

Determination of cadmium, copper and lead in soils, sediments and sea water samples by ETAAS using a Sc + Pd + NH_4NO_3 chemical modifier

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Abstract

Cadmium, copper and lead in soils, sediments and spiked sea water samples have been determined by electrothermal atomic absorption spectrometry (ETAAS) with Zeeman effect background corrector using NH_4NO_3 , Sc, Pd, Sc + NH_4NO_3 , Pd + NH_4NO_3 , Sc + Pd and Sc + Pd + NH_4NO_3 as chemical modifiers. A comprehensive comparison was made among the modifiers and without modifier in terms of pyrolysis and atomization temperatures, atomization and background absorption profiles, characteristic masses, detection limits and accuracy of the determinations. Sc + Pd + NH_4NO_3 modifier mixture was found to be preferable for the determination of analytes in soil and sediment certified and standard reference materials, and sea water samples because it increased the pyrolysis temperature up to 900 °C for Cd, 1350 °C for Cu and 1300 °C for Pb. Optimum masses of mixed modifier components found are 20 μg Sc + 4 μg Pd + 8 μg NH_4NO_3 . Characteristic masses of Cd, Cu and Pb obtained are 0.6, 5.3 and 15.8 pg, respectively. The detection limits of Cd, Cu and Pb were found to be 0.08, 0.57 and 0.83 $\mu\text{g l}^{-1}$, respectively. Depending on the solid sample type, the percent recoveries were increased up to 103% for Cd, Cu and Pb by using the proposed modifier mixture. The accuracy of the determination of analytes in the sea water samples was also increased.

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1. Introduction

Determination of trace amounts of cadmium, copper and lead in environmental samples such as soils and sea water is of great importance due to their toxicological importance, accumulative and persistent character in the environment and living organisms [1]. Electrothermal atomic absorption spectrometry (ETAAS) is one of the most employed analytical techniques available for the determination of low concentrations of toxic elements such as Cd and Pb present in environmental samples due to its high sensitivity, selectivity, simplicity and low detection limits for the analyte determinations [1–5]. However, direct analysis of soil and sea water samples by ETAAS have some difficulties due to high background absorption and inter-

ference effects of complex inorganic matrices and high salt contents, which can have distinct effects on the accuracy of an analysis. In order to overcome these problems, different pre-concentration/separation procedures have been generally used. Most of these analytical procedures are specific, time consuming and subject to contamination [3,6,7].

In the determination of trace elements in soil and sea water samples by ETAAS, a chemical modification technique has been used to minimize both background absorption signals and interference effects prior to the atomization stage [3,6,7]. Different chemical modifiers such as Pd [8–11], W + Pd [10], Ni + Pd + tartaric acid (TA) [11], Pd–Mg(NO_3)₂ [8,12], organic acids [6], ammonium nitrate [3,4,13,14] added to aqueous standards and samples by using platforms have been recommended to overcome these effects, showing improved precision and accuracy [5]. Li and Jiang [14] explained that NH_4NO_3 could delay the vaporization of Cd to 600 °C and

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signals of Cd and Pb could increase slightly when NH_4NO_3 was used as modifier.

In this work, Sc [15], Pd, NH_4NO_3 , Sc + NH_4NO_3 , Pd + NH_4NO_3 , Sc + Pd and Sc + Pd + NH_4NO_3 chemical modifiers were comprehensively examined for the determinations of Cd, Cu and Pb in soil, sediment and sea water matrices because these modifier mixtures have not been studied in earlier works. Addition of ammonium nitrate as a chemical modifier facilitates the removal of chlorides and Na^+ , K^+ , Ca^{2+} , etc ions during pyrolysis, and atomization of the analyte is consequently less susceptible to interference. The background absorption signals in samples are then considerably reduced [3]. Sc + Pd + NH_4NO_3 modifier mixture recommended by using the platform was found to be powerful for the determinations of Cd, Cu and Pb in samples. Microwave assisted sample dissolution was employed for shortening the time required for sample dissolution and to avoid analyte losses and contaminations.

2. Experimental

2.1. Instrumentation

A Hitachi 180/80 atomic absorption spectrometer equipped with a 180/78 graphite furnace, Zeeman effect background corrector and an automatic data processing unit (180/205) was used for all absorption measurements. Hitachi pyrolytic graphite coated graphite tubes (P/N-190/6007) inserted with graphite platforms (P/N-190/6008) were employed throughout the experiment. Hitachi Cd, Cu and Pb hollow cathode lamps were used as radiation sources. Measurements were made at the following analytical wavelengths and bandpass settings: 228.8 and 1.3 nm for Cd, 283.3 and 1.3 nm for Pb, and 324.8 and 1.3 nm for Cu. Instrumental parameters and operating conditions recommended by the manufacturer were used, unless otherwise stated. A 20 μl volume of calibration or sample together with modifier solutions was injected into the platform by an autosampler (P/N-170/126). The measurement of absorbance signals was carried out by the integrated absorbance (peak area) mode throughout. Argon 99.995% was used as the purge gas and interrupted during atomization. A Varian Model 9176 recorder was used in a 20 mV/FS span in order to obtain atomization and background signal profiles. The optimized graphite furnace operating conditions and temperature program for the determinations of Cd, Cu and Pb in sample solutions are summarized in Table 1.

2.2. Reagents and standards

Ultrapure water (resistivity $18 \text{ M}\Omega \text{ cm}^{-1}$) obtained from an ultrapure water system (Nanopure Infinity, Barstead, P/N1161, Germany) was used to prepare the solutions throughout. All acids and reagents used were of analytical reagents grade. Nitric acid (65% w/w), HCl (37% w/w),

Table 1

Heating programs for the determinations of Cd, Cu and Pb in samples with different modifiers

Step	Temperature ($^{\circ}\text{C}$)	Ramp (s)	Hold (s)	Ar flow rate (ml min^{-1})
1	60–130	30	–	250
2	130–200	10	10	250
3	200-Variable ^a	30	30	250
4	Variable ^b	0	5	0
5	2700	0	3	250

^a See Table 2.

^b Optimum atomization temperatures of Cd, Cu and Pb obtained are 1500, 2000 and 2700 $^{\circ}\text{C}$, respectively.

H_2SO_4 (95–98% w/w) and HF (40% w/w) obtained from Merck (Darmstadt, Germany) were used. All solutions prepared were stored in high density polypropylene bottles. Plastic bottles, autosampler cups and pipettes, and glassware materials were cleaned by soaking in 20% (v/v) HNO_3 for 2 days and rinsing six times with ultra pure water and dried. Autosampler washing solution containing 0.2% (v/v) HNO_3 plus 0.2% (v/v) Triton X-100 was used to avoid clogging of the autosampler pipette and to improve dispersion of sample solution onto the platform [16,17].

Palladium standard solution (2.0 g l^{-1}) was prepared by dissolving 506 mg palladium nitrate ($\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, Merck) in 2 ml concentrated HNO_3 and diluting to 100 ml. Scandium(III) stock solution (4.0 g l^{-1}) was prepared by dissolving 307 mg Sc_2O_3 (Merck, 99.99% pure) in 2 ml concentrated HNO_3 with heating on a hot plate and diluting to 50 ml. 0.4% (m/v) NH_4NO_3 (Merck, 99.99% pure) was prepared in ultrapure water.

Stock standard solutions of Cd, Cu and Pb (1.0 g l^{-1}) obtained from BDH chemicals (Poole, UK) were used. Calibration solutions of analytes were freshly prepared by successive dilution of the stock standard solutions to the desired concentrations in 0.25% (v/v) nitric acid solutions immediately before use.

2.3. Decomposition of solid samples by microwave digestion

Buffalo river sediment (2704), estuarine sediment (1646a), san Joaquin soil (2709), Montana II soil (2711) and coal fly ash (1633b) standard reference materials (SRMs) from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), and lake sediment (SL-1) and soil (SL-7) certified reference materials (CRMs) from International Atomic Energy Agency (IAEA, Vienna, Austria) were used for checking the accuracy and precision of the proposed method. Decomposition of samples was performed in Milestone Ethos Sel microwave oven (MLS Ethos 1600, Italy) according to the following procedures described in previous works [16–19].

A portion of sample (0.20–0.25 g) was accurately weighed into a Teflon digestion vessel, then 2.0 ml concentrated HNO_3 , 1.0 ml concentrated HCl and 1.0 ml HF were

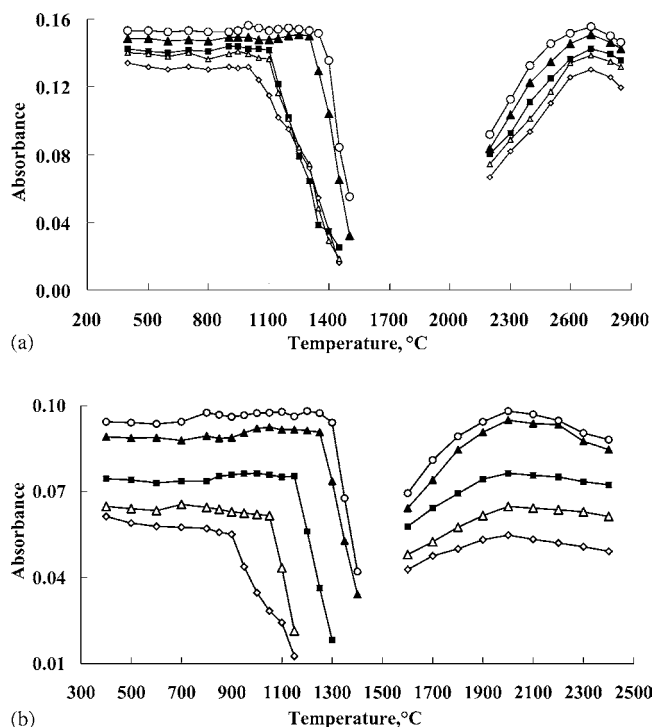


Fig. 1. Pyrolysis and atomization curves for (a) Cu in SRM 2704 ($43.2 \pm 2.2 \mu\text{g l}^{-1}$) and (b) Pb in SRM 1646a ($45.0 \pm 4.6 \mu\text{g l}^{-1}$) without and with modifiers: without (\diamond), $4 \mu\text{g}$ of Pd (\blacksquare), $20 \mu\text{g}$ of Sc (\triangle), $20 \mu\text{g}$ of Sc + $4 \mu\text{g}$ of Pd (\blacktriangle), $20 \mu\text{g}$ of Sc + $4 \mu\text{g}$ of Pd + $8 \mu\text{g}$ of NH_4NO_3 (\circ) as modifiers.

subsequently added to the vessel, with a gentle swirl of the acid mixture. The bomb was closed, placed inside the microwave oven, and decomposition was carried out at 180°C and 700–800 W for 40–45 min. After cooling, the bomb cap was withdrawn, and open vessel was placed on a hot plate. One ml concentrated H_2SO_4 was added and gently boiled near to dryness in order to evaporate the excess acids such as HF. If a residue of material remained, the decomposition procedure was repeated until it was dissolved completely. The final solution was transferred to a 25–50 ml volumetric flask by washing interior surface of digestion vessel with 2% (v/v) HNO_3 three times and the final acidity of flask was adjusted to 1% (v/v) HNO_3 .

After adding 2 ml HNO_3 , 0.5 ml HCl and 0.5 ml HF into the two Teflon bombs for blank solutions, vessels were

heated up to 130°C for 20 min by using microwave heating program. The bombs were washed six times with ultrapure water into a 25–50 ml volumetric flask and diluted to the mark after heating on a hot plate nearly 2 ml and cooling.

2.4. Procedure for preparation of sea water samples

Synthetic sea water was prepared according to the previous works [10,11,20]. 2.66 g of NaCl , 0.55 g of MgCl_2 , 0.10 g of CaCl_2 and 0.09 g of KCl salts (3.40% salinity) were dissolved in a Teflon beaker with ultrapure water. A 1 ml each of Cu and Pb (20 mg l^{-1}), and Cd (2.0 mg l^{-1}) standard solutions was added and this solution was transferred into a 100 ml glass volumetric flask. The interior surface of beaker was washed twice with 1.0% (v/v) nitric acid. Final solution was diluted to the mark with ultrapure water and final acidity was adjusted to 0.25% (v/v) in order to avoid adsorption of analytes onto the glass wall. Sea water samples were collected from the surface layer of the Aegean sea coast near to İzmir in two polyethylene bottles (2 l). Sample portions were transferred into 100 ml volumetric flasks and acidified with 1 ml of concentrated nitric acid. One milliliter each of Cd, Cu and Pb solutions described above was spiked into these flasks because the natural contents of these elements in unspiked sea water are below the detection limits. All flasks were filled with sea water to the mark. Twenty microliter of the sample solution prepared was injected into the platform in the presence or absence of individual or mixed modifiers.

2.5. Analytical procedure

A 1 ml of sufficient concentration of analyte in sample solution was mixed with 1 ml of the modifier solution (2.0 mg ml^{-1} of Sc, 0.4 mg ml^{-1} of Pd, 2.0 mg ml^{-1} of Sc + 0.4 mg ml^{-1} of Pd or 2.0 mg ml^{-1} of Sc + 0.4 mg ml^{-1} of Pd + 0.8 mg ml^{-1} of NH_4NO_3) and injected into the platform inserted in pyrolytic graphite coated tube. Pyrolysis and atomization curves for Cu and Pb obtained in sample solutions with or without of the modifiers are shown in Fig. 1. Maximum pyrolysis temperatures of analytes found are given Table 2.

Table 2

Maximum pyrolysis temperatures, characteristic masses and detection limits of cadmium, copper and lead obtained with different modifiers

Modifier	Pyrolysis temperatures ($^\circ\text{C}$)			m_o (pg)			LOD ($\mu\text{g l}^{-1}$)		
	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb
Without	350	1000	900	3.4	23.6	51.8	0.96	4.79	7.26
NH_4NO_3	400	1050	950	3.3	18.4	45.4	0.78	3.62	5.14
Sc	800	1100	1050	2.9	15.2	41.2	0.64	3.14	3.81
Pd	700	1100	1100	2.5	14.3	38.3	0.56	2.73	3.27
Sc + NH_4NO_3	800	1150	1100	2.3	11.8	32.6	0.42	2.11	2.34
Pd + NH_4NO_3	800	1150	1200	2.0	10.2	29.1	0.31	1.86	2.16
Sc + Pd	850	1300	1250	1.4	6.7	21.3	0.17	1.01	1.64
Sc + Pd + NH_4NO_3	900	1350	1300	0.6	5.3	15.8	0.08	0.57	0.83

3. Results and discussion

3.1. Optimization of ETAAS conditions with modifiers

The solid samples are much more complex than water ones, due to high element contents present in the sample matrix. Therefore, the optimizations of ETAAS conditions were carried out for solid samples and they would be efficient for the determinations of analytes in water samples without significant changes [2]. Effect of mass or mass ratio of modifiers on absorbance values of Cd, Cu and Pb in samples, pyrolysis and atomization temperatures and temperature program conditions such as ramp and hold times given in Table 1 were roughly investigated by preliminary experiments. The effect of mass and mass ratio of Sc and Pd, and NH_4NO_3 together with Sc + Pd modifier mixture on the pyrolysis temperatures and absorbance values of analytes in SRM 2704 (Cd and Cu contents are $3.78 \pm 0.24 \mu\text{g l}^{-1}$ and $43.2 \pm 2.2 \mu\text{g l}^{-1}$, respectively) and SRM 2709 (Pb content is $40.6 \pm 1.1 \mu\text{g l}^{-1}$) samples were studied. The optimum mass and mass ratios of the components obtained were $20 \mu\text{g}$ for Sc, $4 \mu\text{g}$ for Pd and $20 \mu\text{g}/4 \mu\text{g}$ for Sc/Pd. The optimum mass of NH_4NO_3 together with Sc + Pd modifier mixture for analytes was $8 \mu\text{g}$. Mass values of Sc, Pd and NH_4NO_3 obtained were compared with previous works [4,11,15] and similar results were observed.

The pyrolysis and atomization temperature curves studied for analytes in SRM 1633b ($3.92 \pm 0.06 \mu\text{g l}^{-1}$ Cd), SRM 2704 ($43.2 \pm 2.2 \mu\text{g l}^{-1}$ Cu) and SRM 1646a ($45.0 \pm 4.6 \mu\text{g l}^{-1}$ Pb) sample solutions in the absence or presence of modifiers are shown in Fig. 1 as examples. As can be seen in Table 2 and Fig. 1, in the absence of a modifier, Cd, Cu and Pb are lost at temperatures higher than 350 , 1000 and 900°C , respectively. These temperatures are higher than the aqueous standard solutions since the soil samples include complex matrices [9,15,21]. The pyrolysis temperatures of analytes obtained with the Sc + Pd + NH_4NO_3 modifier mixture were compared with the previous studies [9,15,21] and they are similar with aqueous solutions. Small differences in temperatures were ascribed to the instrumental parameters and different tubes or platforms used. These pyrolysis temperatures could be used to remove most of the matrix components and interferences such as chlorides in samples mentioned above without the risk of analyte loss prior to the atomization step [11,21]. As can be seen in Table 2, pyrolysis temperatures of analytes obtained with Sc + Pd + NH_4NO_3 were higher than those obtained with Sc + Pd modifier mixture and a single modifier because the additional effect of NH_4NO_3 for the stabilization of analytes.

The optimum atomization temperatures allow complete atomization of the analytes in samples [5]. Atomization curves by varying temperatures ranging from 1300 to 1800°C for Cd, 2200 to 2850°C for Cu and 1600 to 2400°C for Pb were obtained and shown in Fig. 1 by keeping the pyrolysis temperatures constant in the presence or absence of modifiers. Optimum atomization temperatures obtained from

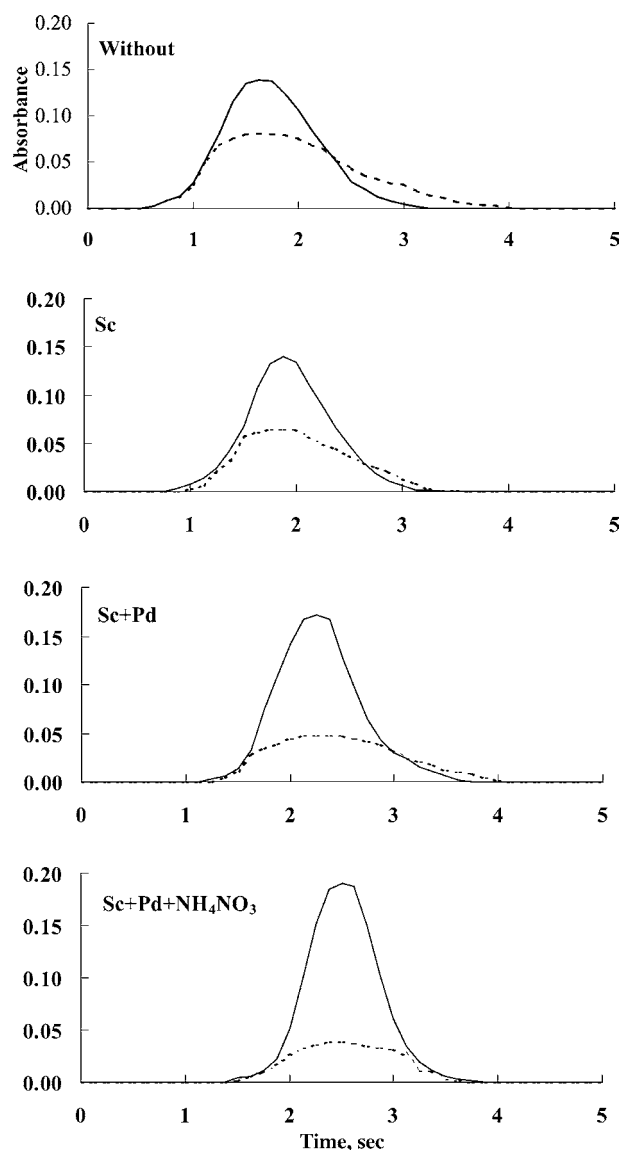


Fig. 2. Atomization profiles of Cu in San Joaquin soil ($49.6 \pm 1.0 \mu\text{g l}^{-1}$) with and without of the modifiers after decomposition with $\text{HNO}_3\text{--HCl--HF}$; where atomization (—) and background (-----) profiles.

Fig. 1 are given in Table 1 and they are similar with the literatures [9,11,12,15,21].

The characteristic mass (m_0) is defined as mass of analyte corresponding to 0.0044 abs unit [11,23]. The limit of detection (LOD) is described as the concentration of an analyte related to three times the standard deviation (3σ) of absorbance units. The characteristic masses and detection limits of analytes were determined in the presence or absence of modifiers from 20 consecutive measurements of the blank solutions [23,24] for the sensitivity of the proposed method. The results obtained are given in Table 2. As can be seen, better m_0 values and lowest detection limits were obtained with Sc + Pd + NH_4NO_3 modifier mixture and they are similar with the results obtained in the previous studies [12,21,22]. Slight inconsistencies in results can be due to

the instrumental and operating parameters used. The reaction mechanism between the analyte and modifier elements has been summarized in previous works [10–12,21,25]. Based on these results, Sc + Pd + NH_4NO_3 modifier mixture was proposed for the determinations of Cd, Cu and Pb in soils, sediments and seawater samples. The Sc + Pd + NH_4NO_3 can help the analyte stabilization onto the platform, allowing higher sensitivity and lower detection limit associated with higher pyrolysis temperatures [2].

3.2. Atomization profiles of analytes

The atomization and background profiles of Cd, Cu and Pb in soil and sea water solutions with and without modifiers were comparatively studied by using integrated absorbance mode in order to show how the modifier affects the absorbance profiles of analytes [8–12,21,22]. Analyte and background atomization profiles of Cu in San Joaquin soil solution obtained in the presence of Sc, Sc + Pd and Sc + Pd + NH_4NO_3 or absence of a modifier are shown in Fig. 2 as example. As can be seen, although the appearance times of the atomic signals of analytes are the same, maximum peak times shifted to a later time were observed when Sc + Pd or Sc + Pd + NH_4NO_3 modifier mixture were used. When no modifier was used, small atomization and higher background signals were obtained. When Sc + Pd + NH_4NO_3 modifier mixture was used, higher atomization and lower background absorption signals were obtained and signal noise ratios of analytes are higher than those obtained in the absence of the modifier. When background signals of analytes with Sc + Pd + NH_4NO_3 are compared with the Sc + Pd modifier mixture, it can be shown that the addition of NH_4NO_3 is important to reduce chloride interferences in samples such as sea water. NH_4NO_3 can convert NaCl to NaNO_3 and NH_4Cl . The NaCl vaporizes at a temperature of 950 °C while NaNO_3 vaporizes nearly 600 °C [4]. So, high salt contents such as chloride and other ion interferences in sample matrix can be reduced by using NH_4NO_3 [14].

3.3. Analytical figures of merit

Cadmium, Cu and Pb in sample solutions were determined in the presence or absence of modifiers by using

the calibration graph method, instead of the analyte addition technique. Calibration graphs were carried out against aqueous standard solutions, with a linear range extending up to $6 \mu\text{g l}^{-1}$ for Cd, $80 \mu\text{g l}^{-1}$ for Cu and Pb. Obtained calibration graphs by using optimum parameters given in Tables 1 and 2, and mass and mass ratio of modifiers described in Section 3.1 were linear. All correlation coefficients (r) for analytes were higher than 0.99, indicating good linearity for the working ranges specified under experimental conditions.

3.4. Applications

An extensive application of single and mixed modifiers selected or without a modifier for the determination of Cd, Cu and Pb in digests of solid reference materials, spiked synthetic and natural sea water solutions was carried out for the accuracy and performance of the proposed method. Heating program (Table 1) and pyrolysis temperatures for analytes (Table 2) were used. In all cases the calibration was run against aqueous standard solutions. The results of analytes found in soils and sediments with Sc + Pd + NH_4NO_3 modifier mixture are given in Table 3. They are presented as the average \pm confidence interval (at 95% confidence level, $t_{\text{Student}} = 2.36$, $n = 8$ replicate measurements of sample solution). As can be seen in Table 3, in the presence of Sc + Pd + NH_4NO_3 , the results obtained are in good agreement with the certified values and the recoveries are in range of 96–103%. Synthetic sea water containing $4 \mu\text{g l}^{-1}$ Cd, $50 \mu\text{g l}^{-1}$ Cu and Pb, and Aegean sea water containing $2.5 \mu\text{g l}^{-1}$ Cd, $30 \mu\text{g l}^{-1}$ Cu and Pb diluted from the stock solutions described in Section 2.4 were analyzed in the presence or absence of modifiers. The obtained percent recoveries of analytes in these solutions are 97–100% in the presence of Sc + Pd + NH_4NO_3 modifier mixture. By using Sc + Pd + NH_4NO_3 , standard deviation of the measurements decreased, the accuracy and precision increased. It can be plausibly concluded that NH_4NO_3 is valid modifier for depressing or reducing the chloride interferences as NH_4Cl (g) at low temperatures. The percent recoveries of analytes found in samples are lower than 88 in the absence of a modifier because of matrix interferences in samples. In addition, percent recoveries of analytes obtained in Aegean sea water are higher than synthetic seawater because the salt

Table 3
Cadmium, copper and lead determination in soil and sediment reference materials

Sample	Concentration ($\mu\text{g g}^{-1}$)					
	Cd		Cu		Pb	
	Certified	Found	Certified	Found	Certified	Found
SRM 2704	3.45 ± 0.22	3.42 ± 0.09	98.6 ± 5.0	99.7 ± 3.8	161 ± 17	160 ± 9
SRM 1646a	0.148 ± 0.007	0.15 ± 0.01	10.01 ± 0.34	9.87 ± 0.16	11.7 ± 1.1	11.6 ± 0.3
SRM 2709	0.38 ± 0.01	0.39 ± 0.01	34.6 ± 0.7	34.4 ± 0.4	18.9 ± 0.5	18.4 ± 0.3
SRM 1633b	0.784 ± 0.006	0.79 ± 0.01	112.8 ± 2.6	112.2 ± 2.1	68.2 ± 1.1	68.4 ± 0.8
SRM 2711	41.7 ± 0.25	40.9 ± 0.1	114 ± 2	113 ± 2	1.16 ± 0.03	1.14 ± 0.01
CRM SL-1	0.26 ± 0.05	0.25 ± 0.01	30.0 ± 5.6	29.7 ± 1.9	37.7 ± 7.4	37.5 ± 2.1
CRM SL-7	$1.3 (1.1–2.7)$	1.31 ± 0.02	$11(9–13)$	11.3 ± 0.3	$60(55–71)$	62 ± 2

contents of natural sea water are lower than synthetic sea water.

4. Conclusion

Direct determinations of Cd, Cu and Pb in soil, sediment and sea water samples containing high element constituents and salinity matrices by using matrix modifiers such as Sc, Pd, Sc + Pd and Sc + Pd + NH_4NO_3 have been investigated. Interference effects and analytical problems arising from the sample matrix could be reduced by using the Sc + Pd + NH_4NO_3 modifier mixture and platform inserted into graphite tube. It can be expected that the recommended chemical modifier mixture is applicable to the trace determinations of Cd, Cu and Pb in various samples such as soil, sediment and sea water although they have highly complex and salinity matrices.

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