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Determination of Cd, Pb and As in sediments of the Sava River by electrothermal atomic absorption spectrometry

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Abstract: The applicability of nitric acid, palladium nitrate and a mixture of palladium and magnesium nitrate as matrix modifiers was estimated for the accurate and reproducible determination of cadmium (Cd), lead (Pb) and arsenic (As) in sediments of the Sava River by electrothermal atomic absorption spectrometry, ETAAS. Decomposition of the samples was done in a closed vessel microwave-assisted digestion system using nitric, hydrochloric and hydrofluoric acids, followed by the addition of boric acid to convert the fluorides into soluble complexes. The parameters for the determination of Cd, Pb and As in sediments were optimised for each individual element and for each matrix modifier. In addition, two sediment reference materials were also analysed. In determination of Cd and Pb, nitric acid was found to be the most appropriate matrix modifier. The accurate and reliable determination of Cd and Pb in sediments was possible also in the presence of boric acid. The use of a mixture of palladium and magnesium nitrate efficiently compensated for matrix effects and enabled the accurate and reliable determination of As in the sediments. Quantification of Cd and As was performed by calibration using acid matched standard solutions, while the standard addition method was applied for the quantification of Pb. The repeatability of the analytical procedure for the determination of Cd, Pb and As in sediments was ±5 % for Cd, ±4 % for Pb and ±2 % for As. The *LOD* values of the analytical procedure were found to be 0.05 mg/kg for Cd and 0.25 mg/kg for Pb and As, while the *LOQ* values were 0.16 mg/kg for Cd and 0.83 mg/kg for Pb and As. Finally, Cd, Pb and As were successfully determined in sediments of the Sava River in Slovenia.

Keywords: cadmium; lead; arsenic; sediments; closed vessel microwave assisted digestion; ETAAS.

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INTRODUCTION

Concern over the presence of pollutants, including metals, has resulted in the development of numerous analytical procedures for their selective and sensitive determination in different environmental and biological samples. Sediments have been frequently analysed in order to estimate the extent of pollution and the impact of anthropogenic activities on the environment. They are known to register changes in the environment and the impact due to industrial pollution, hence providing important information about the contamination of rivers, lakes, estuarine waters and other aquatic systems. Using the results of the analysis, temporal and spatial changes in the concentrations of the pollutants in the environment can be estimated.[1,2] For the evaluation of the metal burden in sediments, the total metal concentration is commonly measured.[1,3–5] In routine analysis, decomposition with strong acid solutions, *e.g.*, different mixtures of concentrated inorganic acids, including hydrofluoric acid[1,6–9] or *aqua regia* digestion[1,9–11] was often applied. The concentration of a particular metal determined after aqua regia treatment was considered as the pseudo total concentration.[1] Determination of trace amounts of Cd, Pb and As in environmental samples (sediment, soil, sewage sludge, coal, fly ash, surface and underground water, *etc*.) is of great importance due to their toxicological importance and persistent character in the environment and living organisms.[12] Numerous analytical techniques, *e.g*., flame or electrothermal atomic absorption spectrometry (FAAS or ETAAS), inductively coupled plasma atomic emission spectrometry (ICP–AES), inductively coupled plasma mass spectrometry (ICP–MS), atomic fluorescence spectrometry (AFS), X-ray fluorescence spectrometry (XRF) and neutron activation analysis (NAA) are available for the determination of trace metals.[13] Among them, ETAAS is one of the most frequently employed analytical techniques for the determination of low concentrations of elements present in environmental samples due to its high sensitivity, selectivity, simplicity and low detection limits. However, when trace metal concentrations in environmental samples are determined by ETAAS, high background absorption and interference effects of complex inorganic matrices and high salt contents, which can have distinct effects on the accuracy of an analysis, have to be considered. For a specific sample matrix, measurement parameters should be optimized for each particular element, or for groups of elements that are simultaneously determined, when a multi-element ETAAS system is applied.[14–16] Additionally, a chemical modification technique was used to minimize both the background absorption signals and interference effects.[17,18] The choice of matrix modifier depended not only on the matrix composition, but also on the specific characteristics of a particular element in ETAAS determinations.[16,19–26]. In the analysis of samples with complex matrices, mixed and composite modifiers rather than individual ones are often preferred. As thermal stabilizers, they often permit higher ashing temperatures than their individual components.[27]

A great number of substances have been investigated as matrix modifiers. Palladium nitrate ($Pd(NO_3)_2$) and magnesium nitrate ($Mg(NO_3)_2$) are considered as universal modifiers for ETAAS.[28–33] The most commonly applied matrix modifiers for Cd and Pb analysis by ETAAS were palladium nitrate and palladium–magnesium nitrate.[28,30,32,33–35] Combined matrix modifier consisting of scandium, palladium nitrate and ammonium nitrate was also proposed for Cd and Pb determinations in environmental samples.[36] For As determination by ETAAS, a mixture of palladium and magnesium nitrate was most frequently used.[24,28–30,32] In addition to palladium nitrate and magnesium nitrate-based modifiers, many other compounds have shown modifier properties. Dilute nitric acid was an appropriate matrix modifier for the determination of trace elements in various biological samples[19] Platinum group elements (Pt, Pd, Ir, Rh and Ru) or carbide forming elements (Zr, Nb, Ta, W) may act as permanent modifiers. Alone or in a mixture, they are frequently used for the determination of Cd, Pb and As in environmental samples.[10,12,25,37–39]

To the best of our knowledge, there are no studies in literature concerning the effects of boric acid on the performance of modifiers in the determination of volatile elements, such as Cd, Pb and As, by ETAAS. These elements are frequently determined in sediments after closed-vessel microwave digestion, which requires the use of nitric acid, hydrochloric acid and hydrofluoric acid, followed by the addition of boric acid to convert the fluorides into soluble complexes. In such complex sample matrixes, the use of an appropriate modifier is of critical importance for their reliable determination. The aim of this study was to optimise the measurement parameters and evaluate the applicability of various matrix modifiers for the determination of Cd, Pb and As in sediment samples after closed-vessel microwave assisted digestion followed by ETAAS. The applicability of various matrix modifiers (nitric acid, palladium nitrate and a mixture of palladium and magnesium nitrate) for the determination of the total metal concentrations was examined by analysis of the sediment reference materials CRM 277 and SRM 2704. The optimized analytical procedures were used for the determination of Cd, Pb and As in sediments of the Sava River in Slovenia.

EXPERIMENTAL

Reagents and reference materials

Merck suprapur acids (hydrochloric, nitric and hydrofluoric acid) were used. Boric acid and a stock standard solution of As (1000±2 mg/L in 5 % nitric acid) were purchased from Fluka. A stock standard solution of Cd and Pb (1000±2 mg L^{-1} in 5 % nitric acid), a stock solution of palladium nitrate and magnesium nitrate (10.0±0.2 g L^{-1}) were obtained from Merck. Fresh working standard solutions were prepared by dilution of a particular stock solution with Milli-Q water (Direct-Q 5 Ultrapure water system, Millipore Watertown, MA, USA) and used in the determination of the total metal concentration. Nitric acid modifier was prepared by dilution of concentrated nitric acid with water 1:3. Palladium nitrate modifier was prepared by dilution of the stock solution with water so that the final concentration of palladium nitrate was 0.2 %. A mixture of palladium and magnesium modifier contained 0.8 mL of 0.2 % palladium nitrate and 0.2 mL of 1 % magnesium nitrate. Two reference materials were used, CRM 277 (trace elements in an estuarine sediment, BCR, Geel, Belgium) and SRM 2704 (Buffalo River sediment, NIST, National Institute of Standards and Technology, USA). All the glassware employed during the analytical procedures was soaked overnight in 10 % (v/v) nitric acid solution, rinsed with Milli-Q water and dried at room temperature.

Instrumentation

Cd, Pb and As were determined by ETAAS on a Hitachi Z-8270 polarized Zeeman atomic absorption spectrophotometer (Tokyo, Japan) equipped with an autosampler. Cd was determined at 228.8 nm, Pb at 283.3 nm and As at 193.7 nm. The spectral bandwidth was 1.30 nm for all analysed elements. The lamp current was 7.5 mA for Cd and Pb and 10 mA for As. 10 μL of sample was introduced into the graphite tube for Cd and Pb determinations and 20 μL for As. 5 μL of modifier was applied into the graphite tube before sample introduction. The wall of pyrolitically coated graphite tubes was used for atomization. The peak areas of the analytical signals were measured.

All samples were digested in a closed-vessel microwave digestion system, CEM MARS 5, CEM Corporation, (Matthews, North Carolina, USA).

Sampling site

The sediments were collected at the sampling sites shown in Fig. 1 along the Sava River in Slovenia. Manual sampling was performed by e use of plastic core liners. The samples of the top layer of the sediment (5 cm) from the shore were collected in polyethylene containers together with surrounding water, transported to the laboratory and stored at 4 °C until analysis., About 3 kg of sample were collected from each location.

Fig. 1. Sampling sites: 1. Mojstrana, 2. Jesenice, 3. Jevnica, 4. Vrhovo, 5. Brežice and 6. Jesenice na Dolenjskem.

In the Slovenian part of the basin, the riverbed is relatively steep and formed from solid rock. Therefore, the samples were taken from the reaches where sediment deposition occurs, usually only a few meters from the riverbank. At the locations Jesenice and Vrhovo, the sediments were sampled just before the hydroelectric dams.

Sample preparation

The sediments were spread on polyethylene foil and divided into four squares. Two diagonal squares were discarded, while other two were mixed and subjected to the same procedure again. The procedure was repeated until approximately 100 g sample remained. The last 100 g of sample was then dried at 40 °C for three days (until constant weight) in the dark, homogenised in an agate mortar and sieved through a 63 μm sieve. Before analysis, the flasks containing the dry sediment samples were shaken virogously for one minute. 0.250±0.001 g of sediment was weighed into a Teflon vessel, 4 mL of nitric acid, 2 mL of hydrofluoric acid and 1 mL of hydrochloric acid were added. Vessels were gently shaken until all the sample was wetted with acid, covered by vessel cups and submitted to closed vessel microwave digestion at the maximal power of 1200 W. The digestion procedure was performed using the following programme, ramp to temperature 30 min (t = 190 °C), hold 60 min (t = 190 °C) and cool 30 min. Subsequently, the Teflon vessels were vented and the vessel caps removed. 12.5 mL of boric acid (4 % w/v) was added to each vessel in order to dissolve the fluorides. The closed-vessel microwave digestion was then applied for a second time using the following programme, ramp to temperature 15 min (t = 190 °C), hold 30 min (t = 190 °C) and cool 30 min. After the digestion, a clear solution was obtained. The contents of the vessels were quantitatively transferred to 30 mL graduated polypropylene flasks and filled to mark with Milli-Q water. These samples were used for the ETAAS determinations. The same digestion procedure, with the exception that no sample was added, was applied to determine blanks. All analyses were realised in duplicate.

Two parallel aliquots of 1 g of the sediment samples were dried to constant weight at 60 °C in order to determine their moisture content. The results of the concentrations of Cd, Pb and As are expressed on the basis of the dry mass.

The ETAAS determinations were realised under clean room conditions (class 10000).

RESULTS AND DISCUSSION

Optimisation of the ashing temperature in electrothermal temperature programme for determination of Cd, Pb and As in sediment samples by ETAAS

For accurate and reliable determinations of the total concentrations of Cd, Pb and As by ETAAS in digested environmental samples, the experimental parameters should be optimised for each particular element and specific sample matrix. In the present work, each stage of the electrothermal temperature programme was optimised with and without modifier with special attention given to the ashing temperature. The efficiencies of three different matrix modifiers, *i.e.*, nitric acid, palladium nitrate, and a mixture of palladium and magnesium nitrate, were compared. In the optimization procedure, the highest ashing temperature was experimentally determined. For this purpose, the intensities (peak area) of the analytical atomic absorption signals and the background absorbance signals of working standard solutions containing 2.5 ng mL^{-1} of Cd and 40 ng mL^{-1} of Pb and As were measured. Aqueous standard solutions were prepared as well as standard solutions in a mixture of acids by applying the sample digestion procedure described above under Sample preparation. The aqueous standard solutions contained 0.5 % (v/v) nitric acid to maintain the analytes in solution. The optimization was commenced without modifier, the addition of modifier followed in the following order: nitric acid, palladium nitrate and the mixture of palladium and magnesium nitrate. To exclude the influence of one modifier on another, the graphite tube was changed after application of a particular modifier. The absorbance signals (peak area) for Cd, Pb and As were measured three times for each parameter under the electrothermal temperature programmes presented in Table I.

TABLE I. Measurement parameters (electrothermal temperature programme) for the determination of Cd, Pb and As in sediments by ETAAS with Zeeman background correction; wavelength, Cd: 228.8 nm; Pb: 283.3 nm; As: 193.7 nm; spectral bandwidth, 1.30 nm; lamp current, 7.5 mA for Cd and Pb, 10 mA for As; sample volume, 10 µL for Cd and Pb, 20 µL for As; modifier volume: 5 µL (before sample introduction)

Stage No.	Metal	Temp. start, °C	Temp. end, °C	Time ramp, s	Time hold, s	Gas flow, mL min^{-1}
1			Dry			
	–	50	90	10	5	200
2			Dry			
	–	90	100	10	5	200
3			Dry			
	–	100	140	10	5	200
3[a]		140	200	20	0	200
4			Ash			
	Cd	140	b	10	15	100
	Pb	140	b	10	15	100
	As	200	b	10	20	100
5			Atomization			
	Cd	1500	1500	0	4	0
	Pb	2000	2000	0	4	0
	As	2500	2500	0	4	0
6			Clean			
	Cd	1800	1800	0	5	200
	Pb	2200	2200	0	5	200
	As	2600	2600	0	5	200
7			Cool			
	–	–	–	0	5	200

[a] Only for As; [b] optimal temperature of the appropriate matrix modifier

Special attention was devoted to the optimisation of the ashing temperature. Hence, for each element, the influence of the ashing temperature on the absorption signal was studied over a wide temperature range. The results of the optimisation of the ashing temperatures for Cd, Pb and As are presented in Figs. 2–4, respectively.

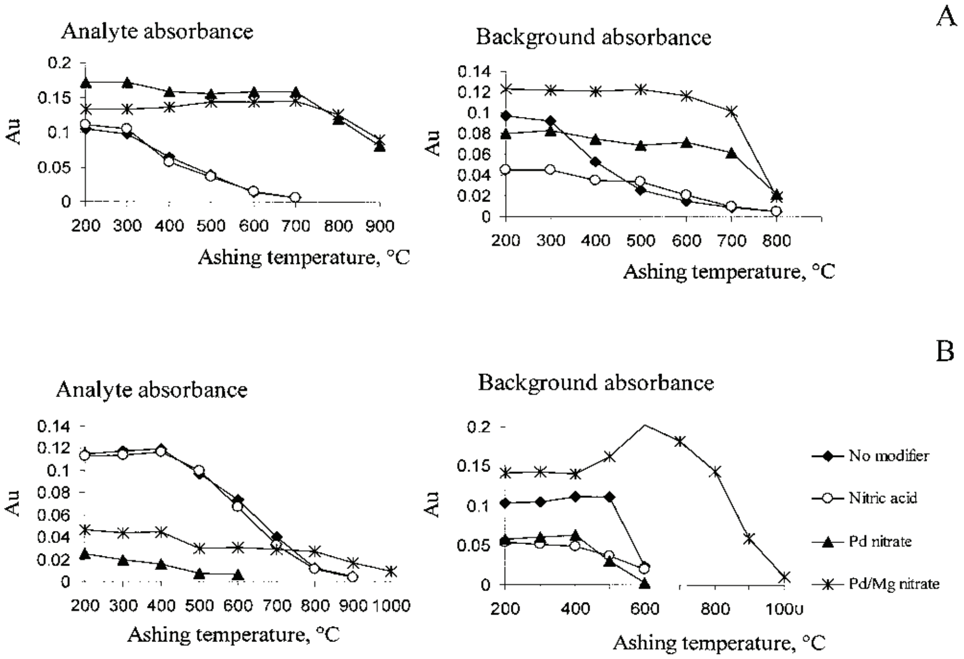

Fig. 2. Optimization of the ashing temperature for Cd in standards (2.5 ng mL^{-1}) prepared in water (A) and in acids used for digestion of the sediments (B). Analyte and background absorbance represent peak area signals expressed in arbitrary units

Data from Fig. 2A and 3A indicate almost the same response of the analytic absorbance signals for Cd and for Pb standards prepared in water if no modifier or nitric acid was used, while the background absorbances were lower when nitric acid was applied. The loss of free Cd and Pb atoms occurred at temperatures higher than 300 and 400 °C, respectively. Palladium nitrate and the mixture of palladium and magnesium nitrate allowed the temperature to be increased up to 700 °C without loss of free Cd atoms and up to 1200 °C without loss of free Pb atoms.

Data from Fig. 2B and 3B further indicate nearly the same response of the analytic absorbance signals for Cd and Pb standards prepared in the acids used for digestion if no modifier or nitric acid was used. Again, the background absorbance was lower when nitric acid was applied. The loss of free Cd atoms occurred at a temperature higher than 400 °C and of free Pb atoms at temperature higher than 300 °C. The addition of palladium nitrate or the mixture of palladium and magnesium nitrate resulted in a substantial losses of free Cd and Pb atoms. The intensity of this effect increased with increasing ashing temperature. It was experimentally proven that these interferences arose from boric acid, which was applied in the closed vessel microwave digestion of the samples. Nitric acid that efficiently transformed the matrix components to nitrates enabled retention of the Cd and Pb atoms within the graphite tube up to temperatures of 400 °C and 300 °C, respectively, also in the presence of boric acid. Since nitric acid also minimized the background absorption signals, accurate and repeatable measurements of Cd and Pb concentrations in the acid mixture were possible.

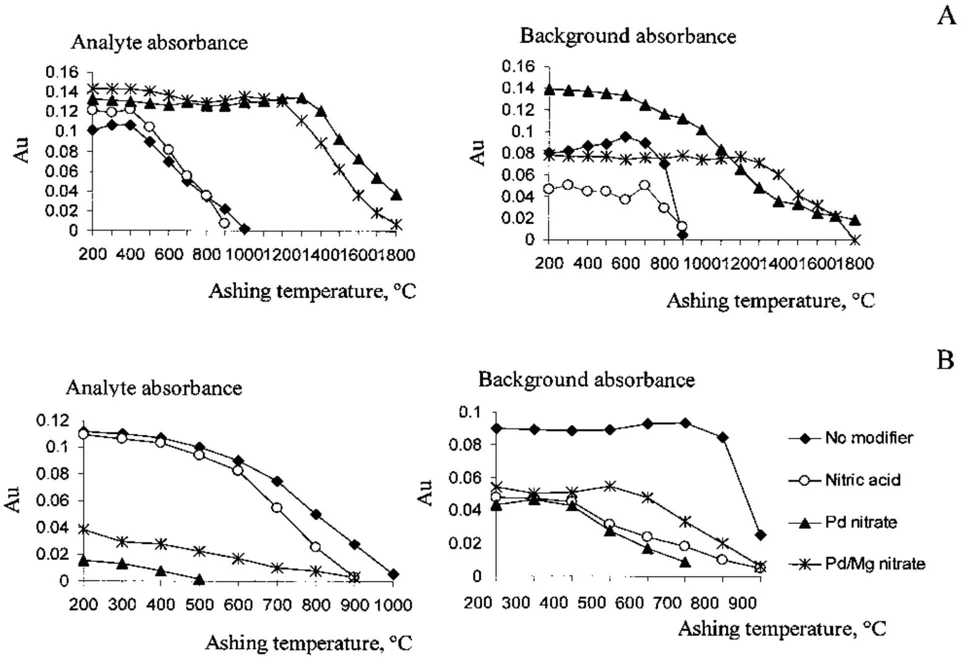

Fig. 3. Optimization of the ashing temperature for Pb in standards (40 ng mL^{-1}) prepared in water (A) and in acids used for digestion of the sediments (B). Analyte and background absorbances represent peak area signals expressed in arbitrary units.

Data from Fig. 4A showed low absorbances for the As standards prepared in water if no modifier was used. This effect is related to the high volatility of As at temperatures as low as 200 or 400 °C.[40] To prevent losses of analyte prior to the atomization step, modifiers based on palladium nitrate or mixtures of palladium and magnesium nitrate are generally recommended.[40] Data from Fig. 4A further indicate that for As standards prepared in water, the use of palladium nitrate and the mixture of palladium and magnesium nitrate enabled the rising of the ashing temperature to be increased up to 1400 °C, while the background absorbance was appreciably lower when a mixture of palladium and magnesium nitrate was applied.

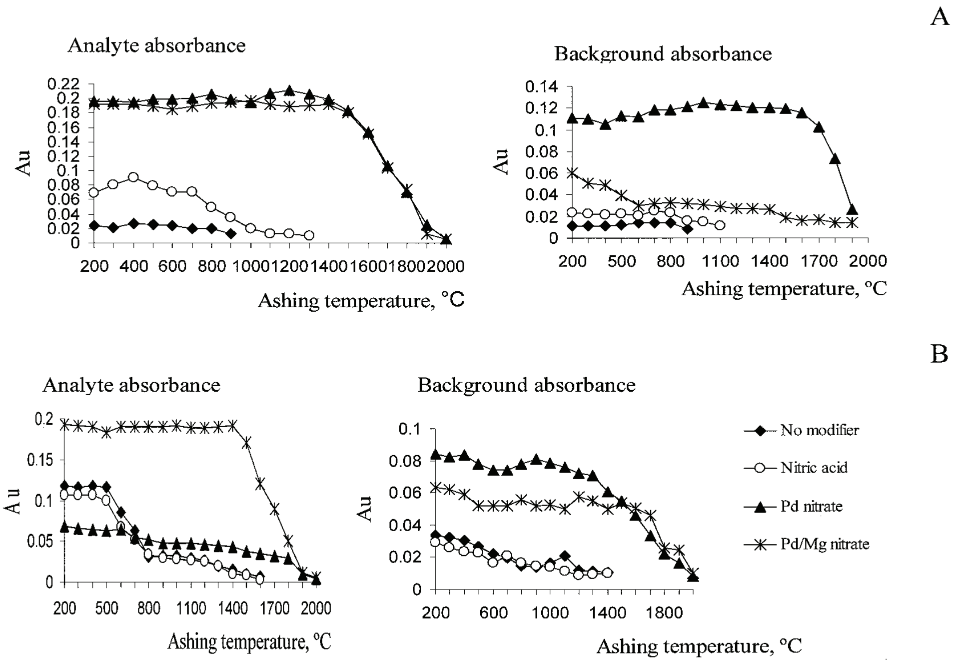

Fig. 4. Optimization of the ashing temperature for As in standards (40 ng mL^{-1}) prepared in water (A) and in acids used for digestion of the sediments (B). Analyte and background absorbances represent peak area signals expressed in arbitrary units.

Data from Fig. 4B indicate that for the As standards prepared in the acids used for digestion, the responses of analytical absorbance signals were low when no modifier, or nitric acid and palladium nitrate modifier were used. The employment of the mixture of palladium and magnesium nitrate modifier efficiently stabilised the free As atoms even in the presence of boric acid up to a temperature of 1400 °C. In addition, the background absorbance was low enough to enable compensation by the Zeeman correction.

Although Cd, Pb and As are all volatile elements, the obtained experimental data demonstrated that there is no universal modifier for all three elements, when they are analysed in the presence of boric acid, making the simultaneous multielement determination of Cd, Pb and As by ETAAS impossible.

To examine the performances of the modifiers in the determination of Cd, Pb and As in sediments by ETAAS, sediment reference materials were further analysed after closed-vessel microwave assisted digestion.

Analysis of sediment reference materials and comparison of the performances of various matrix modifiers

In order to check the accuracy and precision in the determination of Cd, Pb and As in sediments, two reference materials, CRM 277 and SRM 2704, with different concentration ranges of the investigated elements and different sample matrices were analysed. The concentrations of Cd, Pb and As were determined by ETAAS using the optimised electrothermal temperature programme. The samples were digested according to the procedure described above under sample preparation. Three modifiers were used: nitric acid, palladium nitrate and the mixture of palladium and magnesium nitrate. The optimal ashing temperatures based on findings from Figs. 2 to 4 were applied for each element and each matrix modifier. Standards prepared in the acids used for digestion and the standard addition method was used for calibration. Analysis of the reference materials were realised in six parallel determinations. Each sample was measured three times and the average value was calculated. The results of the determination of Cd, Pb and As in the reference materials CRM 277 and SRM 2704 are presented in Table II. The results that agree the best with the certified values are given in bold type. From these data, the optimal modifier and the optimal mode of calibration for an individual element is also evident.

Table II. Concentrations (average of six parallel samples ± standard deviation) of Cd, Pb and As (mg kg^{-1}) in certified reference materials CRM 277 and SRM 2704. The calibration was performed by a working curve using acid-matched standards (A) and by the use of the standard addition method (B). Temperature (t / °C) represents the optimal ashing temperature for Cd and Pb, while t^a / °C is the optimal ashing temperature for As

Element/ /sample	Nitric acid t = 300 °C A / mg kg^{-1}	Pd nitrate t = 300 °C t^a = 400 °C A / mg kg^{-1}	Pd/Mg nitrate t = 400 °C t^a = 700 °C A / mg kg^{-1}	Nitric acid t = 300 °C B / mg kg^{-1}	Pd nitrate t = 300 °C t^a = 400 °C B / mg kg^{-1}	Pd/Mg nitrate t = 400 °C t^a = 700 °C B / mg kg^{-1}	Certified value
Cd CRM 277	11.6 ± 0.2	13.0 ± 0.6	10.8 ± 0.3	16.2 ± 0.2	11.8 ± 0.8	14.0 ± 0.3	11.9 ± 0.4
SRM 2704	3.60 ± 0.17	3.58 ± 0.21	2.38 ± 0.38	5.47 ± 0.17	3.74 ± 0.15	4.18 ± 0.51	3.45 ± 0.22
Pb CRM 277	119 ± 4	179 ± 4	159 ± 4	145 ± 2	143 ± 1	145 ± 2	146 ± 3
SRM 2704	137 ± 6	211 ± 11	154 ± 1	166 ± 6	150 ± 9	146 ± 7	161 ± 17
As CRM 277	29.8 ± 2.9	26.5 ± 3.6	48.5 ± 0.4	60.5 ± 5.6	47.8 ± 4.0	49.1 ± 1.3	47.3 ± 1.6
SRM 2704	14.9 ± 1.2	29.9 ± 2.8	23.7 ± 0.3	11.5 ± 0.6	46.2 ± 7.8	37.4 ± 1.9	23.4 ± 0.8

Data from Figs. 2 and 3, and Table II, indicate that nitric acid is an appropriate modifier for the determination of both Cd and Pb in sediment samples after application of the optimal ashing temperature. Furthermore, the data from Table II indicate good agreement between the determined and certified values of the Cd concentrations in the reference materials when acid-matched standard solutions were used for calibration. The application of other modifiers or the standard addition method gave worse or unsatisfactory recoveries for Cd in the analysed reference sediment materials. It is also evident from the data presented in Table II that good agreement between the determined and certified values were obtained for the Pb concentrations in the reference materials when the standard addition method was applied in the calibration procedure. The employment of other modifiers or acid matched standard solutions gave worse or unsatisfactory recoveries for Pb in the analysed reference sediment materials.

Data from Fig. 4 and Table II indicate that on application of the optimal ashing temperature, a mixture of palladium and magnesium nitrate is an appropriate modifier for the determination of As in sediment samples. Data from Table II further indicate good agreement between the determined and certified values of the As concentrations in the reference materials when acid-matched standard solutions were applied in the calibration procedure. Other modifiers or the use of the standard addition method did not efficiently compensate the matrix effects and, consequently, the agreement between the determined and certified As values was poor.

Based on the present investigation of the performances of nitric acid, palladium nitrate and the mixture of palladium and magnesium nitrate modifiers, and analysis of reference sediment materials after closed-vessel microwave assisted digestion of the samples, it was experimentally demonstrated that the optimal conditions for ETAAS determination of Cd and Pb in sediment samples are when nitric acid at an ashing temperature of 300 °C was applied as the matrix modifier. Accurate and reliable results were obtained for Cd when acid-matched standard solutions were employed for calibration, while for Pb, the standard addition method should be applied in the calibration procedure. For accurate and reliable determination of As in sediments, the optimal modifier is a mixture of palladium and magnesium nitrate at an ashing temperature of 700 °C and the application of acid-matched standard solutions in the calibration procedure.

Linearity, repeatability, limit of detection and limit of quantification

It was experimentally proven that the linearity of the ETAAS determinations ranged from 0.5 to 5 ng mL^{-1} for Cd and from 5 to 50 ng mL^{-1} for Pb and As. The correlation coefficients were better than 0.998 for the three determined elements.

The repeatability of the analytical procedure for the determination of Cd, Pb and As in sediments by ETAAS under optimal conditions was checked by the analysis of six parallel samples of the reference sediment materials CRM 277 and SRM 2704. The results indicated that the repeatability of measurement was ± 5 % for Cd, ± 4 % for Pb and ± 2 % for As.

The limits of detection of the analytical procedure calculated on a 3 *s* basis (the value of three times the standard deviation of the blank) were found to be 0.05 mg kg^{-1} for Cd and 0.25 mg kg^{-1} for Pb and As, while the limits of quantification calculated on a 10 *s* basis (a value of ten times the standard deviation of the blank) were 0.16 mg kg^{-1} for Cd and 0.83 mg kg^{-1} for Pb and As.

Analysis of sediment samples of the Sava River

The optimised analytical procedure for the determination of Cd, Pb and As by ETAAS was applied in the analysis of Sava River sediments. The results of the analysis of the Sava River sediments are presented in Fig. 5. To estimate the environmental status of the sediments of the Sava River, the EPA sediment quality guideline was followed.[41] This guideline proposes the maximal concentrations of chemical compounds that maintain healthy aquatic life associated with bed sediments. The TEL values (threshold effects level) in the EPA guideline refer to the range of concentrations below which adverse toxic effects are not to be expected or are only occasionally observed.[41]

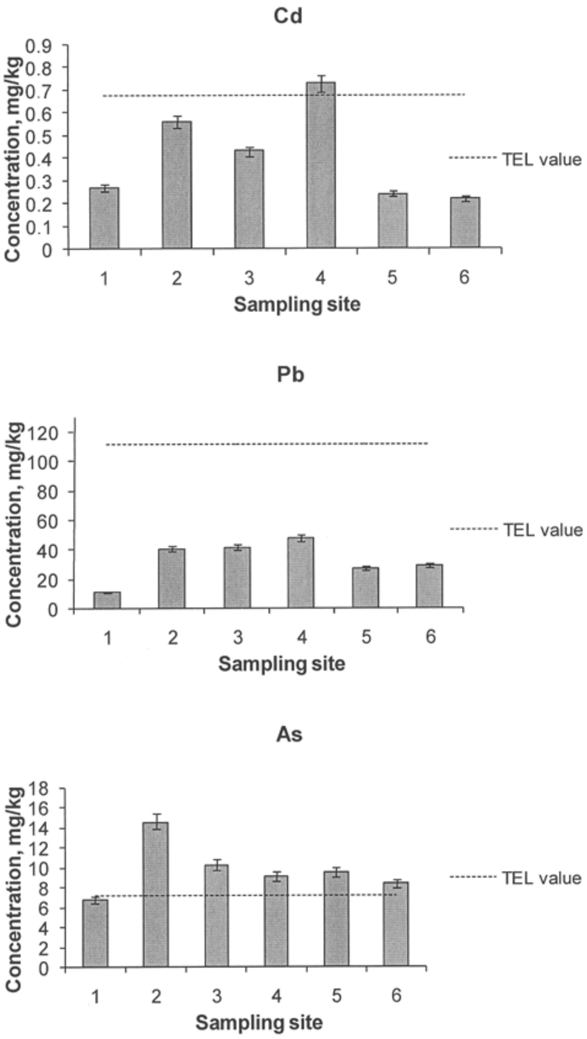

Fig. 5. Concentrations of Cd, Pb and As (mg kg^{-1}) in sediments of the Sava River determined by ETAAS. The results represent the average of two parallel samples. In each bar, the two concentrations that characterize the mean value are indicated.

Data of Fig. 5 indicate that the concentrations of Cd in the sediments of the Sava River were low and ranged between 0.22 and 0.73 mg kg^{-1}. The highest Cd concentration that slightly exceeded the TEL value (0.676 mg kg^{-1})[41] was found in the accumulation basin of the hydroelectric power plant Vrhovo (sampling site 4). The cadmium concentrations in the sediments of the Slovenian part of the Sava River are comparable to previously reported data[42] and to the majority of concentrations determined in River Po (0.4 to 1.4 mg kg^{-1})[43] and are lower than most of the Cd concentrations determined in the sediments of the Danube River (around 2 up to 25 mg Cd kg^{-1})[44] and the Seine River (1 to 2 mg Cd kg^{-1}).[45] Cadmium concentrations are also much lower than those determined at mining area sites (2 to 130 mg Cd kg^{-1}),[2] (around 0.7 up to 7.3 mg Cd kg^{-1})[46] and (2 to 9 mg d kg^{-1})[47]).

Furthermore, the results presented in Fig. 5 indicate that the concentrations of Pb in the sediments of the Sava River ranged between 11 and 48 mg kg^{-1}, which are below the TEL value (112 mg kg^{-1}).[41] The highest Pb concentrations were found in the accumulation basins of the hydroelectric power plants at Jesenice (sampling site 2) and Vrhovo (sampling site 4), as well as at Jevnica (sampling site 3). The lead concentrations in the Slovenian part of the Sava River are in general comparable to previously reported data (around 40 up to 60 mg Pb kg^{-1})[48] and to concentrations of Pb in River Po (40 to 70 mg Pb kg^{-1})[45] and in the Danube River (30 to 100 mg Pb kg^{-1})[44] and are much lower than those reported for mining areas (100 to 9000 mg Pb kg^{-1})[2] and (500 to 5000 mg Pb kg^{-1}).[47]

From the data of Fig. 5, it can be also seen that the concentrations of As in the Slovenian part of the Sava River sediments range from 6.8 to 14.6 mg As kg^{-1}. These As concentrations in general slightly exceed the TEL value (7.24 mg kg^{-1})[41] Since the As concentrations are also close to the TEL value at the sampling site Mojstrana, an unpolluted area near the origin of the Sava River, the concentrations of As in the investigated sediments are most probably characterized by the natural background value of As. The arsenic concentrations in the sediments from the Slovenian part of the Sava River are in general comparable to those of its tributary Savinja and the Rivers Voglajna and Hudinja (around 16 mg As kg^{-1})[46] and are in general lower than those reported for the Danube River (9.0 to 68.9 mg As kg^{-1}).[45]

CONCLUSIONS

The parameters for the determination of Cd, Pb and As in sediments after closed-vessel microwave assisted digestion by ETAAS with Zeeman background correction were optimised. For the decomposition of the samples, a mixture of nitric, hydrochloric and hydrofluoric acids was applied, followed by the addition of boric acid to dissolve the insoluble fluorides. To compensate the matrix effects, the applicability of nitric acid, palladium nitrate and a mixture of palladium and magnesium nitrate modifiers were evaluated for accurate and reproducible determination of Cd, Pb and As in sediments. Nitric acid, which was applied for the first time in the analysis of sample matrixes, that contained boric acid, was found to be the most efficient matrix modifier for the determination of Cd and Pb in sediment samples. By chemical transformation of the matrix components to nitrates with consequential reduction of the background signal, accurate and reliable determinations of Cd and Pb were achieved at an ashing temperature of 300 °C. For the determination of As, the optimal modifier was found to be a mixture of palladium and magnesium nitrate. It allowed the efficient compensation of matrix effects, prevented the loss of analyte at an ashing temperature of 700 °C, and enabled the accurate and reliable determination of As in sediments. For the quantification of Cd and As, the best results were obtained when acid-matched standard solutions were employed in the calibration procedure, while for the quantification of Pb, the standard addition method should be applied.

The optimised analytical procedures were successfully applied in the determination of Cd, Pb and As in sediments of the Sava River in Slovenia. The results indicated that the concentrations of Cd, Pb and As were in general lower than those reported for other moderately polluted rivers in Europe.

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ИЗВОД

ОДРЕЂИВАЊЕ Cd, Pb И As ИЗ НАСЛАГА РЕКЕ САВЕ ЕЛЕКТРОТЕРМИЧКОМ АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОМЕТРИЈОМ

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Примењљивост азотне киселине, паладијум-нитрата и смеше паладијум- и магнезијум-нитрата као модификатора матрице оцењена је у случају поузданог и репродуктивног одређивања кадмијума, олова и арсена из наслага реке Саве електротермичком атомском апсорпционом спектрометријом, ETAAS. Узорци су разграђени у затвореном микроталасном дигестору помоћу азотне, хлороводоничне и флуороводоничне киселине, уз накнадно додавање борне киселине, чиме су флуориди преведени у растворне комплексе. Параметри одређивања Cd, Pb и As у наслагама оптимизовани су за сваки елемент и сваки модификатор матрице понаособ. Такође су анализирана два референтна материјала наслага. Азотна киселина се показала као најпогоднији модификатор матрице за одређивање Cd и Pb. Тачно и поуздано одређивање Cd и Pb из наслага било је могуће и у присуству борне киселине. Утицај матрице је успешно компензован употребом смеше паладијум- и магнезијум-нитрата, што је омогућило тачно и поуздано одређивање As из наслага. Квантитативно одређивање Cd и As урађено је помоћу калибрације стандардим растворима за киселу средину, док је за квантитативно одређивање Pb примењена стандардна метода адиције. Репродуктивност аналитичке процедуре за одређивање Cd, Pb и As из наслага износила је ±5, ±4 и ±2 %, редом. *LOD* вредности аналитичке процедуре износиле су 0,05 mg/kg за Cd и 0,25 mg/kg за Pb и As, док

су *LOQ* вредности износиле 0,16 mg/kg за Cd и 0,83 mg/kg за Pb и As. На крају, Cd, Pb и As су успешно одређени из наслага реке Саве дуж тока кроз Словенију.

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