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Journal of Chromatography A, 915 (2001) 167–175

JOURNAL OF
CHROMATOGRAPHY A

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Ion chromatographic preconcentration of Cu and Cd from ultra-high-purity water and determination by electrothermal atomic absorption spectrometry

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Received 22 March 1999; received in revised form 9 February 2001; accepted 9 February 2001

Abstract

A method based on preconcentration of Cu and Cd from ultra-high-purity water by ion chromatography (IC) and determination by electrothermal atomic absorption spectrometry is described. A small low-capacity ion-exchange concentrator Dionex HPIC-CG5 and mobile phase of 3 mM pyridine-2,6-dicarboxylic acid (PDCA) are used. Water samples are loaded onto the preconcentration column at a flow-rate ranging from 1 to 3.5 ml min⁻¹. Large sample volumes (up to 200 ml) can be loaded onto the concentrator without losing metal ions. Elution is carried out in the reverse direction of sample loading and the volumes of effluent are as small as 0.150 and 0.200 ml for copper and cadmium, respectively. Under these conditions the preconcentrated ions coelute. The detection limits, based on the Hubaux–Vos method, for Cu using a 1300-fold preconcentration in the IC step was found to be 1 pg ml⁻¹, and was limited due to impurity in PDCA, while the detection limit found for Cd using a 1000-fold preconcentration was 0.02 pg ml⁻¹. Ultra-high-purity water produced by a Millipore system is successfully analysed by the proposed method and the content of Cu and Cd are found to lie in the range 1–10 pg ml⁻¹. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Sample handling; Detection, IC; Atomic absorption spectrometry; Copper; Cadmium; Pyridinedicarboxylic acid; Metal cations

1. Introduction

Nowadays, the electronic industries often make use of a wide variety of high-purity materials in the

manufacture of semiconductor materials. The presence of impurities below $\mu\text{g g}^{-1}$ levels affects the mechanical and electrical properties of semiconductors and must be strictly controlled. Ultra-high-purity water is employed in the construction of electronic devices and water quality monitoring is needed to reduce the manufacturing of faulty products. The determination of elements at very low levels in

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ultra-high-purity water is not possible by measuring the resulting resistivity, therefore sensitive analytical methods are required. Preconcentration is often a necessary step to enhance the analyte concentration in the sample solution. Chelating ion-exchange resins are commonly used for preconcentrating metal ions from aqueous solutions [1–6]. Ion chromatography (IC) has been successfully used in the analysis of anions and cations in pharmacopoeial water and ultra pure water [7–9]. IC is a satisfactory tool for preconcentrating trace levels of metals from water samples, which avoids risk of contamination through additional sample handling [10,11]. Aqueous samples with low content of metals can be concentrated on the guard column in a simple and effective manner provided that the total exchange capacity of the column is not exceeded. Recently, determination of transition metals in drinking water below the $\mu\text{g l}^{-1}$ level has been reported by chelation ion chromatography with spectrophotometric detection [12].

Among the atomic spectroscopy techniques that have been coupled with IC, atomic absorption spectrometry with electrothermal atomization (ETAAS) is the most sensitive and less expensive and sophisticated technique for detection of elements at very low levels. ETAAS has been coupled to IC in the analysis of high-purity materials [13] and in the analysis of As and Se compounds in lake and river waters [14–17], because it is a specific-element detector compared to conductometric and UV–Vis spectrophotometric ones. On-line coupling between chromatographic systems and ETAAS, which allows the monitoring of effluent in real time, have been proposed [18–20]; however the interfacing device is not yet commercially available. The off-line sampling of effluents remains the most simple procedure for interfacing IC to ETAAS, and by proper selection of volume effluent and volume injected into the furnace tube low detection limits can be attained [21].

In the present work a method based on IC–ETAAS coupled for the analysis of Cu and Cd from ultra-high-purity water is described. Some parameters of the chromatographic process, such as the flow-rate during sample loading and volume of effluent are optimized to get shorter analyses time and high enrichment factors.

2. Experimental

2.1. Instrumentation

The ion chromatograph was a QIC Ion Chrom Analyzer (Dionex, Sunnyvale, CA, USA), which includes a post-column derivatization reaction system, an Opti-ion UV–Vis detector and a Shimadzu Chromatopac C-R6A integrator (Shimadzu, Kyoto, Japan). A Dionex HPIC-CG5 guard concentrator (50×3.5 mm I.D.), containing pellicular polystyrene–divinylbenzene cation and anion-exchangers (capacity $6 \mu\text{equiv g}^{-1}$), was used in place of the normal $50 \mu\text{l}$ sample loop in the injector. An extra Dionex model DQP-1 pump was used to load the water samples. All connections were made with Dionex fittings and PTFE tubing. The outlet end of the guard concentrator was connected to an Isco 3100 programmable fraction collector (Isco Lincoln, NE, USA) for collecting the fractions of effluent.

An Instrumentation Laboratory IL VIDEO 22 dual channel dual AA/AE spectrophotometer (Allied Systems, MA, USA), operating in simultaneous mode, was equipped with an IL 655 graphite furnace and a D_2 background correction system. Westinghouse hollow cathode lamps of Cu and Cd were used as sources. Pyrolytic graphite-coated graphite tubes were used. Argon (99.999%) gas was fluxed in the graphite tube. The sample volume was $10 \mu\text{l}$, unless otherwise stated. Peak height absorbance signals were measured by the AAS instrument. In Table 1 are listed the operating conditions and the heating cycle program.

High-density polyethylene volumetric flasks for storage of all solutions and cups (Nalgene, Nalge, Rochester, NY, USA) for the collection of eluate were soaked in dilute nitric acid (3%) for 24 h and rinsed several times with deionized water before use. Eppendorf micropipettes were used to prepare solutions and to inject sample solution into the graphite furnace.

2.2. Reagents and solutions

Ultra-high-purity water with a specific resistance of $18 \text{ M}\Omega \text{ cm}$ obtained from a Millipore Super-Q System (Millipore, Bedford, MA, USA) and filtered

Table 1
Operating conditions in AAS and graphite furnace temperature program for copper and cadmium

	Element			
	Cu	Cd		
Wavelength (nm)	324.7	228.8		
Spectral bandwidth (nm)	1	1		
Lamp current (mA)	5	3		
Photomultiplier (V)	620	700		
Sample volume (μl)	10	10		
Peak measurement type	Height	Height		
Heating program	Step	Temperature ($^{\circ}\text{C}$)	Hold (s)	Ar flow-rate (ml min^{-1})
	dry			
	I	70	5	40
	II	120	45	40
	ash			
	I	550	15	40
	II	600	15	100
	atomize			
	I	2000	5	0

through a 0.22 μm membrane filter was used for all preparations and dilutions. Multi-element working standard solutions for Cu and for Cd were prepared fresh daily by making serial dilutions of the stock solutions containing 1000 mg l^{-1} of the analyte as nitrate (Fisher Scientific, Schwerte, Germany). Blank was prepared in a separate flask using the same procedure as that used for making working standard solutions without adding standard.

The eluent was a solution of 3 mM pyridine-2,6-dicarboxylic acid (PDCA) (Aldrich, Milwaukee, WI, USA) adjusted to pH 4.8 with LiOH (Aldrich) [22]. Post-column reagent solution (0.3 mM) was prepared by dissolving 4-(2-pyridylazo)resorcinol (PAR) (Merck, Darmstadt, Germany) in 400 ml of 7.4 M ammonium hydroxide (Merck) and then slowly adding 600 ml of 1.7 M acetic acid (Merck). The PAR solution should be prepared in a hood. Both eluent and post-column reagent solutions were degassed by sonication with a Branson 1200 ultrasonic cleaner (Branson Ultrasonics, Danbury, CT, USA). All solutions were stored under a purified N_2 atmosphere to avoid air contamination.

2.3. Chromatographic process

The guard concentrator column was flushed with

deionized water and then conditioned with the PDCA eluent at a flow-rate of 1 ml min^{-1} to remove trace metal impurities from the chromatographic system before use. Different volumes (1–5 ml) of water sample solutions, spiked with Cu and Cd, were loaded on the column by means of an extra pump at flow-rates between 1.0 and 3.5 ml min^{-1} . A higher value of flow-rate has not been assessed because non-uniformity of sample volumes loaded could occur by air blockages [23]. The exact loaded sample volume was controlled by weighing the sample bottle before and after loading. By means of the inject valve the eluent was flushed at 1 ml min^{-1} and at the exit of column the effluent was mixed in a T-connection with the PAR solution at flow-rate of 0.5 ml min^{-1} . The derivative was detected at 520 nm using the UV-Vis detector. The chromatographic system is schematically shown in Fig. 1(a). Large volumes of water sample (25–200 ml) spiked with Cu (5–25 ng) and Cd (50–200 ng) were loaded on the column and analysed with the configuration above-described.

Subsequently, the outlet end of the concentrator was disconnected from the post-column derivatization reaction system and connected to the programmable fraction collector [Fig. 1(b)]. A volume of 2 ml of water sample spiked with 4 ng Cu and 0.2 ng

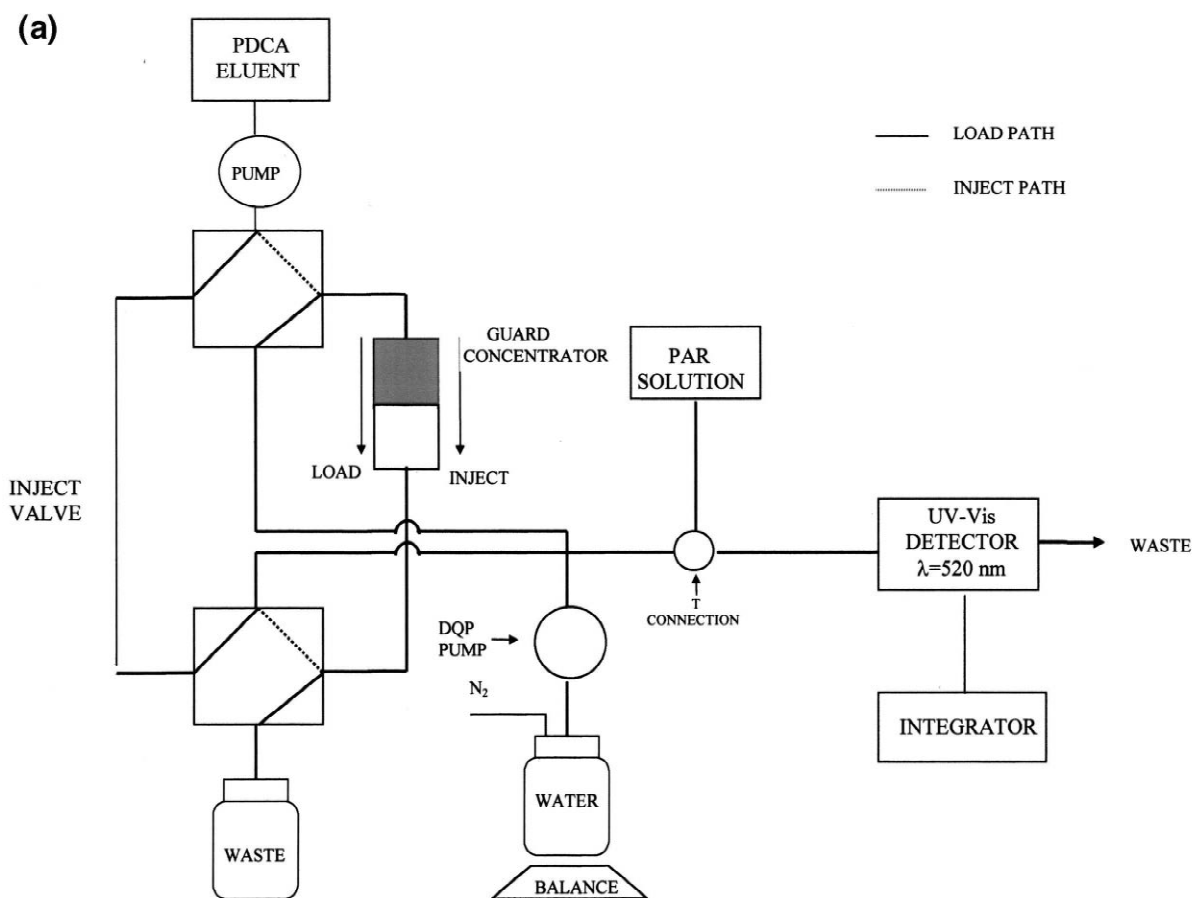


Fig. 1. Schematic diagram of IC with UV-Vis detector (a) and of IC coupled to ETAAS (b).

Cd was delivered to the concentrator at 3.5 ml min^{-1} flow-rate and eluted in the opposite direction from loading. The timing of the injector valve of the chromatograph was synchronized with the fraction collector, which was programmed to take fractions of effluent in small cups every 3 s. The exact eluate fraction volume was measured by weighing the cups before and after collection. Aliquots of each collected fraction were transferred into the graphite tube of the spectrometer and analysed for the copper and cadmium content. Care should be taken during transferring of the aliquots of effluent to the graphite furnace to avoid contamination problems. Chromatograms are presented as histograms, where the abscissa corresponds to the time necessary to collect each

fraction and the ordinate, the absorbance measured in the fraction. The absorbance is related to the mass of analyte by calibration against aqueous standard solutions processed by the same method as the sample. Large volumes of water sample (25–200 ml) spiked with Cu (1–5 ng) and Cd (0.1–0.5 ng) were loaded on the column and analysed with the configuration above-described. Finally, measured volumes of Millipore water (20–200 ml) were loaded onto the column and analysed. All preconcentration procedures were done in a class 100 laminar flow hood.

2.4. ETAAS detection

The ETAAS optimized conditions for the determi-

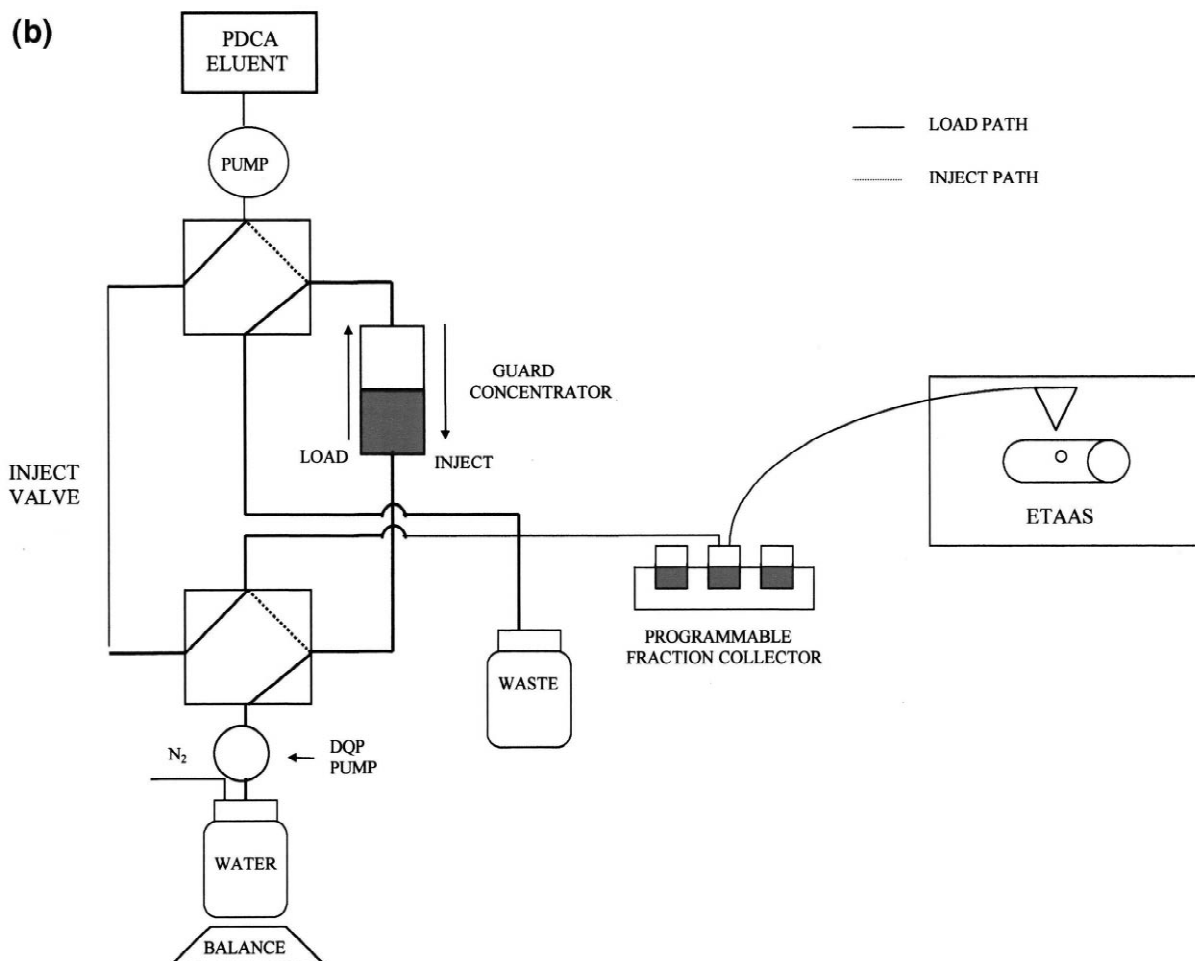


Fig. 1. (continued)

nation of each of the two elements were selected by varying the temperature and time of drying, ashing and atomization steps of the furnace programs (Table 1). As the capacity of a graphite furnace is usually 50 μ l sample volume, larger sample volumes were accommodated in it by using four successive injections with two drying steps at 70°C (5 s) and 120°C (45 s), respectively, between them. Subsequently, sequential drying at 120°C (45 s); ashing in two steps at 550°C (15 s) and 600°C (15 s), respectively, and atomization at 2000°C (4 s) of furnace program was run and integrated absorbance recorded.

3. Results and discussion

3.1. Ion chromatographic preconcentration

Preconcentration of solute ions by passing a large sample volume through a concentrator before the analytical column is a common method to enhance the sensitivity of most popular chromatography techniques. Copper and cadmium ions are trapped onto the HPIC-CG5 concentrator and eluted through a purely anionic exchange mechanism using the chelating eluent PDCA, which forms strong anionic complexes with heavy metals, as evidenced by the

Table 2

Recoveries (%) and precision of analytes from different volumes of high-purity water spiked with 0.1 µg Cu and Cd loaded onto concentrator at different flow-rates, eluent 3 mM PDCA, configuration: on-line IC post-column derivatization–UV–Vis detector (see Fig. 1a)

Sample loading flow-rate (ml min ⁻¹)	Sample volume loaded (ml)	Recovery (%)	
		Cu	Cd
1.0	1.0	98±2 ^a	99±2 ^a
	2.5	98±2 ^a	100±2 ^a
	5.0	100±2 ^a	99±2 ^a
2.0	1.0	98±2 ^a	98±2 ^a
	2.5	100±2 ^a	100±2 ^a
	5.0	99±2 ^a	99±2 ^a
3.5	1.0	98±2 ^a	99±2 ^a
	2.5	100±2 ^a	100±2 ^a
	5.0	99±2 ^a	98±2 ^a

^a Mean and relative standard deviation of three replicate runs.

large values of the complex formation constants for Cu (log K_f =16.6) and Cd (log K_f =11.6).

In the preliminary experiments we use an on-line post-column derivatization–UV–Vis detection for the IC (see Fig. 1a) to optimise some parameters of the

preconcentration process, such as the sample loading flow-rate and sample volume. The effect of varying the flow-rate during water sample loading onto the concentrator was evaluated in order to speed up the chromatographic process and shorten the analysis time. Different volumes (1–5 ml) of water solutions spiked with 0.1 µg of each metal are loaded onto the concentrator at a given value of flow-rate. Elution was carried out with 3 mM PDCA at flow-rate of 1 ml min⁻¹ in the conventional flow direction and the colored metal PAR complexes detected at 520 nm. In Table 2 are reported the recoveries for the pre-concentrated ions with enrichment factors of 20, 50 and 100 (calculated with respect to 50 µl sample loop) at each value of loading flow-rate investigated. There is no loss of solute ions seen by enhancing the sample loading flow-rate up to 3.5 ml min⁻¹ for either element. Analyte recovery remains within 98–100% under these conditions. The relative standard deviation (RSD), based on three replicate runs, is within 2%. The loading flow-rate selected for subsequent experiments was 3.5 ml min⁻¹.

The effect of varying the sample volume on the preconcentration process was studied by pumping onto the short column 25–200 ml of water samples spiked with copper and cadmium. As shown in Table

Table 3

Recoveries (%) of analytes from different sample volumes of high-purity water spiked with Cu and Cd, loading sample flow-rate at 3.5 ml min⁻¹, eluent 3 mM PDCA, configuration: on-line IC post-column derivatization–UV–Vis detector (see Fig. 1a)

Sample volume (ml)	Cu			Cd		
	Concentration loaded (ng ml ⁻¹)	Mass loaded (ng)	Recovery (%)	Concentration loaded (ng ml ⁻¹)	Mass loaded (ng)	Recovery (%)
25	0.2	5	101±2 ^a	2.0	50	99±2 ^a
	0.4	10	99±2 ^a	4.0	100	100±2 ^a
	1.0	25	100±2 ^a	8.0	200	99±2 ^a
50	0.1	5	99±2 ^a	1.0	50	101±2 ^a
	0.2	10	101±2 ^a	2.0	100	98±2 ^a
	0.5	25	99±2 ^a	4.0	200	99±2 ^a
100	0.05	5	98±2 ^a	0.5	50	100±2 ^a
	0.1	10	99±2 ^a	1.0	100	99±2 ^a
	0.2	20	101±2 ^a	2.0	200	101±2 ^a
200	0.025	5	99±2 ^a	0.25	50	99±2 ^a
	0.05	10	101±2 ^a	0.5	100	100±2 ^a
	0.1	20	100±2 ^a	1.0	200	101±2 ^a

^a Mean and relative standard deviation of three replicate runs.

3, the recoveries for 500–4000-fold pre-concentrated ions are quantitative, being within a range of 98–101% for both the analytes. All metals show good linearities up to 200 ml. These results suggest that the short concentrator is able to treat quantitatively large volumes of dilute aqueous solution.

Five-point calibration curves were obtained for Cu ($0.1\text{--}1\ \mu\text{g ml}^{-1}$) and for Cd ($0.5\text{--}5\ \mu\text{g ml}^{-1}$). The goodness of fit for three replicates was assessed by examining the y -residuals, which are random about zero [24]. The correlation coefficients r , were better than 0.999 and the intercepts did not deviate significantly from zero at 95% confidence level.

3.2. IC-ETAAS coupled

Fig. 2 shows the histograms for copper and cadmium obtained by the IC-ETAAS coupled method. Preconcentration was obtained by passing 2 ml of water solution spiked with 4 ng Cu and 0.2 ng Cd onto the concentrator and eluting with PDCA in the reverse direction to sample loading (see Fig. 1b). Each fraction collected (50 μl volume as determined by weighing) was analysed by AAS using single injection into the graphite tube. As can be seen from Fig. 2, the metal ions coelute under these conditions because the concentrated ions at the top of the column eluted together as a narrow band, rather than as separated peaks resulting from the ion-exchange process, which would occur in the conventional flow elution mode. However, the selectivity of ETAAS for metals allows the simultaneous determination of copper and cadmium without chromatographic separation. The reverse elution method has been introduced [27,28] to minimize peak spreading for best separation of inorganic anions, to avoid problems of irreversible ion-exchange of ions [29] and to reduce the dip peak [30]. It is here used with the purpose of getting smaller volumes of effluent collected from the chromatographic system to make it suitable for use with the graphite tube. From Fig. 2, it can also be seen that the times needed to elute completely the analytes from the chromatographic system are 9 and 12 s for Cu and Cd, respectively. At the eluent flow-rate of $1\ \text{ml min}^{-1}$ these times correspond to a volume of 0.150 ml for Cu and 0.200 ml for Cd. Therefore the total volume of effluent to elute both analytes can be accommodated in the graphite fur-

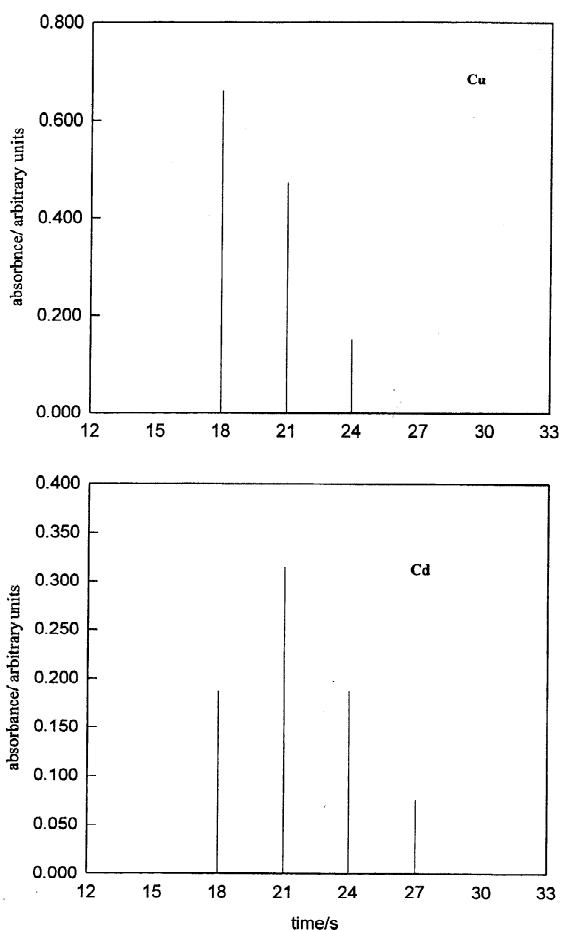


Fig. 2. IC-ETAAS histogram of 2 ml pre-concentrated high-purity water spiked with 4 ng Cu and 0.2 ng Cd. Elution with PDCA in the reverse direction to sample loading. Found 4.08 ng Cu and 0.204 ng Cd.

nace using four successive injections. In this way the maximum sensitivity is obtained and the time of analysis in AAS is reduced.

Calibration curves were obtained for Cu ($1\text{--}40\ \text{ng ml}^{-1}$) and Cd ($0.02\text{--}1\ \text{ng ml}^{-1}$) using five aqueous standard solutions processed by IC-ETAAS coupled method using single and successive injection techniques. In Table 4 are displayed the linear range, correlation coefficients, and the slopes of the calibration curves. The curves were linear over the entire concentration range studied with correlation coefficients better than 0.999 and the intercepts did not significantly deviate from zero at 95% confidence

Table 4

Calibration slopes, correlation coefficient (r) and detection limits (D.L.) for Cu and Cd obtained by the IC–ETAAS coupled method using single and successive injections in the graphite tube (see Fig. 1b)

Analyte	Matrix	Slope of the regression lines		Correlation coefficient		D.L. (ng ml ⁻¹) ^a	
		Single injection ^b (10 μl)	Successive injections ^c (4×50 μl)	Single injections ^c (10 μl)	Successive injections ^c (4×50 μl)	3σ Approach ^d	Hubaux–Vos method ^e
Cu	PDCA	0.0154	0.0153	0.9999	0.9998	1	1
Cd	PDCA	0.1870	0.1850	0.9999	0.9999	0.01	0.02

^a Detection limits calculated with calibration graphs obtained using 10 μl injections into graphite tube.

^b Based on a calibration curve constructed using 10 μl injections into graphite tube of standard solutions at 1, 5, 10, 20 and 20 ng ml⁻¹ for Cu and 0.01, 0.25, 0.5, 1, and 2 ng ml⁻¹ for Cd.

^c Based on a calibration curve constructed using successive injections (4×50 μl) into graphite tube of standard solutions at 0.1, 0.2, 0.4, 0.6 and 0.8 ng ml⁻¹ for Cu and 0.01, 0.025, 0.05, 0.75 and 0.1 ng ml⁻¹ for Cd.

^d Based on three times the standard deviation of seven measurements of blank.

^e Based on the recursive formula proposed in Ref. [10]; $\alpha = \beta = 0.05$.

level for three replicates, except for Cu due to impurity in the PDCA. As can be seen from Table 4, there was any loss of sensitivity comparing the slopes of the curves obtained with single injection and four successive injections. No interference effects produced by PDCA matrix present in the collected fractions is observed on the absorbance signal of copper. In contrast, PDCA matrix causes a signal increase for cadmium by about 25% as compared to aqueous standard solution directly performed in ETAAS, probably because the organic complex stabilises the cadmium atoms in the graphite tube with respect to the cadmium atoms alone [25]. However, under the conditions reported in Table 1 both elements can be simultaneously determined in AAS. The appearance of a background absorbance due to the PDCA matrix is not seen.

The detection limits were calculated according to the recursive formula proposed in Ref. [10], which is based on the Hubaux–Vos (H–V) method [26]. This method is more statistically sound compared to the 3σ approach, because it takes into account calibration curves, the probability of false positives (α), and the probability of false negatives (β) bias and non-constant σ , producing more realistic values of the detection limit. The detection limits (H–V method) for $\alpha = \beta = 0.05$ are shown in Table 4. A detection limit of 1 ng ml⁻¹ was found for Cu, limited due to impurity in the eluent, and 0.02 ng ml⁻¹ for Cd. For comparison in Table 4 are also shown the detection limits calculated, on the basis of the 3σ approach.

The sensitivity of IC is enhanced using ETAAS detection with respect to commonly employed direct UV absorbance [8] with enrichment factors up to 1300 using 200 ml of water sample. When the enrichment factor resulting from the coupling of the IC preconcentration step to the ETAAS method is applied, the detection limits as presented in Table 4 are extended to much lower values. The detection limits for the IC–ETAAS coupled method, based on the H–V method, for Cu using a 1300-fold preconcentration in the IC step was found to be 1 pg ml⁻¹, and was limited due to impurity in PDCA, while the detection limit found for Cd using a 1000-fold preconcentration was 0.02 pg ml⁻¹. The application range for the investigated analytes was examined by analysing water sample volumes (25–200 ml) spiked with different masses of Cu and Cd. The recoveries are quantitative, being in the range 97–102% (Table 5). The RSD, based on three replicate runs, is within 3%.

The highest purity water available in our laboratory is the Millipore water. Three replicate measurements for each loaded water volume (20–200 ml) have been performed and the content of Cu and Cd and were found to be 8 and 3 pg ml⁻¹, respectively.

4. Conclusions

The IC provides an automated manner of preconcentrating Cu and Cd from high-purity water prior to determination by ETAAS, allowing one to

Table 5

Recoveries (%) of analytes from different sample volumes of water spiked with Cu and Cd, loading sample flow-rate at 3.5 ml min⁻¹, eluent 3 mM PDCA, flow-rate at 1 ml min⁻¹, IC-ETAAS coupled method using successive injections in the graphite tube (see Fig. 1b)

Sample volume (ml)	Cu			Cd		
	Concentration loaded (ng ml ⁻¹)	Mass loaded (ng)	Recovery (%)	Concentration loaded (ng ml ⁻¹)	Mass loaded (ng)	Recovery (%)
25	0.05	1.2	98±3 ^a	0.05	0.12	101±3 ^a
	0.1	2.5	99±3 ^a	0.01	0.50	99±3 ^a
	0.2	5.0	97±3 ^a	0.02	0.50	99±3 ^a
50	0.025	1.2	101±3 ^a	0.0025	0.12	101±3 ^a
	0.05	2.5	99±3 ^a	0.005	0.25	99±3 ^a
	0.1	5.0	98±3 ^a	0.01	0.50	98±3 ^a
100	0.01	1.0	101±3 ^a	0.001	0.10	97±3 ^a
	0.025	2.5	98±3 ^a	0.0025	0.25	98±3 ^a
	0.05	5.0	97±3 ^a	0.005	0.50	97±3 ^a
200	0.005	1.0	98±3 ^a	0.0005	0.10	101±3 ^a
	0.01	2.0	102±3 ^a	0.001	0.20	99±3 ^a
	0.025	5.0	99±3 ^a	0.002	0.40	98±3 ^a

^a Mean and relative standard deviation of three replicate runs.

achieve low detection limits for the analytes analyzed. The method can be extended to other metal ions (Fe, Zn, Co and Ni).

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