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On-line pretreatment and determination of Pb, Cu and Cd at the μg l^{-1} level in drinking water by chelation ion chromatography

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Abstract

A novel, highly sensitive method for the simultaneous separation and determination of lead, copper, cadmium and other transition metals in drinking water was achieved by on-line sample pretreatment of chelation ion chromatography. Manganese, which coeluted with cadmium, was oxidized to permanganate by ammonium persulfate before injection. Permanganate, with bulk quantity of alkali, alkaline earth metals, iron and aluminum, was eliminated by pyrophosphoric acid–ammonium acetate buffer solution (pH 5.5), while retaining heavy and transition metals on a selective chelating resin (MetPac CC-1 column). Then, they were disabsorbed and transferred to a sulfonated cation exchanger (TMC-1 column). Finally, the concentrated trace metals were separated on a bifunctional ion-exchange column (CS5A) by a concentration gradient of oxalic acid and sodium nitrate eluents, coupled with post-column spectrophotometric detection with 2-[(5-bromo-2-pyridyl)azo]-5-diethylaminophenol (5-Br-PADAP) at 560 nm. The separation and color-development conditions were optimized. The detection limits for the method (signal-to-noise ratio=3:1) were at or below the μg l^{-1} level. The results of drinking water analyses were satisfactory. © 1998 Elsevier Science B.V.

Keywords: Water analysis; Lead; Copper; Cadmium; 2-[(5-Bromo-2-pyridyl)azo]-5-diethylaminophenol

1. Introduction

The determination of trace metals in real matrices has received increasing attention in recent years. Heavy and transition metals are toxic when their concentrations in water exceed certain values. The most toxic heavy and transition metals are Hg^{2+}, Cu^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+}. They have special importance from the ecotoxicological point of view, both because of the high toxicity of their compounds and because they can accumulate in various organisms [1–3]. So, it was an important task to analyze these metals in drinking water.

Ion chromatography (IC) has been used for a long time for the separation of trace metals [4–18]. Most methods were based on cation exchange with reversible complexation [11–13], while fewer studies have explored anion-exchange with irreversible complexation. The anion-exchange approach did offer some advantages with respect to selectivity and the analysis of complex samples [19,20]. At present, the bifunctional ion-exchange column (CS5 or CS5A column) is the most effective analytical column for separating heavy and transition metals. The common

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eluent used is oxalic acid (Ox) [4,9] or pyridine-2,6-dicarboxylic acid (PDCA) [4–8,10]. When Ox was used, cadmium and manganese coeluted. Furthermore, iron and aluminum could not be eluted from the analytical column. When PDCA was used, although heavy and transition metals could be well separated, it reduced the sensitivities because the metal–PDCA complexes were more stable than the corresponding metal–Ox complexes. Moreover, the concentrations of metals in drinking water were usually at $\mu g\ l^{-1}$ levels or less. However, the concentrations of alkali and alkaline earth metals were high, thus hampering the direct determination of trace metals. Therefore, the separation (to eliminate alkali, alkaline earth metals and other interfering components present in samples) and preconcentration of trace metals on chelating resins might be used as a complementary method for their determination. Due to the high selectivities of iminodiacetate-based resins (IDA) towards transition metals and the property of the complexes of being kinetically labile, they have been widely used for enrichment from complex matrices in conjunction with spectrometric methods of analysis [21–23].

In order to eliminate the remaining interferences in complex matrices, chelation ion chromatography was developed as a new technique that combined on-line analyte concentration and matrix elimination [24–26,28]. Unlike conventional ion-exchange concentration methods, which were typically not selective for metal ions of the same valency [23,27], chelation concentration was a selective concentration method. Using this method, Caprioli and Torcini [26] determined Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+} in seawater while eliminating high concentrations of alkali and alkaline earth metals. However, Pb^{2+} and Cd^{2+} could not be determined. Because the Pb–PDCA complex was more stable than the corresponding chelate complex with the 4-(2-pyridylazo)resorcinol (PAR) reagent and Cd^{2+} was difficult to separate from Co^{2+} [29,30]. Cardellicchio et al. [28] determined Pb^{2+} and Cd^{2+} in aqueous matrices while eliminating high concentrations of alkali, alkaline earth metals. However, the other transition metals could not be determined. Thus, using these methods, Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} could not be determined simultaneously. Furthermore, tervalent cations, such as iron and aluminium, could not be eliminated while the trace metals were being concentrated. In this paper, the method development and application for the simultaneous determination of Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} in drinking water by chelation ion chromatography is described. This is the first time that aluminium, iron and manganese have been eliminated prior to ion chromatographic separation and a novel elution system was chosen.

A number of post-column derivatizing agents were used for the determination of metals with high sensitivity, e.g., dithizone [31], PAR [4–10] and 8-hydroxyquinoline-5-sulfonate (HQS) [32]. However, dithizone and HQS could not be used under the same conditions for different metals. Therefore, they were not suitable for the simultaneous detection of metals in ion chromatographic analysis. PAR is a commonly used derivatizing agent and it could develop color with most metals under the same conditions. However, its molar absorptivities were not very high ($>2\times10^4$). 2-[(5-Bromo-2-pyridyl)azo]-5-diethylaminophenol (5-Br-PADAP) is a novel derivatizing agent whose metal complexes showed relatively high molar absorptivities ($>10^5$) in the range 550–570 nm and it had a relatively low background absorbance [33,34]. In this paper, the optimum wavelength was determined to be 560 nm.

2. Experimental

2.1. Instrumentation

Chromatographic analyses were performed on a metal-free Dionex DX-300 ion chromatography (Dionex, Sunnyvale, CA, USA) equipped with two advanced gradient pumps (AGP), a MetPac CC-1 chelation column (50×4 mm I.D., packed with styrene-based macroporous 12% cross-linked iminodiacetate-functionalized chelating resin, the particle size was 20 μm and the capacity of the resin was about 0.9 mequiv.), a TMC-1 concentrator column (25×3 mm I.D. containing fully sulfonated PS-DVB cation-exchange resin with a high capacity of 2.2 mequiv.), an IonPac CG5A Guard column and an IonPac CS5A analytical column (250×4.6 mm I.D., 9 μm bead diameter, ethylvinyl benzene-functionalized with both quaternary ammonium and sulfonate functional groups), a 3.66-ml injection loop and a Dionex variable wavelength detector with a post-

column reactor. MetPac CC-1 and TMC-1 columns were used for sample pretreatment. The separation of heavy and transition metals was performed on an IonPac CS5A column.

All measurements were made at room temperature and all samples were filtered through a 0.45-μm filter prior to injection.

Data collection and the operation of all components in the system were controlled by Dionex AI-450 chromatographic software interfaced via an ACI-2 advanced computer interface to an AST Power Premium 3/33 computer.

2.2. Reagents and standards

Ammonium hydroxide, glacial acetic acid, Triton X-100, sodium hydrogen carbonate, sodium nitrate, ammonium persulfate, silver nitrate, mercury nitrate, ammonium acetate, ethanol, lithium chloride, 2-[(5-bromo-2-pyridyl)-azo]-5-diethylaminophenol and lithium hydroxide monohydrate were analytical-reagent grade reagents (Peking Chemical Works, Peking, China), sodium hydroxide, nitric acid, potassium hydroxide and oxalic acid dehydrate were of guaranteed-reagent grade (Peking Chemical Works), pyridine-2,6-dicarboxylic acid (PDCA) was of chromatographic grade (Aldrich, USA), pyrophosphoric acid was a chemical-grade reagent.

Iminodiacetate-based resins (D401, 50–100 mesh, >0.6 Cu^{2+} mequiv. ml^{-1}) were from Chemical Works (Nankai University, China).

Working standard solutions were prepared daily using standards (100 μg ml^{-1}) that were obtained from the Research Center for Eco-Environmental Sciences of Academia Sinica (Beijing, China).

All standards, samples and reagents were stored in polyethylene bottles that had been cleaned and conditioned following the recommended procedures for trace metal determination [24,25].

All solutions were prepared with pretreated water purified with a Milli-Q system (>18 MΩ, Millipore, Waters Chromatography Division, Oslo, Norway).

2.3. Eluents and post-column reagent solution

2.3.1. Purification of D401 resin

Approximately 40 g of D401 resin were weighed in a 1-l polyethylene bottle and then cleaned with a 1.0 *M* NaOH solution, 2.0 *M* nitric acid and deionised water in turn. Finally, the resin was stored in 200 ml of 2.0 *M* ammonium acetate solution, pH 5.5, until required.

Eluents: E_1, 0.18% $NaNO_3$; E_2, 20 m*M* $H_4P_2O_7$, 2.0 *M* NH_4OAc, pH 5.5; E_3, 0.5 *M* HNO_3; E_4, 0.9% $NaNO_3$; E_5, 168 m*M* Ox, pH 4.7; E_6, 18 MΩ deionised water; E_7, 0.012 *M* PDCA, 0.02 *M* LiOH and 0.10 *M* LiCl; ''carrier'' acid, 0.1 *M* HNO_3. E_2, 20 m*M* pyrophosphoric acid, 2.0 *M* ammonium acetate, pH 5.5.

A 3.7-g amount of pyrophosphoric acid was dissolved in 1 l of 2.0 *M* ammonium acetate, pH 5.5. Since pyrophosphoric acid is not available in ultrapure grade, the trace heavy and transition metal contaminants in the solution were removed using D401 resin. The cleaned D401 resin was placed in the solution. After stirring for 60 min, the pyrophosphoric acid–ammonium acetate solution was decanted into an eluent container.

The post-column reagent comprised 0.3 m*M* 5-Br-PADAP, 0.8% Triton X-100, 0.5 *M* ammonium hydroxide and 0.3 *M* sodium hydrogen carbonate solution.

2.4. Samples and sample preparation

The drinking water used in this study was from the Research Center for Eco-Environmental Sciences of Academia Sinica.

A 150-ml volume of drinking water was placed in a beaker. Then, 10 ml of HNO_3 (1.2 g ml^{-1}) and 5 ml of 0.1 *M* $Hg(NO_3)_2$ were added and the solution was boiled for 5 min. All Cl^- and reducible organisms were eliminated and adsorbed metals were released from organic colloids. Then, 10 ml of a 10% $(NH_4)_2S_2O_8$ solution (newly synthesized) was added and the mixture was boiled for 5 min. All Mn^{2+} was oxidized to permanganate (MnO_4^-). After allowing the mixture to cool, the solution was diluted to 200 ml with 0.1 *M* HNO_3, before being transferred to a closed polytetrafluoroethylene beaker.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \xrightarrow{Ag^+} 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

2.5. Experimental procedure

A detailed scheme of the chelation ion chromatographic system is shown in Fig. 1.

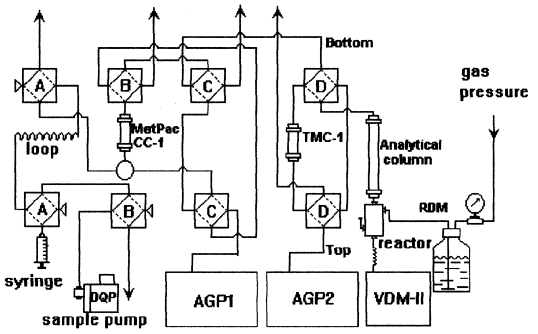

Fig. 1. Scheme of the chelation ion chromatographic system.

Table 2
Gradient separation program for the analysis of heavy and transition metals (AGP-2 program)

Time (min)	E_4 (%)	E_5 (%)	E_6 (%)	Valve D[b]
0.0	7	27	66	Off
16.1[a]	7	27	66	On
24.0	7	27	66	On
24.1	7	60	33	On
34.0	7	60	33	On
34.1	7	27	66	Off

[a] Begin sample analysis.
[b] Off: real line connected; on: dotted line connected.
Flow-rate: 1.0 ml min^{-1}.

The AGP1 pretreatment program (shown in Table 1) was entered as a method file in the AI-450 operating software and subsequently downloaded onto AGP1. The AGP2 concentration gradient program listed in Table 2 was entered through the AGP2 front panel. These eluent containers were pressurized with nitrogen to 3500 Pa. When the operation started, sample was flushed by the acid carrier to a mixing tee, where it was buffered with a pyrophosphoric acid–ammonium acetate buffer before entering the MetPac CC-1 column. None of the anions (including permanganate) and monovalent cations were retained. Alkaline earth metals, iron and aluminum were selectively removed using a pyrophosphoric acid–ammonium acetate buffer. Then, the retained metals were transferred to a TMC-1 column by 0.5 *M* HNO_3 and rinsed with a 0.18% $NaNO_3$ solution to convert the TMC-1 column from the hydrogen form to the sodium form. Finally, the TMC-1 column was linked to the CS5A column; AGP2 delivered $NaNO_3$ and Ox eluents to the column and the different metals were separated. All metals were detected after post-column reaction with 5-Br-PADAP at 560 nm.

3. Results and discussion

3.1. Spectrophotometric detection

3.1.1. Choice of 5-Br-PADAP concentration

5-Br-PADAP could form stable metal complexes

Table 1
Chelation concentration and matrix elimination operating conditions for analysis of heavy and transition metals (AGP-1 program)

Time (min)	E_1 (%)	E_2 (%)	E_3 (%)	Valve A[b] Valve B[b]	Valve C[b]	Flow-rate (ml min^{-1})	Sample pump
0.0	0	100	0	Off	On	1.0	On
3.0	0	100	0	Off	On	1.0	Off
3.1	0	100	0	Off	On	2.5	Off
5.0	0	100	0	Off	On	2.5	Off
5.1	0	0	100	On	On	2.0	Off
8.0	0	0	100	On	On	2.0	Off
8.1	100	0	0	Off	Off	2.5	Off
16.0[a]	100	0	0	Off	Off	2.5	Off
16.1	0	100	0	On	Off	2.0	Off
20.0	0	100	0	On	Off	0.0	Off
35.0	0	100	0	Off	Off	2.0	Off
40.0	0	100	0	On	Off	0.0	Off

[a] Begin sample analysis.
[b] Off: real line connected; on: dotted line connected.
Sample pump flow-rate: 1.5 ml min^{-1}.

with metal ions. Its concentration had a great influence on the absorbance of the complexes. When the concentration of 5-Br-PADAP was increased, their absorbance would also increase. However, when the concentration of 5-Br-PADAP reached a certain value, there was no obvious increase in their absorbance. However, the background absorbance also increased. This resulted in increased signal-to-noise ratios. Thus, a compromise had to be obtained and a 0.1 m*M* 5-Br-PADAP solution was determined to be the best.

3.1.2. Choice of Triton X-100 concentration

Since the surface active agent adds the functions of solubilization, sensitization, dispersion and stabilization to the color-development system, it could be used to enhance the sensitivity and solubility of spectrophotometric detection for Pb^{2+}, Cu^{2+} and Cd^{2+} in an aqueous system. Several surface active agents, including Triton X-100, Tween 80, poly-(vinyl alcohol) (PVA) and cetyltrimethyl ammonium bromide (CTAB), were tested. Of them, Triton X-100 was the best. The influence of the concentration of Triton X-100 on Cu^{2+}, Pb^{2+} and Cd^{2+} is shown in Fig. 2. When the Triton X-100 concentration was 0.16%, the absorbance of Cu^{2+} and Pb^{2+} was the highest. However, when the Triton X-100 concentration was 0.24%, the absorbance of Cd^{2+} was the highest. We chose 0.24% Triton X-100 as the optimal concentration as the absorbance values for Cu^{2+} and Pb^{2+} differed only slightly from their highest values at this concentration.

3.1.3. Choice of pH for the color-development system

The pH can influence the 5-Br-PADAP complexation process. A high pH increases the ionization of 5-Br-PADAP, thus exploiting its complexing capabilities. However, the background absorbance would be high also. Moreover, hydrolysis of metals could be observed along with the simultaneous disappearance of their signals, whereas using very low pH values could result in decreasing their complexing capabilities. The optimal pH value for color-development was 10.5 for Cu^{2+} and Cd^{2+}. However, the higher the pH was, the higher the absorbance for Pb^{2+} was (Fig. 3). So, when we wanted to determine Cu^{2+} and Cd^{2+}, pH 10.5 was chosen, but when we wanted to determine Pb^{2+}, a higher pH value was chosen.

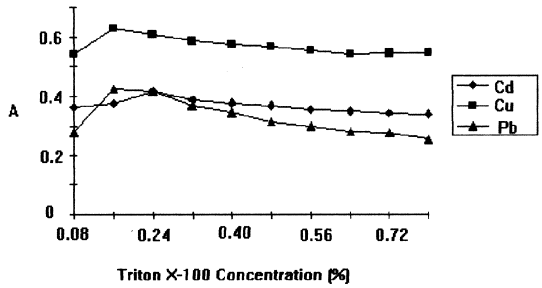

Fig. 2. Effects of Triton X-100 concentration of the chromophoric reaction on absorption.

3.2. Matrix elimination and concentration

The matrix elimination step was to remove anions, alkali metals, alkaline earth metals, manganese, iron and aluminium from the sample matrix. The MetPac CC-1 column contained macroporous iminodiacetate chelating resin, which has a very high affinity for transition and heavy metals compared to alkali and alkaline earth metals. Before the sample stream passed through the MetPac CC-1 column, the sample that had been loaded previously into the sample loop was flushed out by the acid carrier and buffered on-line with 20 m*M* pyrophosphoric acid–2.0 *M* ammonium acetate eluent, pH 5.5. No anions or monovalent cations were retained. By using this eluent further, alkaline earth metals, iron and aluminum could be selectively eluted, while Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} quantitatively remained on the column. The recoveries of Pb^{2+}, Cu^{2+}, Cd^{2+},

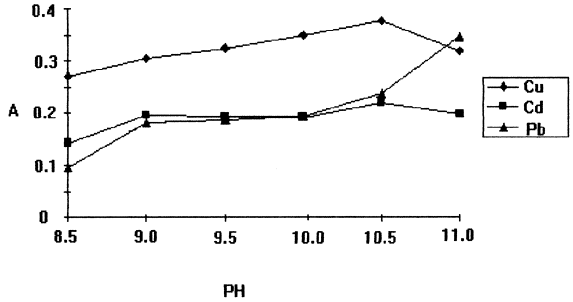

Fig. 3. Effects of acidity of the chromophoric reaction on absorption.

Co^{2+} and Ni^{2+} were higher than 90% at $\mu g\ l^{-1}$ levels. A 10-mg amount of Ca could be eluted completely with 5 ml of eluent. The results were the same for the other alkaline earth metals. Changing the flow-rate from 1 to 3 ml min^{-1} did not influence the recoveries of retained metals. Before each analysis, the flow paths had to be rinsed with 0.1 *M* HNO_3, otherwise, the reductive component would reduce permanganate to Mn^{2+}.

As iron and aluminium could not be eluted from the analytical column, they had to be removed beforehand. Pyrophosphoric acid can selectively bind iron and aluminium, thus preventing their uptake by the chelating resin during concentration. This approach not only prevented precipitation of iron and aluminium at high concentrations, but it also allowed the effective removal of iron and aluminium from the MetPac CC-1 column. Table 3 shows the constants for metals–IDA and metals–pyrophosphate. It was found that the constants between IDA and Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} were far bigger than those between pyrophosphate and these metals. However, for iron and aluminium, the metal–pyrophosphate complexes formed during the on-line neutralization step (in-situ) were more stable than metal–IDA complexes, which were not retained on the column. More than 99.8% of a 2-mg amount of iron or aluminium could be eluted with 6 ml of eluent. The scheme for selective concentration using the MetPac CC-1 column with complexing agents is as follows:

In situ

$$M^{3+} + HPP^{3-} \overset{K_{MHPP}}{\Rightarrow} MHPP$$

$$M^{3+} + 2HPP^{3-} \overset{K_{M(HPP)_2}}{\Rightarrow} M(HPP)_2^{3-}$$

Resin

$$M^{3+} + R\text{-}N(CH_2COO^-)_2 \overset{K_R}{\Rightarrow} R\text{-}N(CH_2COO)M^+$$

$$M^{3+} + 2R\text{-}N(CH_2COO^-)_2 \overset{K_{R_2}}{\Rightarrow} 2R\text{-}N(CH_2COO)M^-$$

$(M^{3+} = Al^{3+}, Fe^{3+})$

All of the metals retained in the MetPac CC-1 column could be eluted completely to the TMC-1 column using 0.5 *M* HNO_3. However, before the TMC-1 column is linked with the CS5A column, it must be converted from the hydrogen form to the sodium form, otherwise, the peaks of Pb^{2+}, Cu^{2+} and Cd^{2+} would be within a big negative peak and could not be determined accurately. Table 1 shows the optimization procedure for chelation concentration and matrix elimination.

Table 3
Constants for the metals and IDA or pyrophosphate acid (H_4PP)

	Fe	Al	Co	Ni	Cu	Cd	Pb
M(IDA)	10.07	8.10	6.78	7.92	10.62	6.88	7.39
$M(IDA)_2$	–	15.07	12.33	14.24	15.64	–	–
M(HPP)	–	–	3.4	3.71	4.45	3.1	4.2
$M(HPP)_2$	22.2	25.3	–	–	–	–	–

3.3. Chromatographic separation

Since IonPac CS5A has both anion- and cation-exchange capacity, metals could be separated by cation- and anion-exchange. Thus, major selectivity changes could be made by simply changing the eluent. Hydrated and weakly complexed metals could be separated as cations on cation-exchange sites. By adding chelating carboxylic acid to the eluent, the net charge on the metal was reduced. Also, if the chelating agent concentration was high and the β constant was $>10^3$, then the net charge of the metal complexes was negative and the metal ion complex could be separated by anion exchange. Therefore, when the metals were separated with Ox eluent, the separation had both anion- and cation-exchange components. Since Pb^{2+} and Cd^{2+} formed relatively weak complexes with oxalate, they were separated by cation-exchange. However, the other metals formed stable complexes and were separated by anion-exchange [9]. The elution order was Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+} and Ni^{2+}. However, the peaks of Pb^{2+} and Cd^{2+} tailed seriously. The use of $NaNO_3$ in the eluent reduced the tailing and improved the peak shape considerably, as Na^+ could compete with Pb^{2+} and Cd^{2+} for the cation-exchange sites. This lead to a decrease in the interactions between the cation-exchange sites and Pb^{2+} and Cd^{2+}, which resulted in shorter elution times and better peak shapes. A series of separating

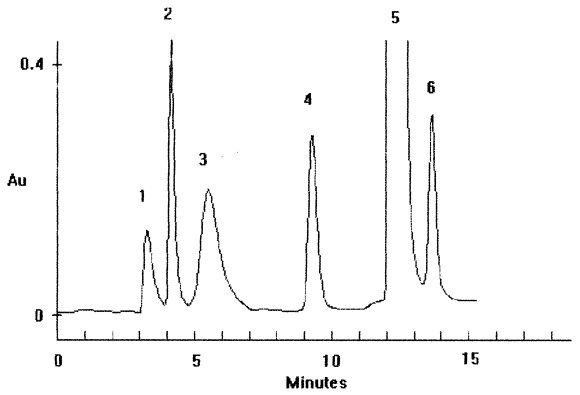

Fig. 4. Chromatogram of metals in a synthetic standard solution. Chromatographic conditions are the same as in Tables 1 and 2. Post-column reagent: 0.3 m*M* 5-Br-PADAP, 0.8% Triton X-100, 0.5 *M* ammonia and 0.3 *M* sodium hydrogen carbonate. Flow-rate: 0.5 ml min^{-1}. Detection was at 560 nm. Peaks: 1, Pb (80 ng ml^{-1}); 2, Cu (30 ng ml^{-1}); 3, Cd (24 ng ml^{-1}); 4, Co (24 ng ml^{-1}); 5, Zn; 6, Ni (24 ng ml^{-1}), Al (2.0 mg ml^{-1}), Fe (2.0 mg ml^{-1}), Ca (5.0 mg ml^{-1}) and Mg (5.0 mg ml^{-1}), respectively.

conditions were tested. From these experiments, the optimum conditions was chosen (shown in Table 2). A typical chromatogram of a synthetic standard solution is illustrated in Fig. 4. All individual metal peaks were well separated. Even though there were a lot of alkaline earth metals, aluminium and iron in the solution, they did not affect the separation or the determination of heavy and transition metals.

Before starting each analysis, the analytical column had to be equilibrated with Ox and $NaNO_3$ eluent for 16 min. This could be done while the sample pretreatment steps were being performed.

The analytical column frequently had to be eluted using PDCA to remove iron and aluminium, which are commonly found in eluents and, if not removed, could lead to column overload.

Table 5
Analytical results of drinking water

Metal	IC[a] (ng ml^{-1})	Spiked (ng ml^{-1})	Recovery (%)
Pb	0	50	104
Cu	5.20	15	96
Cd	0	30	104
Co	0.25	15	99
Ni	1.20	15	99

[a] Observed in drinking water.

3.4. Accuracy and detection limit

In this work, an optimized program was selected (Tables 1 and 2). It gave rise to sharper peaks with good peak separation and excellent calibration curves. Table 4 illustrates the linear ranges, correlation coefficients, relative standard deviations (R.S.D.) and detection limits for the method. All metals had good linearities with correlation coefficients that were greater than 0.999. The R.S.D., based on $>10\times$ the detection limit, was found to be in the range of 1.8–5.0% and the detection limit (signal-to-noise ratio of 3:1) of this method was at or below the $\mu g\ l^{-1}$ level. The data confirmed that the precision of this method was good.

3.5. Analysis of drinking water

The data shown in Table 5 represents averages of three totally independent analyses involving sample digestion and chelation ion chromatography. The results were obtained using the system that was

Table 4
Linear ranges, correlation coefficients, R.S.D. values and detection limits for heavy and transition metals

Metal	Concentration range (ng ml^{-1})	Correlation coefficient (r)[a]	R.S.D. (%)[b]	Detection limit[c] (ng ml^{-1})
Pb	5–640	0.9995	5.1	2.0
Cu	1.5–192	0.9990	4.7	0.2
Cd	3–384	0.9999	1.8	0.6
Co	1.5–192	0.9999	3.8	0.2
Ni	1.5–192	0.9996	4.3	0.2

[a] Diluted 1:1, 1:2, 1:4, 1:8, 1:16, 1:32, 1:64 and 1:128.
[b] Concentration $>10\times$ the detection limit ($n=7$).
[c] Signal-to-noise ratio = 3:1.

calibrated using our standards. The concentrations of Pb^{2+} and Cd^{2+} in drinking water were below the detection limits and, therefore, could not be determined (Fig. 5.). We obtained good recovery rates for all of the metals.

Blanks were well below the detection limits for Pb^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+}. The major contributors to contamination were Cu^{2+} and Zn^{2+}. These contaminations could be reduced by using ultrapure reagent and water. Washing the flow paths with 0.1 *M* oxalic acid could also reduce contamination levels. However, some of the contaminants dissolved in the system and could not be eliminated completely. However, the content of Cu^{2+} was constant, it could not affect its determination. Moreover, there was no indication of any memory effect when a blank was run immediately after a sample with a high concentration of metals. These results indicate that the present chelation ion chromatographic system was useful for the determination of heavy and transition metals in drinking water. One of the most important advantages gained by using this method was that the analytical media could be injected directly after sample digestion.

However, this method essentially measured the ''labile dissolved'' fraction in solution and not the non-labile fraction, which included stable metal complexes with fulvic acid or humic acid. Complexation of trace metals by fulvic acid or humic acid was dependent on the pH value. After the sample was digested, its pH was one. However, after being buffered on-line with 2.0 *M* pyrophosphoric acid–ammonium acetate buffer, the pH increased up to 5.5. Under these conditions, there was a low concentration of H^{+} to compete for binding sites on the fulvic acid or humic acid. Thus, metals would bind more tightly to fulvic acid or humic acid [8]. A large fraction of the transition metals was present as complexes. However, the ''labile dissolved'' fraction more closely represented the metal that was actually available to species and gave important information on potential toxicity [35]. If the total concentration was required, the sample must be digested further.

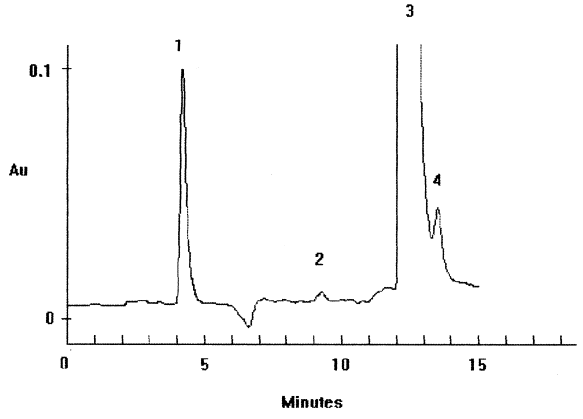

Fig. 5. Chromatogram of metals in drinking water. Chromatographic conditions were similar to those in Fig. 4. Peaks: 1, Cu (5.2 ng ml^{-1}); 2, Co (0.25 ng ml^{-1}); 3, Zn and 4, Ni (1.2 ng ml^{-1}).

4. Conclusions

An on-line chelation ion chromatographic technique was developed that could be used to accurately and precisely analyse Pb^{2+}, Cu^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} at the $\mu g\ l^{-1}$ level in drinking water. Sample preconcentration and matrix elimination covered a wide range of sample matrix concentrations. The method was not only adaptable to simple samples, such as drinking water, but also to complex samples. As a further application of this technique, five standard reference samples, peach leaves, tea, mussel, prawn and pork liver, were analyzed. The ion chromatographic values obtained were in good agreement with the certified values.

References

[1] O. Ravera, Experientia 40 (1984) 2.
[2] D.F. Flick, H.F. Kraybill, J.M. Dimitroff, Environ. Res. 4 (1971) 71.
[3] G.W. Bryan, in R. Johnston (Editor), Marine Pollution — Heavy Metal Contamination in the Sea, Academic Press, London, 1976, p. 185.
[4] P.L. Buldini, S. Cavalli, A. Mevoli, E. Milella, J. Chromatogr. A 739 (1996) 131.
[5] P.L. Buldini, S. Cavalli, A. Mevoli, J. Chromatogr. A 739 (1996) 167.
[6] P. Janvion, S. Motellier, H. Pitsch, J. Chromatogr. A 715 (1995) 105.
[7] C. Sarzanini, M. Aceto, G. Sacchero, E. Mentasti, Ann. Chim. (Rome) 84(1) (1994) 71.

[8] N. Cardellicchio, P. Ragone, S.Cavalli, J.M. Riviello, II CS'96 International Ion Chromatography Symposium, No. 102, The University of Reading, Reading, UK, 1996.
[9] A.W. Al-Shawi, R. Dahl, II CS'96 International Ion Chromatography Symposium, No. 59, The University of Reading, Reading, UK, 1996.
[10] K.A. Ruth, R.W. Shaw, J. Chromatogr. 546 (1991) 243.
[11] Y.B. Liu, Q. Wang, J. Chromatogr. 644 (1993) 73.
[12] S. Reiffenstuhl, G. Bonn, J. Chromatogr. 482 (1989) 289.
[13] A. Rahmalan, M.Z. Abdullah, M.M. Sanagi, M. Rashid, J. Chromatogr. A 739 (1996) 233.
[14] I.N. Voloschik, M.L. Litvina, B.A. Rudenko, J. Chromatogr. A 671 (1994) 205.
[15] W. Shotyk, I. Immenhauser-Potthast, J. Chromatogr. A 706 (1995) 167.
[16] A.R. Timerbaev, G.K. Bonn, J. Chromatogr. 640 (1993) 195.
[17] K. Robards, P. Starr, E. Patsalides, Analyst 116 (1991) 1247.
[18] T.S. Stevens, G.L. Jewett, R.A. Bredeweg, Anal. Chem. 54 (1982) 1206.
[19] T. Tanaka, Fresenius' Z. Anal. Chem. 320 (1985) 125.
[20] O.N. Obrezkov, V.I. Slyamin, O.A. Shpigun, Anal. Sci. 6 (1990) 617.
[21] R.R. Greenberg, H.M. Kingston, J. Radioanal. Chem. 71 (1982) 147.
[22] Y. Liu, J.D. Ingle Jr., Anal. Chem. 61 (1989) 520.
[23] J.P. Riley, D. Taylor, Anal. Chim. Acta 40 (1968) 479.
[24] S. Motellier, H. Pitsch, J. Chromatogr. A 739 (1996) 119.
[25] B. Paull, M. Foulkes, P. Jones, Analyst 119 (1994) 937.
[26] R. Caprioli, S. Torcini, J. Chromatogr. 640 (1993) 365.
[27] D. Chambaz, W. Haerdi, J. Chromatogr. 600 (1992) 203.
[28] N. Cardellicchio, S. Cavalli, J.M. Riviello, J. Chromatogr. 640 (1993) 207.
[29] M. Betti, M.P. Colombini, R. Fuoco, P. Papoff, Mar. Chem. 17 (1985) 313.
[30] A.W. Struempler, Anal. Chem. 45 (1973) 2251.
[31] P. Jones, K. Barron, L. Ebdon, Anal. Proc. 22 (1985) 373.
[32] P. Jones, P.J. Hobbs, L. Ebdon, Anal. Chim. Acta 149 (1983) 39.
[33] W. Jin, Physical Testing and Chemical Analysis, Part B, Chem. Anal. 31(1) (1995) 53.
[34] Y.X. Yuan, H.Q. Liu, Y.J. Wang, Anal. Chem. (Chinese) 19(4) (1991) 460.
[35] T.M. Florence, Water Res. 11 (1977) 681.