures of 420 and 2200 °C, respectively, using the mixture of $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ as the chemical modifier [45], which differ from those obtained in this study (m_o values of 28 μg for Cu and 46.5 μg for Pb, Table 4).

The differences between the m_o values obtained in this work compared with other investigations are mainly due to the conditions of analysis. Among these studies, only Gupta et al. [45] applied simultaneous determination by ET AAS of the total content of Ag, Cd, Pb, Bi, Mn, Co, Ni, Cr, Li, Be, Cu, and Sb in sediments. Other studies that have determined the available fraction of metals in extracts of sediments obtained by the modified BCR sequential extraction scheme, do not report the characteristic masses [23,29,30,32].

3.2.2. Limits of detection

Limits of detection are shown in Table 4. In general, the LOD obtained for the matrices analyzed (STD, SS1 and SS2) are comparable to those obtained in the standard aqueous solution (SAS), indicating absence of matrix effects. This is expected due to the high dilution factors used. Differences among limits of detection may be due to differences in sample preparation, specifically as regards as the amount of sediment used for analyses, as suggested by Felipe-Sotelo et al. [27]. The limits of detection values obtained in this study were better for Cd and Cr, and comparable for Cu, Ni and Pb, to those reported in the extracts of sediments totally digested [45], obtained by the BCR procedure [11,29,31] or analyzed by slurry sampling [25–27] indicating that simultaneous analysis of sediment by ET AAS by the methodology proposed in this work does not affect the sensitivity of the elements.

3.3. Accuracy and precision

The results of the analysis of the certified materials are shown in Tables 5 and 6. The total metal content determined in the total digestion (STD) solutions of the certified reference materials (stream sediments, CRM NCS DC 73315, and lake sediments, LKSD-4) (Table 5), agreed with the certified values ($P=0.05\%$) for Cd, Cu, Ni and Pb. For Cr method recoveries of 89% and 94% were obtained satisfying the requirements for quantitative analysis. Regarding As, the $\%R_m$ obtained for the CRM NCS DC 73315 sample was low (69%), however a satisfactory recovery was obtained ($\%R_i=106$). This suggests that losses of the analyte could have occurred during total digestion of the sediments, possibly due to the instability of As in nitric acid solutions [56] and/or the transfer of the solution, before its analysis by ET AAS.

Table 5
Total content ($\mu\text{g g}^{-1}$) in certified reference materials of sediments determined by simultaneous ET AAS^a.

Element	CRM NCS DC 73315			LKSD-4		
	Certified	Obtained	%R _m	Certified	Obtained	%R _m
As	75 ± 4	52 ± 6	69	NC	31 ± 4	ND
Cd	0.82 ± 0.03	0.78 ± 0.05	95	1.9 ± 0.5	2.1 ± 0.2	110
Cr	70 ± 3	62 ± 2	89	33 ± 6	31 ± 2	94
Cu	137 ± 3	139 ± 4	101	31 ± 4	34 ± 2	109
Ni	34.0 ± 1.2	32.5 ± 2.8	96	31 ± 5	33 ± 2	107
Pb	112 ± 4	116 ± 4	104	91 ± 6	101 ± 3	110
Tl	1.16 ± 0.12	1.12 ± 0.04	97	NC	0.58 ± 0.08	ND

^a Concentrations expressed as mean values ± standard deviation ($n=3$); %R_m: Method recovery; ND: Not determined; NC: Not certified.

Table 6
Available concentrations ($\mu\text{g g}^{-1}$) in the BCR-701 sediment sample, following to the modified BCR sequential extraction scheme, determined by simultaneous ET AAS^a.

Elements	Certified	Obtained	%R _m
SS1: Sequential extraction solution stage 1			
As	NC	2.1 ± 0.1	ND
Cd	7.34 ± 0.35	7.7 ± 0.9	105
Cr	2.26 ± 0.16	2.31 ± 0.09	102
Cu	49.3 ± 1.7	48.3 ± 0.8	98
Ni	15.4 ± 0.9	15.1 ± 1.1	98
Pb	3.18 ± 0.21	3.23 ± 0.02	102
Tl	NC	ND	ND
SS2: Sequential extraction solution stage 2			
As	NC	21.2 ± 1.1	ND
Cd	3.77 ± 0.28	3.9 ± 0.2	103
Cr	45.7 ± 2	45 ± 5	98
Cu	124 ± 3	105 ± 7	85
Ni	26.6 ± 1.3	26.03 ± 0.02	98
Pb	126 ± 3	111 ± 4	88
Tl	NC	ND	ND

^a Concentrations expressed as the mean values ± standard deviation ($n=3$); ND: Not determined; NC: Not certified; %R_m: Method recovery.

The concentrations of the metals obtained from the matrices of the SS1 and SS2 extracts of the BCR-701 certified reference sediment sample agreed with the certified values ($P=0.05\%$), except for Cu and Pb in SS2, for which however, satisfactory %R_m were achieved (85% and 88%, respectively) (Table 6). For Tl and As, elements which are not certified in the reference sample, %R_i between 101% and 114% were obtained. The extraction efficiency of As in stage 1 and stage 2 of the modified BCR procedure using the same certified material and its analysis by ET AAS has been shown [32], therefore the results obtained for the instrumental recovery of As in this work would indicate a good accuracy of the analytical procedure.

The precision (RSD) obtained in this study for triplicates analysis was between 0.6% and 6% in most cases, which is comparable to that reported in sediment analyses by ET AAS (2.5%–3.3% [25], 2.35% [26], 10%–12% [27], 2%–28% [31]) and by plasma mass techniques (3%–10% [5]). The highest RSD value was obtained for the total content of Tl in the SDT solution of the reference sample LKSD-4 (14%), probably because the concentration of this element in the sample is close to the LOD of the method. In the case of As in the STD of both reference samples (CRM NCS DC 73315 and LKSD-4), the RSD observed (12% and 13%, respectively) may be associated with losses of this element during sample treatment. Other factors that may affect precision are the reproducibility of the sample treatment methods employed, mainly during the sequential extraction procedure,

and possible contamination effects, this last observed specifically for Cu and Cr.

The determination of total content of Cd, Cr, Cu, Ni, Pb and Tl and available fractions of As, Cd, Cr, Cu, Ni, Pb and Tl in sediments by simultaneous ET AAS performed under the optimized conditions established by this study, showed good accuracy and precision, validating the analytical method employed. According to the results, the filtration of the SS1 and SS2 extracts during the sequential extraction procedure does not affect the accuracy and precision of the BCR procedure. The high dilution factors used in the analysis explain the similar behavior of the analytes in the matrices studied and in the standard aqueous solution. We can thus assume that there are neither complex matrices to be destroyed, nor interferences that could affect the thermal stability of the volatile elements. It is important to note that the use or not of chemical modifiers depends on the needs of each particular investigation. This explains why analysis with a pyrolysis step at a low temperature and none chemical modifiers (unusual in ET AAS), enabled to perform a quantitative analysis of the reference samples of sediments in this study.

There is a claim for further studies that should involve methodologies that avoid As losses attributed to the use of HNO₃ during sediment samples digestion. However, since good results were obtained for the rest of the elements in the matrices considered in this study, changes to the method used for total sediment digestion were not undertaken here.

4. Conclusions

The determination of the total content and available fractions of As, Cd, Cr, Cu, Ni, Pb and As in sediments was accomplished using simultaneous analysis by ET AAS. The optimized compromise conditions used to perform the simultaneous determination, allowed the analysis of different matrices employing a single calibration curve. Due to the high dilution factors applied during the analysis of the different solutions, no matrix interferences effects were observed. The benefits obtained from the reduction in the time of analysis should prove extremely valuable for environmental investigations.

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