

Determination of cadmium, copper and lead in soils, sediments and sea water samples by ETAAS using a Sc + Pd + NH₄NO₃ chemical modifier

Orhan Acar*

Department of Nuclear Chemistry, Ankara Nükleer Araştırma ve Eğitim Merkezi, 06100 Ankara, Turkey

Received 8 March 2004; received in revised form 31 May 2004; accepted 23 July 2004

Available online 25 August 2004

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 NH₄NO₃, Sc, Pd, Sc + NH₄NO₃, Pd + NH₄NO₃, Sc + Pd and Sc + Pd + NH₄NO₃ 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 + NH₄NO₃ 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 NH₄NO₃. 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 µg 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.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Soil; Sediment; Sc + Pd + NH₄NO₃; Cadmium; Lead; ETAAS

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(NO₃)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 NH₄NO₃ could delay the vaporization of Cd to 600 °C and

* Tel.: +90 312 2126230; fax: +90 312 2234439.

E-mail address: orhana@taek.gov.tr.

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

Download English Version:

<https://daneshyari.com/en/article/10561576>

Download Persian Version:

<https://daneshyari.com/article/10561576>

[Daneshyari.com](https://daneshyari.com)