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Talanta 64 (2004) 1241–1246

Talanta

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Flow injection in-valve-mini-column pretreatment combined with ion chromatography for cadmium, lead and zinc determination

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Received 26 March 2004; received in revised form 28 May 2004; accepted 28 May 2004
Available online 25 August 2004

Abstract

A flow injection (FI) in-valve-mini-column packed with Chelex-100 resin is proposed for on-line sample pretreatment for some metal ions, namely, Cd(II), Pb(II) and Zn(II), prior to simultaneous determination using ion chromatography (IC). A solution containing a mixture of the cations was first passed through the in-valve-mini-column, followed by on-line elution. The eluate was then flowed further to an injection valve and was injected into an ion chromatograph. Conditions of the system were optimized. A single standard calibration was possible. The recoveries of cations were found to be in the range of 95–105%. The developed method was applied to the accurate analysis of zinc ore samples.

Keywords: Sample pretreatment; In-valve-mini-column; Ion chromatography; Flow injection; Ores; Cadmium; Lead; Zinc

1. Introduction

Sample pretreatment is necessary when the analytical method cannot provide good separation and quantification due to interferences from sample matrix components [1]. Sample preparation has been a growing area in chromatography over the past several years, since samples containing interfering substances can affect chromatographic performance. These substances may mask the peak of interest or irreversibly retain on the analytical column, permanently damaging the column. To eliminate these problems, such samples need to be treated before injection [2]. A common problem in ion chromatography is poor resolution of an analyte ion from matrix ions that are present in relatively high concentrations [3–9]. Post column derivatization with a color reagent such as 4-(2-pyridylazo) resorcinol (PAR) or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) for visible spectrophotometric detection [10–13] has been used for good sensitivity and stable baselines. One of the most important aspects of developing an IC method is the ability to recognize when undesirable chromatographic effects are derived from sample matrix interferences. Sample matrix effects can include shortened retention times, poor peak efficiency, poor resolution, poor reproducibility and irregular baseline [1].

A flow injection (FI) system can be used to introduce samples into a detector such as atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP–AES), inductively coupled plasma-mass spectroscopy (ICP–MS) and ion-selective electrode (ISE) and

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doi:10.1016/j.talanta.2004.05.060

to enhance the pretreatment step. FI systems with on-line sample pretreatment are very beneficial. Automation of sample pretreatment and manipulation within the manifold have increased sample throughput and decreased the potential for sample contamination [14,15]. These include, for examples, column retention, gas diffusion, and solvent extraction [16,17]. The on-line column in a FI system could be used for sample pretreatment for complicated matrix samples prior to the determination step.

In the present work, a simple flow injection system with an in-valve-mini-column has been coupled with a simple ion chromatograph (IC) with a conductivity detector without suppressor, for on-line sample cleaning or pretreatment for the determination of Cd, Pb and Zn in a complicated matrix sample such as in a zinc ore sample, prior to their determination. An additional advantage of prolonging the life-time of the IC column is also gained.

2. Experimental

2.1. Standard solutions

Standard solutions of each cation were prepared by appropriate dilution of a stock standard solution (1000 mg l^{-1}, Merck, Germany). Ultrapure water (resistivity 18 mΩ cm^{-1}) was produced by a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Buffer solutions and eluents

For the FI system, ammonium acetate buffer solution (1.0 M, pH 5.4) was prepared by mixing 57 ml of glacial acetic acid (99.8% (w/v), Merck, Germany) and 75 ml of 25% ammonia liquor (25% (w/v), Merck, Germany) and diluting to 1000 ml. Sodium citrate buffer solution pH 3 was prepared from reagent-grade chemical obtained from Merck (Germany). The eluent was 2.0 M HNO_3 (65% (w/v) HNO_3, Merck, Germany).

For the IC system, a mixture of tartaric acid and oxalic acid was employed as the eluent. The eluent concentration optimized for the best resolution was: 3 mM tartaric acid/1 mM oxalic acid.

All solutions were degassed using an ultrasonic bath before use.

2.3. FI in-valve-mini-column

Chelex-100 (sodium form, 50–100 mesh; Bio-Rad Laboratories) was packed in a mini-column, made of acrylic tubing (3 mm i.d. × 2 cm), similarly described in [16]. Teflon frits were placed at each end of the column to prevent the loss of the resin when a solution passed through the column, as shown in Fig. 1. The two ends of the column were connected to a six-port injection valve by replacing a sample loop of the valve.

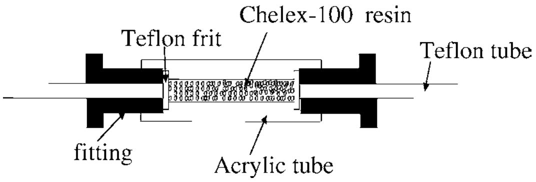


Fig. 1. Ion exchange mini-column.

2.4. Instruments

2.4.1. FI system

The FI system consisted of two peristaltic pumps (MP-3, EYELA, Tokyo Rikakikai, Tokyo, Japan and Ismatec, Glattbrugg-Zurich, Switzerland), and a Rheodyne (model 7725i) injection valve with in-valve-mini-column.

2.4.2. Ion chromatograph

The ion chromatographic system without chemical suppression (Metrohm Ltd., Switzerland) used this study consisted of a Metrohm isocratic pump, a six-port valve with 20 μl sample loop, and a Metrohm 732 conductivity detector (without suppressor). The analysis column used for the cation separation was a universal cation column (4.6 mm × 100 mm; Altech, USA). The column was packed with polybutadiene-maleic acid (PBDMA) coated on silica material. The chromatograms were recorded and handled with Metrohm software (Metrohm Ion analysis, Metrohm Ltd., Switzerland), which was also used for controlling the pump and injection valve.

2.5. Procedure

The FI–IC manifold (Fig. 2) operation was controlled by two injection valves under manual control for timing as indicated in Fig. 3. Standard/sample solution was mixed with buffer to adjust the pH for adsorption of cations on the resin, and flowed through the column with the FI-valve in the load position, with various loading times, while the unretained cations were passed to waste. After that the valve was switched to the injection position and 2.0 M HNO_3 was flowed through the mini-column to elute cations from the column. The eluate was neutralized with 2.0 M NaOH and then controlled for pH with citrate buffer. When the elapsed time was 24 s after switching the FI valve to the injection position, the zone of cations was moved into the sample loop and was injected into the IC via the IC valve.

2.5.1. Preparation of zinc ore samples

A portion (0.1 g) of a zinc ore sample was accurately weighed and digested with concenterated nitric acid (25 ml) by heating on a hot plate until it became clear (about 4 h). It was filtered and transferred into a 250 ml volumetric flask and made to the volume with 1% nitric acid.

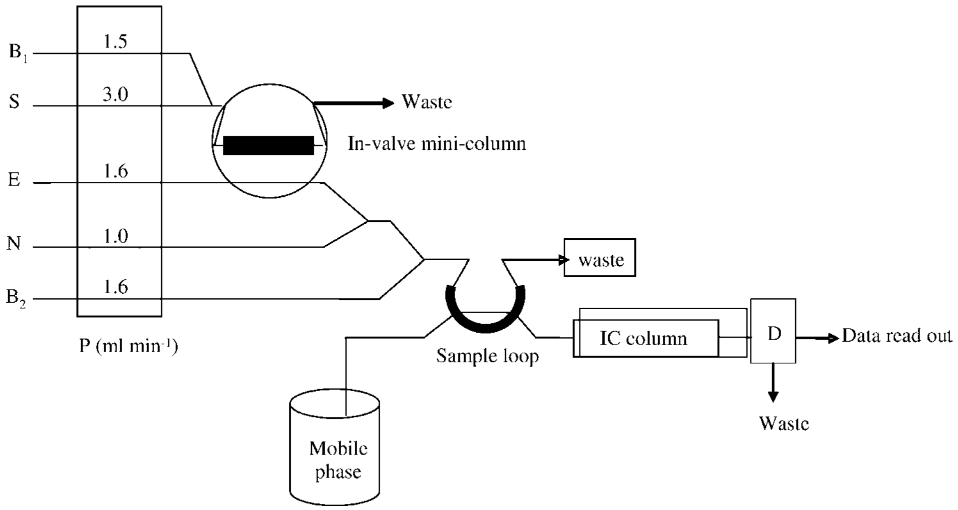
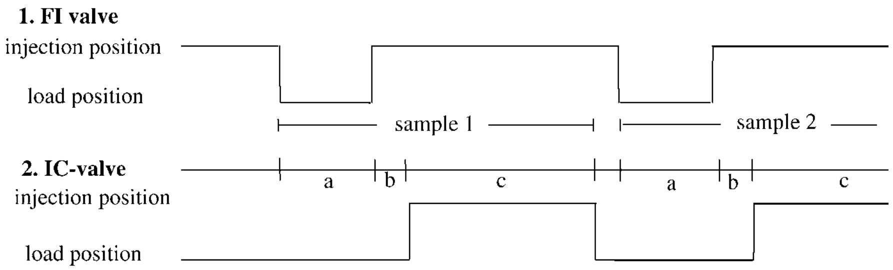


Fig. 2. Manifold of FI–IC combination; P: peristaltic pumps; B_1: ammonium acetate buffer; B_2: sodium citrate buffer; S: sample or standard solution; E: 2.0 M nitric acid; N: 2.0 M sodium hydroxide; mobile phase: mixture of tartaric acid and oxalic acid; sample loop: 20 µl loop of IC; IC column: universal cation column 100 mm × 4.6 mm; D: conductivity detector (without suppressor).



a = loading time: varying as desire
b = elapsed time (24 seconds)
c = analysis time of IC (35 minutes)

Fig. 3. Schematic diagram of timing control for operation of valves in the FI–IC system.

3. Results and discussion

3.1. Ion chromatography

The conditions, mobile phase concentration, and flow rate of mobile phase for ion chromatographic separation were optimized. Results are summarized in Table 1 and Fig. 4(a)–(d). For the flow rate studies (1.0, 1.5 and 2.0 ml min^{-1}), the lower the flow rate employed, the better sensitivity obtained, but a lower flow rate resulted in longer analysis time, as expected. Chromatograms of a blank solution and of cations obtained from conventional ion chromatography are shown in Fig. 5(a) and (b), respectively. Milli-Q water was used as a blank solution and a mixture of cations containing 3 mg l^{-1} Cu, 3 mg l^{-1} Zn, 5 mg l^{-1} Cd and 10 mg l^{-1} Pb in 20 µl was injected directly into the ion chromatograph with a mobile phase flow rate of 1.5 ml min^{-1} and an injection volume of 20 µl. In the chromatographic separation similar to a previous report [8], a mixture of 3 mM tartaric acid/1 mM oxalic acid was used as the mobile phase since this organic acid eluent can separate Cd, Cu, Pb and Zn on the PBDMA stationary phase, which is polybutadienemaleic acid coated on silica material of the

Table 1
Concentrations of tartaric acid and oxalic acid

Concentration (mM)		Retention time (min)				Total analysis time (min)	Comments
Tartaric acid	Oxalic acid	Cu	Zn	Cd	Pb		
3.0	2.0	1.1	4.4	11.8	12.9	17	Bad resolution of Cd and Pb (Fig. 4a)
1.5	2.0	1.1	5.2	15.4	15.4	20	Co-elution of Cd and Pb (Fig. 4b)
3.0	1.5	1.4	6.5	17.0	20.5	25	Good resolution of all cations (Fig. 4c)
3.0	1.0	1.9	9.4	23.0	31.3	35	Good resolution of all cations (Fig. 4d)

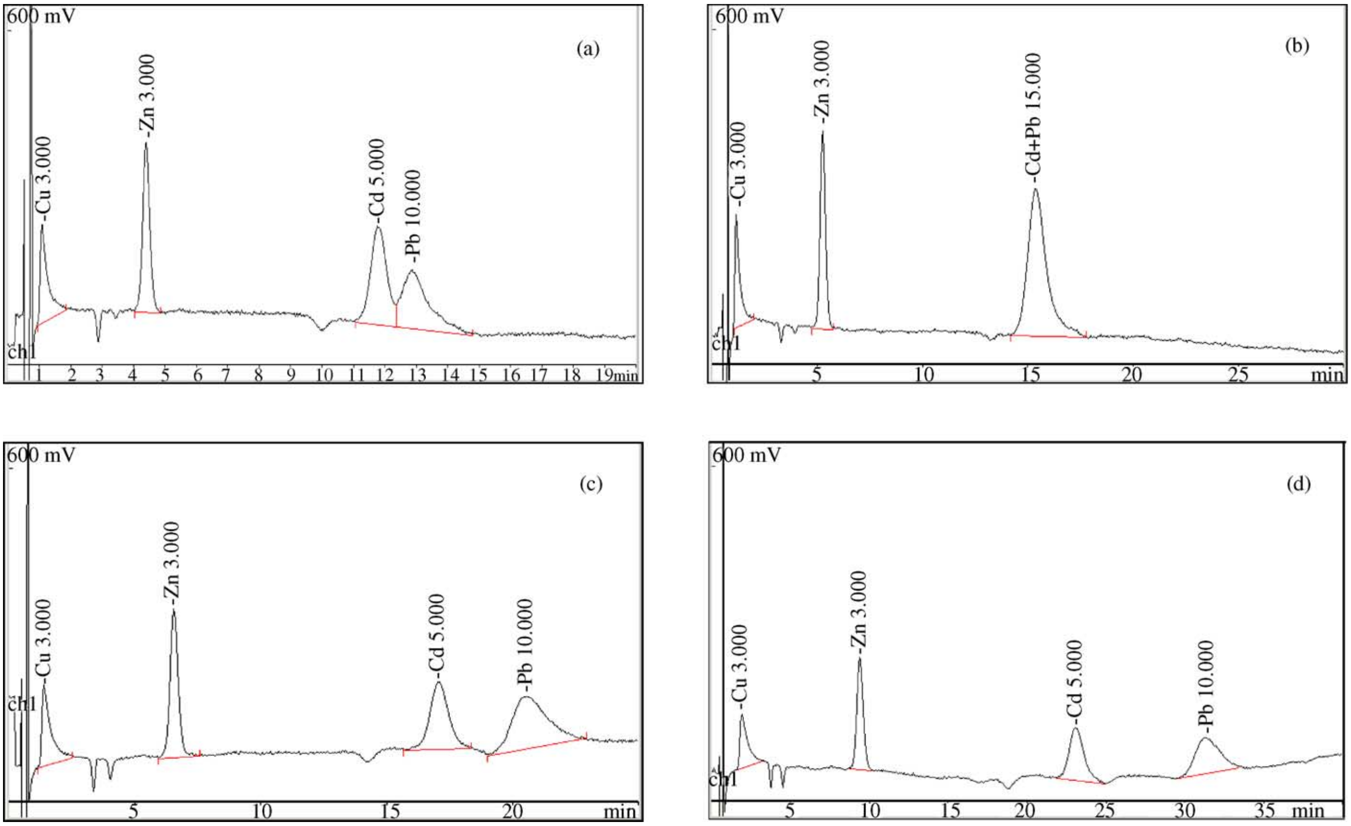


Fig. 4. Chromatograms of cations in Milli-Q water at different concentrations and ratios of tartaric acid and oxalic acid as a mobile phase: (a) 3 mM tartaric acid/2 mM oxalic acid, (b) 1.5 mM tartaric acid/2 mM oxalic acid, (c) 3 mM tartaric acid/1.5 mM oxalic acid and (d) 3 mM tartaric acid/1 mM oxalic acid. The values on the peak tops are concentrations (mg 1–7).

universal cation column. The retention time of the cations of interest in the presence of the mobile phase followed the order Cu < Zn < Cd < Pb, and the separation was achieved within 35 min at a flow rate of 1.5 ml min^{-1}.

3.2. Flow injection-ion chromatography

Using the FI–IC system and optimal conditions of the FI system in Table 2, the results in Fig. 6a show the chromatogram of a blank solution obtained on-line from the FI system to the ion chromatograph. A blank solution (without cations) was loaded on the in-valve-mini-column and followed by the on-line elution process with 2.0 M HNO_3 for FI operation. The eluate acid solution from the FI system was neutralized with 2.0 M NaOH and the pH controlled with sodium citrate buffer solution before flowing into the IC injection valve, because highly acid solution will affect the analytical column. The baseline of the blank solution in the chromatogram exhibits a large, early elution peak, which is that of a high concentration of unretained Na^+ ion. Because the conductivity of Na^+ ion is lower than that of H^+ ion, a baseline drift occurs from the change of the Na^+/H^+ ratio leading to stepwise fashion at the about 20–25th and 25–27th min.

Table 2
Proposed conditions for FI system with in-valve-mini-column

Parameters	Conditions
Buffer for adsorption process	1.0 M ammonium acetate buffer pH 5.4
Loading flow rate	3 ml min^{-1}
Eluent	2.0 M Nitric acid
Eluent flow rate	1.6 ml min^{-1}
Base for neutralized eluate	2.0 M sodium hydroxide
Buffer for eluate	Sodium citrate buffer pH 3

In Fig. 6b, the chromatogram of a mixture of cations (Cd, Cu, Pb and Zn) was obtained by using the same conditions as for the blank. From the chromatogram, the high conductivity of the unretained Na^+ ion causes a large peak and interferes with the Cu peak (t_R = 1.4 min).

Reproducibility tests were carried out for estimating the relative standard deviation (R.S.D.) of the chromatographic peak areas. This data was obtained from five repeated injections at a loading time of 40 s for a concentration of 1 μg ml^{-1} of all interested cations. Average R.S.D. values of 3.1, 3.5 and 5.1% for Zn, Cd and Pb, respectively, were obtained.

Calibration plots, with various loading times, were constructed with single standard calibration by using a plot of peak area (*y*-axis) and micrograms of cation loaded (*x*-axis). The microgram of cation was calculated by concentration (μg ml^{-1}) of a standard solution used × loading flow rate

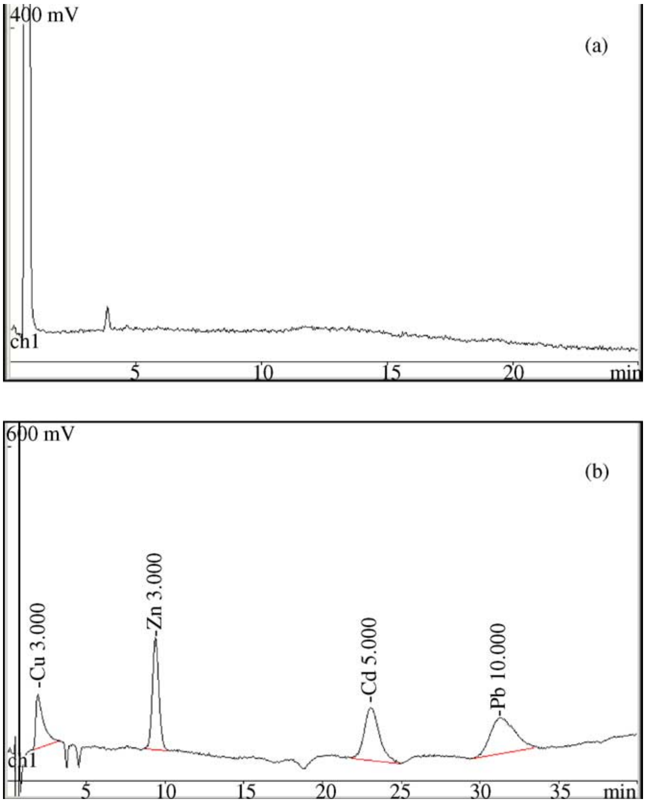


Fig. 5. Chromatograms: (a) blank solution without cations using Milli-Q water (b) cations (Cd = 5 mg l^{-1}, Pb = 10 mg l^{-1}, Zn = 3 mg l^{-1}) in Milli-Q water by direct injection into ion chromatograph without FI system. Peaks: Cd (t_R = 24.1 min), Pb (t_R = 32.5 min) and Zn (t_R = 9.8 min); column: universal cation (100 mm × 4.6 mm); eluent: 3 mM tartaric acid/1 mM oxalic acid; flow rate 1.5 ml min^{-1}; injection volume: 20 μl; detector: conductivity without suppressor.

(ml min^{-1}) × loading time (min). The plots were found to be linear. For each cation, two breaks of linear calibration ranges were obtained; for Cd: $y = 105x - 99$ ($r^2 = 0.989$) (for 6−25 μg) and $y = 44x + 1035$ ($r^2 = 0.981$) (for 25–60 μg); for Pb: $y = 93x + 762$ ($r^2 = 0.983$) (for 18–54 μg) and $y = 43x + 3559$ ($r^2 = 0.992$) (for 54–180 μg) and for Zn: $y = 89x - 553$ ($r^2 = 0.986$) (for 60–200 μg) and $y = 59x + 5561$ ($r^2 = 0.992$) (for 200–600 μg). Under such conditions, detection limits were: 5, 3 and 4 μg for Cd, Pb and Zn, respectively.

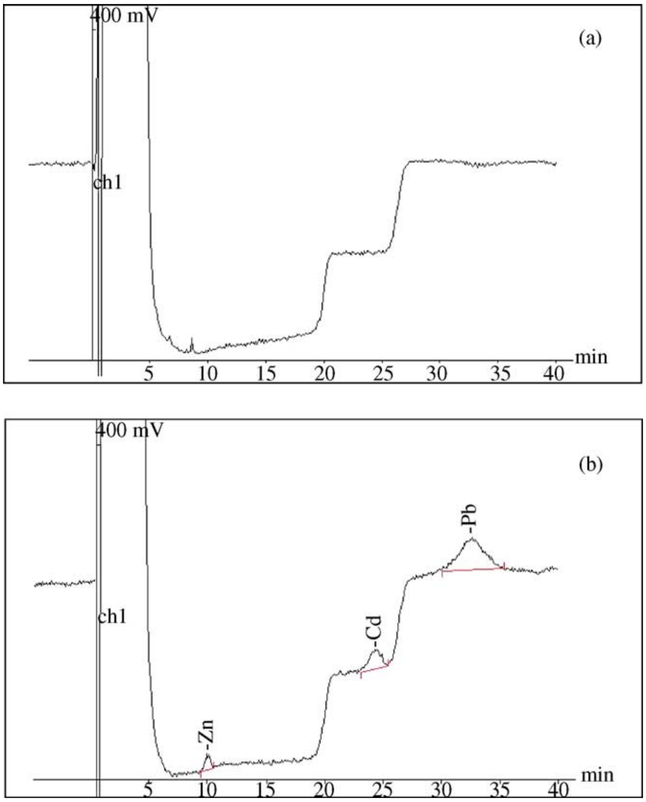


Fig. 6. Chromatograms: (a) blank solution without cations, using the FI–IC system (b) cations (Cd = 5 mg l^{-1}, Pb = 10 mg l^{-1}, Zn = 3 mg l^{-1}) by using the FI on-line sample pretreatment with loading time 1 min and loading flow rate 3 ml min^{-1} before injecting into ion chromatograph with elapsed time 24 s. Peaks: Cd (t_R = 24.3 min), Pb (t_R = 32.6 min) and Zn (t_R = 9.9 min); column: universal cation (100 mm × 4.6 mm); eluent: 3 mM tartaric acid/1 mM oxalic acid; flow rate 1.5 ml min^{-1}; injection volume: 20 μl; detector: conductivity without suppressor.

The proposed method was applied to the determination of cation mixtures in zinc ore samples and ore samples with spiked cations. To determine Cd, Zn and Pb in zinc ore samples which have high matrix content, the digested sample solution was on-line pretreated using the in-valve column FI system. The pretreated sample zone was injected into the ion chromatograph. The results obtained agree with reference methods (AAS and ICP–AES), all from triplicate

Table 3
Analysis of zinc ore samples

Sample	Concentration found (%)								
	Zn			Cd			Pb		
	FI–IC[a]	ICP–AES[b]	AAS[b]	FI–IC[a]	ICP–AES[b]	AAS[b]	FI–IC[a]	ICP–AES[b]	AAS[b]
A	25.3 ± 0.6	30.4 ± 0.2	30.4 ± 0.2	0.27 ± 0.01	0.33 ± 0.02	0.32 ± 0.02	6.0 ± 0.2	5.8 ± 0.3	5.7 ± 0.3
B	49.5 ± 1.2	45.1 ± 0.5	45.1 ± 0.5	0.19 ± 0.01	0.20 ± 0.02	0.20 ± 0.02	5.4 ± 0.2	6.3 ± 0.3	6.3 ± 0.3
C	42.4 ± 0.8	45.1 ± 0.5	45.1 ± 0.5	0.20 ± 0.01	0.20 ± 0.02	0.19 ± 0.02	4.4 ± 0.2	6.3 ± 0.3	6.3 ± 0.3
D	26.9 ± 0.4	27.8 ± 0.2	27.8 ± 0.3	0.18 ± 0.01	0.19 ± 0.02	0.19 ± 0.02	4.6 ± 0.1	4.8 ± 0.3	4.8 ± 0.3
E	28.5 ± 0.4	27.9 ± 0.3	27.8 ± 0.3	0.18 ± 0.01	0.19 ± 0.02	0.18 ± 0.02	4.6 ± 0.2	4.8 ± 0.3	4.8 ± 0.3

Both (a) and (b) were from triplicate results: mean ± S.D.

[a] The proposed method.

[b] Analyzed by the Mineral Resources Region 3 (Chiang Mai).

determination with standard deviation as represented in Table 3. The recoveries of cations were found to be in the range of 95–105%. The proposed procedure offers simultaneous determination of Cd, Pb, and Zn. This is advantageous over the AAS, in which simultaneous determination is not possible. The proposed pretreatment using FI column reduces IC column damage. The FI–IC procedure is cheaper than the ICP–AES method, both in instrumentation and operation aspects.

4. Conclusion

In-valve column in FI system for sample pretreatment coupled to a simple IC with conductivity detector without suppressor for simultaneous determination of some cations in zinc ore samples which have high amounts of matrix interference, has been successfully applied. The on-line sample matrix interference removals are easily automated, and eliminate costly and time consuming off-line operations, and reduce IC column damage. The developed FI–IC method offers advantages over traditional analytical procedures. It allows a range of some cations to be simultaneously analyzed, and is accurate, reliable and uses readily available chemicals. The on-line sample preparation FI-column can also potentially be combined with IC using PAR/absorbance detection.

Acknowledgements

Thanks are due to the National Research Council of Thailand (NRCT) and the Thailand Research Fund (TRF) for research grant support, the Post Graduate Education and Research Program in Chemistry, the Commission for Higher Education and the Graduate School, Chiang Mai University, Thailand for partial support.

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