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Trace analysis of heavy metals in groundwater samples by ion chromatography with post-column reaction and ultraviolet–visible detection

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Abstract

Groundwaters originating from local and regional aquifers surrounding ash deposits produced by a coal-fired power plant were collected. These water samples were chemically analyzed for quantifying their heavy metal composition at trace levels. A highly sensitive analytical technique based on ion chromatography with a UV–Vis detector and under isocratic eluent flow-rate conditions was used. In order to quantify the major heavy metals (Pb, Cu, Cd, Co, Zn and Ni), three ionic separation column systems were evaluated: (1) a cationic column (HPIC-CS2, Dionex) tested with two eluents (10 mM oxalic acid–7.5 mM citric acid; and 40 mM D-tartaric acid–12 mM citric acid); (2) an anionic column (HPIC-AS4, Dionex) evaluated with 25 mM oxalic acid as eluent; and (3) a bifunctional ion-exchange column (Ionpac CS5, Dionex) which was also tested with two eluents (6 mM pyridine, 2,6-dicarboxylic acid; and 50 mM oxalic acid/95 mM lithium hydroxide). The lowest detection limits achieved with the Ionpac CS5 column and the 50 mM oxalic acid–95 mM lithium hydroxide eluent enabled the heavy metal analysis in groundwater samples to be reliably performed. Details of this comparative study, including the ion chromatography procedure selected and its application to heavy metal analysis of groundwater samples, are presented in this work. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Water analysis; Environmental analysis; Mobile phase composition; Metals; Inorganic cations

1. Introduction

The accelerated industrialization process of developing countries in combination with their rapid population growth and some agricultural activities have brought a risk of increasing the pollution index in natural environments such as soils, waters or air [1–3]. Low efficiency in industrial production pro-

cesses (e.g. energy power plants, petrochemical and chemical industries, etc.), or the unsuitable handling and management of the industrial wastes have been recognized as pollution sources responsible for producing considerable loading of heavy metals (Pb, Cu, Cd, Co, Zn, and Ni) to the environment [4,5].

The presence of residual ash deposits derived from the coal combustion process in an energy power plant could be a possible source of metallic pollutants. Traces of heavy metals, such as Cd, Pb, and Zn, can have their origin from combustion residues, which could migrate or infiltrate into the aquifers for

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interacting and dissolving with natural groundwater [2,5]. Such hydrogeochemical transport and interaction processes could affect the composition of local and regional waters and therefore produce a direct effect on the ecosystem. In order to predict its impact to water aquifers surrounding the coal power plant, an environmental protection program for monitoring heavy metal contents in groundwater samples was carried out. This application required a sensitive and reliable analytical technique to be developed for determining the concentration of heavy metals (Pb, Cu, Cd, Co, Zn, and Ni) at trace levels ($\mu\text{g/l}$).

The analytical determination of metal ions at low concentration levels has received considerable attention in the last few years [6,7]. Chemical analyses of heavy metals have traditionally been carried out by atomic absorption spectrometry (AAS) [3,5]. However, the detection limits of AAS have usually been high and consequently unsuitable for a direct trace analysis in complex matrices [6].

A more complex system consisting of a graphite furnace with atomic absorption spectrometry (GF-AAS) has better detection capabilities, but some chemical, ionization, spectral or physical interferences have limited their generalized use [6,8]. Moreover, other methods based on the use of simple or standard inductively coupled plasma (ICP) instruments have not totally demonstrated to be sensitive analytical tools for achieving the low detection limits required for trace analyses [8]. Therefore, new and more complex technology such as inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled argon plasma spectroscopy (ICAP) have required to be coupled with liquid chromatography for measuring heavy metals at lower detection limits [8–12]. Unfortunately, these new high-cost technologies are often beyond the reach of most laboratories in developing countries. Hence, a great need still persists for investigating cheaper, faster, accurate, and highly sensitive analytical methods for the determination of heavy metals at trace levels.

High-performance liquid chromatography (HPLC) in its different technical modes (ion chromatography, chelation-ion chromatography, reversed-phase liquid chromatography or ion-interaction chromatography)

has become one of the main powerful analytical tools available for analyzing heavy metals [6]. Most of these techniques offer several advantages for the determination of metals, including the ability for oxidation state speciation and multi-elemental capability in a single analysis [6,13]. Ion chromatography (IC) has been applied for measuring heavy metals as well as other inorganic ions (e.g. rare-earth elements) [7]. Numerous IC papers dealing with new developments and a wide variety of applications have been published, e.g. [12–20]. However, use of IC for heavy metal analysis has still been somewhat limited, due to certain matrix interference problems. Generally low concentrations of heavy metals in the presence of high contents of alkali and alkaline-earth elements in geohydrological samples have been identified as one of the main factors responsible of these interferences [13]. Significant progress has, however, been made in IC methodology in terms of the eluent (composition and pH), the detection mode, and the chromatographic operating conditions, for minimizing interferences and obtaining lower detection limits [13].

Detection of heavy metal ions after an ion chromatographic separation has generally been carried out by UV-Vis spectrophotometry after a post-column derivatization reaction (using a membrane reactor) of metal ions by mixing them with various metal-chromic reagents to form chelate complexes that absorb at approximately 520 nm (e.g. [21–24]). Most frequently metal-chromic reagents such as 4-(2-pyridylazo)resorcinol (PAR); 2,7-bis(*o*-arsenophenyl)azo-1,8 dihydroxynaphthalene-3,6-disulfonic acid (arsenazo III) or 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) are used [13,25–27].

Most of these IC methodologies use a rather complex instrumentation (detectors, gradient pumps, and several arrays of separation columns) for achieving a better separation and detection of these elements as well as for optimizing the analysis time. Gradient pumps, for example, enable IC analyses to be carried out with gradient concentration programs of eluent. Such an instrumental feature constitutes a strong limitation, especially for laboratories which are still using either a former or a standard IC instrumentation based on the use of an isocratic high-pressure pump. Additional laboratory work

should therefore be carried out to estimate the most optimum IC conditions for measuring heavy metals under isocratic eluent flow-rate conditions.

The present work reports a simple and accurate IC procedure for an efficient separation and quantification of heavy metals at trace levels under isocratic eluent flow-rate conditions. Three different separation column systems (based on anionic, cationic, and bifunctional mixed-bed exchanges) were evaluated for selecting the most appropriate analytical column to carry out heavy metal analysis. In this paper, the application of the best of these three separation systems for a simultaneous determination of heavy metals in groundwater samples is also reported.

2. Experimental

2.1. Instrumentation

Chromatographic analyses were carried out on a metal-free high-pressure ion chromatograph, model 2010i (Dionex, Sunnyvale, CA, USA), which is equipped with an isocratic pump, a post-column pneumatic controller for post-column reagent addition (equipped with a semipermeable membrane reactor), and a variable-wavelength absorbance detector (at 520 nm). The ion chromatograph was interfaced to an integrator unit Spectra-Physics model SP4270 (Spectra-Physics, San Jose, CA, USA) for collecting chromatographic data.

Three ionic separation column systems (250×4 mm I.D., Dionex) were used during the experimental tests: (1) a cationic separation column (HPIC-CS2); (2) an anionic separation column (HPIC-AS4); and (3) a bifunctional mixed-bed ion-exchange column (Ionpac CS5). The separation column systems were protected from fouling problems by fixing their respective guard columns (50×4 mm I.D., Dionex): HPIC-CG2, HPIC-AG4 and Ionpac CG5, respectively.

All the experimental tests were carried out under isocratic eluent flow-rate conditions and at room temperature. A 100- μ l sample loop was used for all measurements. At the sampling site, groundwater samples were pre-filtered through a filter-membrane

of 0.20 μ m (Millipore, Bedford, MA, USA) for removing suspended and colloidal matter before acidifying. At the laboratory, water samples were again filtered and injected at least in triplicate. The operating conditions and eluents used by the IC system during a phase of experimental tests are summarized in Table 1. Even though such operating parameters have commonly been suggested in technical literature on ion chromatography for analyzing metal ions (e.g. [22,23]), they were modified and optimized to increase the detection sensitivity, and hence to achieve the required trace concentration levels.

2.2. Chemical reagents and standards

All chemical reagents were analytical grade and contained negligible concentrations of trace metals. Nitric and hydrochloric acids were ultra-pure reagents (Merck, Mexico). Pyridine-2,6-dicarboxylic acid (PDCA) and PAR monosodium salt were obtained from Aldrich. Oxalic acid, citric acid, D-tartaric acid, lithium hydroxide, sodium hydroxide, ammonium hydroxide (30%), and acetic acid were also analytical reagent grade (Baker, Mexico). Working standard solutions of metals ranging from 0.00195 to 100 mg/l (1.9 to 1×10^5 μ g/l) were prepared each working day by serial dilution of certified AAS standard solutions of each metal containing 1000 mg/l (Merck). Deionized water with a conductivity lower than 0.1 μ S was used. Normal precautions for trace analysis were taken, e.g., all glassware material was carefully cleaned in concentrated nitric acid and vigorously washed with deionized water.

2.3. Eluents and post-column reagents

Five different eluents were prepared for use with three ionic separation columns. Table 1 also summarizes all the eluents used (composition, pH, and flow-rate conditions) as well as the corresponding analytical column where they were used. Theory of Van-Deemter curves (height equivalent to a theoretical plate versus flow-rate) was used for fixing the optimum eluent flow-rate conditions (0.9–1.0 ml/min) [23]. Post-column reagent (PAR) was prepared

Table 1
Separation of heavy metals by ion chromatography technique using various commercial Dionex analytical columns and eluents under isocratic conditions

| | Separating cationic column: HPIC-CS2 | | Separating anionic column: HPIC-AS4 | Bifunctional mixed-bed ion-exchange column: Ionpac CS5 | |
|--------------------------------------------|---------------------------------------------------------------|-----------------------------------------------------------------|-----------------------------------------|-----------------------------------------------------------|--------------------------------------------------------------------|
| | Eluent (A) | Eluent (B) | Eluent (C) | Eluent (D) | Eluent (E) |
| Composition | 10 mM oxalic acid 7.5 mM citric acid pH=4.2 (with LiOH) | 40 mM D-tartaric acid 12 M citric acid pH 4.3 (with LiOH) | 25 mM oxalic acid pH 4.8 (with NaOH) | 6 mM PDCA pH 4.8 (with LiOH) | 50 mM oxalic acid 95 mM lithium hydroxide pH 4.8 (with LiOH) |
| Post-column derivatization (0.8 ml/min) | 0.2 mM PAR | 0.2 mM PAR | 0.2 mM PAR | 0.2 mM PAR | 0.2 mM PAR |
| <i>UV detection conditions</i> | | | | | |
| Sensitivity (AUFS) | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Wavelength (nm) | 520 | 520 | 520 | 520 | 520 |
| <i>Isocratic conditions</i> | | | | | |
| Injection volume (μl) | 100 | 100 | 100 | 100 | 100 |
| Flow-rate (ml/min) | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |

with a mixture of 0.2 mM PAR, 3 M ammonium hydroxide, and 1 M acetic acid (adjusted to pH=10.2). Prior to use, all the reagents were filtered through a 0.2- μ m filter-membrane and degassed to avoid air bubble problems within the high-pressure pump. Since PAR reagent is easily oxidized, it was quickly degassed and stored under a helium atmosphere.

2.4. Samples

Groundwaters were sampled and pre-filtered in polypropylene bottles (volume 125 ml) previously washed with nitric acid and deionized water according to the sampling techniques recommended for collecting geothermal fluids [28]. All samples (~124 ml) were then acidified immediately after collection by adding 1 ml of 6 M hydrochloric acid and stored at ~5°C for their subsequent chemical analysis. All samples were again filtered through a filter-membrane (0.2 μ m) before injection into the IC system to prevent fouling problems.

3. Results and discussion

3.1. Conditioning and operation of the IC instrument

Before initiating the experimental tests, traces of metals in the IC system (flowing paths, pump and columns) were removed by flushing the system with a 0.2 M oxalic acid solution (at a flow-rate of 1 ml/min) for ~1 h, followed by rinsing with deionized water (15 min). The instrument was then set in operation for 30 min with an optimum flow-rate of working eluent solution according to the analytical column chosen (Table 1).

3.2. Heavy metals separation

An efficient separation of metal ions at trace levels by IC technique is a challenging analytical task [13,19,20]. Hydrated and weakly heavy metals can be eluted either as cations on a cation-exchange column or as anions using an anion-exchange column [13]. Separation of these elements can also be achieved by use of a bifunctional or mixed bed

ion-exchange column having both a cation- and anion-exchange capacity. After an efficient separation of metal ions, a continuous mixing process with PAR (at 0.9 or 1.0 ml/min) as post-column derivatization reagent must be performed for finally measuring the metal ions by spectrophotometric detection at 520 nm. The present work involved two experimental phases: (i) three separation modes were evaluated, in terms of individual detection limits of each metal ion, for selecting the most appropriate ion separation column, and (ii) the selected analytical column was then applied for the analysis of metal ions in groundwater samples.

3.2.1. Detection limits

The limit of detection (LOD) was interpreted as the metal ion concentration below which the chromatographic procedure can not detect a reliable response [29]. The LODs for all the chromatographic tests were determined using the '3 σ method' which has been widely used by many authors (e.g. [30,31]). This 3 σ method gives, in a very simple form, a LOD based on either the blanks or a trace-level standard alone. In most of the analyzed cases, seven replicates of the lowest-level metal ion standard were injected. The standard deviation of these replicate intensities divided by the slope of the corresponding calibration curve enabled a standard deviation (SD) value in concentration units to be estimated. This SD was then multiplied by the appropriate value of student's *t* (for a 99% confidence level and for *n*–1 degrees of freedom) for finally computing the LOD of the metal ion.

3.2.2. Selection of the best separation column

The first experimental phase was initiated with the evaluation of the three available ion separation columns: (1) a cationic separation column (HPIC-CS2), which depends on the ability of metal ions to form neutral or anionic complexes (in reversible mode) and the formation constants of these complexes for increasing selectivity [23]; (2) an anionic separation column (HPIC-AS4), which uses the apparent ability of metal ions to form stable anionic complexes [23]; and (3) a bifunctional mixed-bed ion-exchange column (Ionpac CS5) that offers a cation and anion-exchange capacity to enable metal ions to be eluted as cations and anions according to

the different degrees of association between metal ions and the chelating agent [13].

HPIC-CS2 column was evaluated with two eluents: (A) 10 mM oxalic acid–7.5 mM citric acid; and (B) 40 mM D-tartaric acid–12 mM citric acid. The chromatographic operating conditions initially used for trying to separate heavy metals at trace concentration levels are presented in Table 1. These working conditions were compiled from experimental results reported by Weiss [23] who recommended them for analyzing metal ions at concentration levels ranging from 0.5 to 5 mg/l (500 to 5000 µg/l). The corresponding ionic chromatograms, taken from Ref. [23], are presented in a schematic form in Fig. 1A and B. These two plots show the separation of metal ions (at these concentration levels) by using either an oxalate eluent (A) for a standard containing Fe^{3+} ,

Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , and Fe^{2+} or a D-tartaric acid eluent (B) for a standard containing Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , Fe^{2+} , Cd^{2+} , and Mn^{2+} . Although, these chromatograms were related to metal ions at higher concentration levels (compared to the required trace levels in µg/l), they were only used as a reference for identifying the elution sequence of the metal ions and the corresponding retention times. The original chromatographic conditions (Table 1) were therefore modified and optimized for increasing the detection sensitivity at trace levels of concentration expected for later applications. Trace analyses required that diluted standard solutions (ranging from 0.00195 to 10 mg/l) of each metal were injected. Fe^{2+} , Fe^{3+} , and Mn^{2+} metal ions were not added to the working standards because they were not required by the environmental

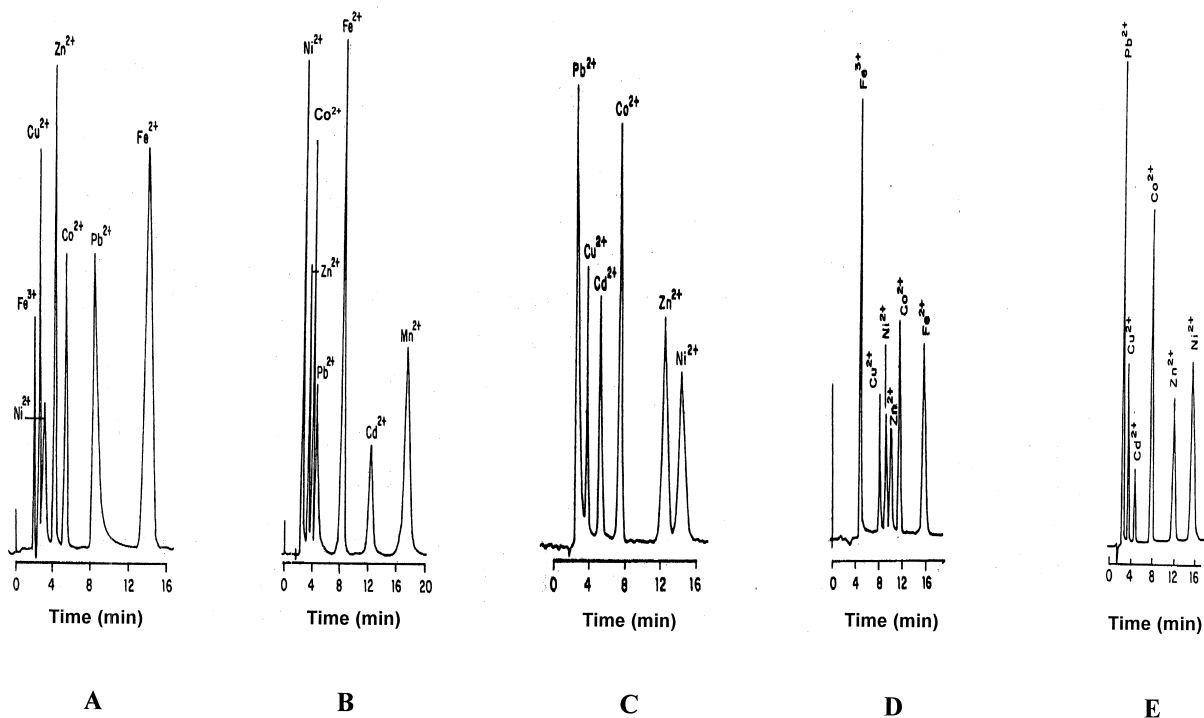


Fig. 1. Typical ion chromatograms of heavy metals using: (A) HPIC-CS2 column with an eluent of 10 mM oxalic acid–7.5 mM citric acid [peaks: Fe^{3+} (5 mg/l), Cu^{2+} (0.5 mg/l), Ni^{2+} (0.5 mg/l), Zn^{2+} (0.5 mg/l), Co^{2+} (1 mg/l), Pb^{2+} (1 mg/l), and Fe^{2+} (5 mg/l)]; (B) HPIC-CS2 column with an eluent of 40 mM D-tartaric acid–12 mM citric acid [peaks: Ni^{2+} (1 mg/l), Zn^{2+} (0.5 mg/l), Co^{2+} (0.5 mg/l), Pb^{2+} (5 mg/l), Fe^{2+} (3 mg/l), Cd^{2+} (2 mg/l), and Mn^{2+} (2 mg/l)]; (C) HPIC-AS4 column with an eluent of 25 mM oxalic acid [peaks: Pb^{2+} (3 mg/l), Cu^{2+} (0.2 mg/l), Cd^{2+} (3 mg/l), Co^{2+} (0.5 mg/l), Zn^{2+} (1 mg/l), and Ni^{2+} (0.5 mg/l)]; (D) Ionpac CS5 analytical column with an eluent of 6 mM pyridine-2,6-dicarboxylic acid; [peaks: Fe^{3+} (1 mg/l), Cu^{2+} (1 mg/l), Ni^{2+} (3 mg/l), Zn^{2+} (4 mg/l), Co^{2+} (2 mg/l), and Fe^{2+} (3 mg/l)]; and (E) Ionpac CS5 column with an eluent of 50 mM oxalic acid–95 mM lithium hydroxide [peaks: Pb^{2+} (4 mg/l), Cu^{2+} (2 mg/l), Cd^{2+} (4 mg/l), Co^{2+} (2 mg/l), Zn^{2+} (2 mg/l), and Ni^{2+} (4 mg/l)]; Weiss [23]. Chromatographic operating conditions are given in Table 1.

Table 2
Reproducibility and detection limits obtained during the experimental tests using three ionic separation column systems (HPIC-CS2, HPIC-AS4 and Ionpac CS5)^a

| Heavy metal | HPIC-CS2 | | | | | | HPIC-AS4 | | | Ionpac CS5 | | | | | |
|------------------|---------------------------------|------------|----------------------------|---------------------------------|------------|----------------------------|---------------------------------|------------|----------------------------|---------------------------------|------------|----------------------------|---------------------------------|------------|----------------------------|
| | Eluent (A) | | | Eluent (B) | | | Eluent (C) | | | Eluent (D) | | | Eluent (E) | | |
| | t_R (± 1 SD) $n=7$ | RSD (%) | LOD ($\mu\text{g/l}$) | t_R (± 1 SD) $n=7$ | RSD (%) | LOD ($\mu\text{g/l}$) | t_R (± 1 SD) $n=3$ | RSD (%) | LOD ($\mu\text{g/l}$) | t_R (± 1 SD) $n=7$ | RSD (%) | LOD ($\mu\text{g/l}$) | t_R (± 1 SD) $n=7$ | RSD (%) | LOD ($\mu\text{g/l}$) |
| Cd ²⁺ | n.e. | – | n.e. | 10.2 (0.1) | 1.0 | 224 | 5.23 (0.08) | 1.5 | 4000 | n.e. | – | n.e. | 6.0 (0.2) | 3.3 | 2.7 |
| Co ²⁺ | 6.30 (0.02) | 0.3 | 132 | 3.30 (0.01) | 0.3 | 112 | 7.51 (0.07) | 0.9 | 900 | 11.85 (0.03) | 0.3 | 0.9 | 9.5 (0.1) | 1.0 | 0.6 |
| Cu ²⁺ | 1.80 (0.02) | 1.1 | 144 | n.e. | – | n.e. | 3.5 (0.2) | 5.7 | 500 | 8.51 (0.02) | 0.2 | 0.9 | 4.1 (0.1) | 2.4 | 1.1 |
| Pb ²⁺ | 8.4 (0.1) | 1.2 | 173 | 3.81 (0.04) | 1.0 | 213 | 2.52 (0.07) | 2.7 | 4500 | n.e. | n.e. | n.e. | 2.05 (0.01) | 0.5 | 1.8 |
| Ni ²⁺ | 2.87 (0.02) | 0.7 | 248 | 2.20 (0.01) | 0.4 | 200 | 15.0 (0.5) | 3.3 | 1800 | 9.53 (0.06) | 0.6 | 1.3 | 16.5 (0.5) | 3.0 | 1.3 |
| Zn ²⁺ | 4.62 (0.06) | 1.3 | 189 | 2.7 (0.1) | 3.7 | 210 | 12.9 (0.4) | 3.1 | 2250 | 10.5 (0.4) | 3.8 | 1.3 | 12.92 (0.15) | 1.2 | 0.9 |

^a t_R , retention time (min); SD, standard deviation; LOD, limit of detection ($\mu\text{g/l}$); n , number of injections of the trace-level standard; n.e., not eluted.

hydrogeochemical study. The lowest detection limits of HPIC-CS2 column with the eluents A and B were obtained when the detector sensitivity was increased up to 0.1 AUFS. The calculation of LODs, in $\mu\text{g/l}$, was then performed using the 3σ approach. The LODs and the retention time reproducibility found for HPIC-CS2 are summarized in Table 2. The LODs for Cu^{2+} , Ni^{2+} , Zn^{2+} , Co^{2+} , and Pb^{2+} were calculated to be 144, 248, 189, 132, and 173 $\mu\text{g/l}$ respectively, when the oxalate eluent A was used. The LODs for Ni^{2+} , Zn^{2+} , Co^{2+} , Pb^{2+} , and Cd^{2+} were calculated to be 200, 210, 112, 213, and 224 $\mu\text{g/l}$, respectively, when the D-tartaric acid eluent B was used. Reproducibility was evaluated by injecting the standard solutions seven times. Relative standard deviation (RSD) values of the retention times varied from 0.3 to 1.3% and from 0.3 to 3.7% for eluents A and B, respectively. The analysis times required for a complete separation of heavy metals with these two eluents (A and B) were about 12 min and 14 min, respectively.

The HPIC-AS4 column used 25 mM oxalic acid as eluent (C). The initial chromatographic conditions used with this anionic column are also reported in Table 1. An expected separation of metal ions (Pb^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+}) under these operating conditions is presented in Fig. 1C. This chromatogram was also published by Weiss [23] who suggested the application of HPIC-AS4 for eluting metal ions at concentration levels ranging from 0.5 to 5.0 mg/l. Considering the elution sequence of these metal ions and their retention times, the LODs provided by this column were evaluated in a similar operational mode as for the HPIC-CS2 column (i.e. modifying the initial chromatographic conditions by injections of standards at a maximum sensitivity of 0.1 AUFS). Considerably higher LODs for Pb^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+} were found to be 4500, 500, 4000, 900, 2250, and 1800 $\mu\text{g/l}$, respectively. Thus, the use of this column exhibited a very poor sensitivity for trace analysis of heavy metals. In fact, the metal ion concentration levels indicated in Fig. 1C and previously reported by Weiss [23] were never achieved. A possible damage in the column packing or a deterioration of the column efficiency due to a long working use could be responsible of the poor detection observed. Nevertheless, it is very important to note that HPIC-AS4 is more suitable for

anion analyses where it has been demonstrated to be a powerful chromatographic tool. Reproducibility was evaluated by injecting the heavy metal standard solutions in triplicate. The retention time reproducibility in terms of the RSD values ranged from 0.9 to 5.7%. The analysis time required for a complete separation was around 16 min.

The Ionpac CS5 analytical column was also evaluated with two different eluents: (D) 6 mM pyridine, (PDCA), and (E) 50 mM oxalic acid–95 mM lithium hydroxide. All the initial chromatographic conditions used with this bifunctional mixed-

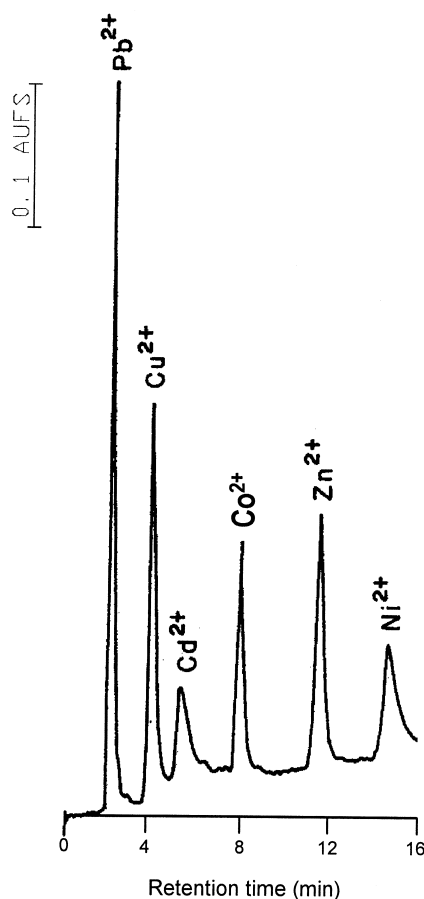


Fig. 2. Ion chromatogram of a standard solution of heavy metals containing Pb^{2+} (62.5 $\mu\text{g/l}$), Cu^{2+} (31 $\mu\text{g/l}$), Cd^{2+} (62.5 $\mu\text{g/l}$), Co^{2+} (31 $\mu\text{g/l}$), Zn^{2+} (31 $\mu\text{g/l}$), and Ni^{2+} (62.5 $\mu\text{g/l}$). Eluent (E): 50 mM oxalic acid–95 mM lithium hydroxide; a detector sensitivity of 0.1 AUFS and a post-column reagent of 0.2 mM PAR, 3 M ammonium hydroxide, and 1 M acetic acid. The remaining operating conditions are given in Table 1.

Table 3

Reproducibility and linearity results of the IC procedure using an Ionpac CS5 analytical column with an eluent of 50 mM oxalic acid–95 mM lithium hydroxide

| Heavy metal | Retention time (% RSD) | Peak area (% RSD) | Linear correlation coefficient, r (n) ^a |
|-----------------------------|------------------------|-------------------|----------------------------------------------------------|
| Cadmium (Cd ²⁺) | 3.3 | 6.8 | 0.991 (5) |
| Cobalt (Co ²⁺) | 1.0 | 6.4 | 0.924 (8) |
| Copper (Cu ²⁺) | 2.4 | 8.5 | 0.937 (8) |
| Lead (Pb ²⁺) | 0.5 | 7.7 | 0.820 (8) |
| Nickel (Ni ²⁺) | 3.0 | 6.3 | 0.984 (5) |
| Zinc (Zn ²⁺) | 1.2 | 3.9 | 0.978 (5) |

^a n : number of data points considered for the linear regression.

bed column are also given in Table 1. They were directly taken from technical literature provided by the column manufacturer. Fig. 1D shows the separation of Fe³⁺, Cu²⁺, Ni²⁺, Zn²⁺, Co²⁺, and Fe²⁺ when the PDCA eluent (D) was used. The separation of heavy metal ions by using an oxalate eluent for a standard solution containing Pb²⁺, Cu²⁺, Cd²⁺, Co²⁺, Zn²⁺, and Ni²⁺ is shown in Fig. 1E. According to the analytical procedure adopted in all the previous experimental tests, chromatograms in Fig. 1D and E were again utilized as a chromatographic reference. These operating conditions were modified and optimized for achieving the required LODs for trace analyses (i.e. at a maximum detection sensitivity of 0.1 AUFS). The experimental results related to the LODs and the retention time reproducibility of Ionpac CS5 are summarized in Table 2. The LODs for Cu²⁺, Ni²⁺, Zn²⁺, and Co²⁺ were calculated to be 0.9, 1.3, 1.3 and 0.9 µg/l, respectively, when the PDCA eluent D was used. The LODs for Ni²⁺, Zn²⁺, Co²⁺, Pb²⁺, and Cd²⁺ were found to be 1.3, 0.9, 0.6, 1.8, and 2.7 µg/l, respectively, when the oxalate eluent E was used. It is important to mention that these computations agree with the LOD estimations performed by Cardellicchio et al. [13]. Reproducibility tests were evaluated by injecting the standard solutions thirteen times. RSD values of the retention times ranged from 0.2 to 3.8% and from 0.5 to 3.3% for eluents D and E, respectively. The analysis time required for a complete separation of heavy metals with any of these two eluents (D and E) was approximately 16 min.

These results clearly show that Ionpac CS5 is a suitable column for determining heavy metals at lower concentration levels, using either a PDCA

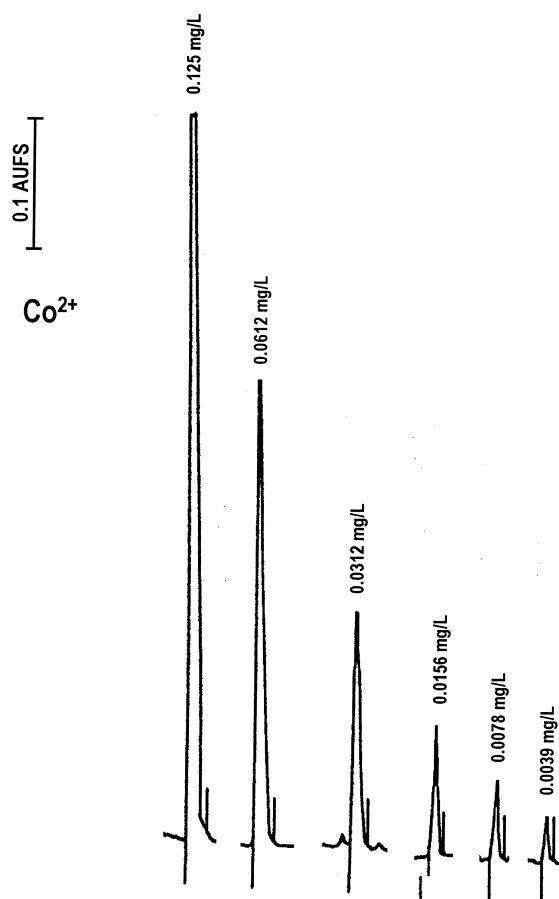


Fig. 3. Schematic diagram showing the calibration results of six injections of various standard solutions of Co²⁺ at trace concentration levels. Eluent (E): 50 mM oxalic acid–95 mM lithium hydroxide; a detector sensitivity of 0.1 AUFS and a post-column reagent of 0.2 mM PAR, 3 M ammonium hydroxide and 1 M acetic acid. The remaining chromatographic operating conditions are included in Table 1.

eluent or an oxalate eluent. In the first case, PDCA eluent forms strong and stable anionic complexes with most metal ions (except Cd and Pb which cannot be separated with this eluent, see Fig. 1D) by an anion-exchange process. In the second case, the oxalate eluent enables both anion- and cation-exchange processes to occur simultaneously. The cation-exchange process dominates for the separation of Pb and Cd, while for the other metal ions, the anion-exchange process controls the formation of stable complexes (Fig. 1E).

On the basis of these chromatographic results, the analytical column with the lowest detection limits was selected for routine applications. Clearly, the most effective separation and detection results were provided by use of the Ionpac CS5 column. The oxalate eluent, which provided an appropriate separation of Pb^{2+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , and Ni^{2+} , was chosen as working eluent. Therefore, this bifunctional analytical column was used for a reliable and accurate analysis of heavy metals at trace levels for the second experimental phase of this work. A standard solution containing a working standard mixture of heavy metals was analyzed by using the best operating parameters (i.e. at a detector sensitivity of 0.1 AUFS). The corresponding ion chromatogram is presented in Fig. 2 where an

efficient elution for all metal ions is clearly shown. The analysis time required for a complete separation of all metal ions was about 16 min.

3.3. Precision and calibration tests

Additional reproducibility tests were also carried out for estimating the RSD values of peak area chromatographic data. A summary of the reproducibility results related to retention times and peak areas have been included in Table 3. These data were obtained from three replicated injections at a concentration range from 3.9 to 500 $\mu\text{g/l}$. An average RSD value of about 6.6% for the peak area of all metal ions was obtained.

With respect to the calibration curves, most of the metals, except Pb, showed a good linear correlation ($r > 0.92$; $5 \leq n \leq 8$) for concentrations ranging from 0.0039 to 0.5 mg/l (3.9 to 500 $\mu\text{g/l}$; Table 3). Even though the linear correlation coefficient for Pb was apparently low ($r = 0.82$ for $n = 8$), it has an acceptable linearity (statistically significant at the 99% confidence level), considering a high degree of probability $P_c(r, n) > 0.01$ [32]. A typical calibration curve related to chromatograms for Co^{2+} at different concentration levels (ranging from 3.9 to 125 $\mu\text{g/l}$) is schematically shown in Fig. 3.

Table 4

Ion chromatography results obtained during the analysis of heavy metals in groundwater samples collected from local and regional aquifers surrounding the coal power plant^a

| Water sample | pH | Temperature (°C) | Salinity (mg/l) | Cd^{2+} (± 1 SD) ($\mu\text{g/l}$) | Co^{2+} (± 1 SD) ($\mu\text{g/l}$) | Cu^{2+} (± 1 SD) ($\mu\text{g/l}$) | Pb^{2+} (± 1 SD) ($\mu\text{g/l}$) | Ni^{2+} (± 1 SD) ($\mu\text{g/l}$) | Zn^{2+} (± 1 SD) ($\mu\text{g/l}$) |
|--------------|-----|------------------|-----------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|----------------------------------------------------|
| C-6 | 7.3 | 23 | 968 | 10.2 (0.7) | 12.9 (0.8) | n.d. | <1.8 | 48 (3) | <0.9 |
| E-1 | 7.8 | 23 | 4350 | 27 (2) | 34 (2) | 10.0 (0.8) | <1.8 | 4.0 (0.2) | <0.9 |
| ED-50 | 7.1 | 23 | 1089 | n.d. | 29 (2) | n.d. | 4.9 (0.4) | <1.3 | 4.0 (0.2) |
| H-1 | 7.7 | 22 | 1475 | 14 (1) | 16 (1) | 63 (5) | 6.4 (0.5) | n.d. | 7.0 (0.3) |
| H-2 | 8.2 | 22 | 2660 | <2.7 | 16 (1) | 9 (1) | 5.6 (0.4) | <1.3 | 7.0 (0.3) |
| N-3 | 7.1 | 23 | 1650 | <2.7 | 222 (14) | n.d. | 5.5 (0.4) | n.d. | <0.9 |
| N-5 | 7.5 | 23 | 670 | 26 (2) | 12.0 (0.8) | <1.1 | 6.8 (0.5) | <1.3 | <0.9 |
| N-25 | 7.0 | 24 | 3770 | <2.7 | 112 (7) | <1.1 | <1.8 | <1.3 | 7.8 (0.3) |
| N-214 | 7.0 | 24 | 1360 | 78 (5) | 32 (2) | n.d. | 5.5 (0.4) | 48 (3) | <0.9 |
| N-417 | 7.1 | 23 | 1146 | 17 (1) | 20 (1) | <1.1 | <1.8 | 8.9 (0.6) | <0.9 |
| N-500 | 7.1 | 23 | 961 | 21 (1) | 19 (1) | n.d. | <1.8 | 10.4 (0.7) | <0.9 |
| P-30 | 7.6 | 23 | 852 | 15 (1) | 19 (1) | <1.1 | 4.5 (0.3) | 5.1 (0.3) | <0.9 |
| P-45 | 7.1 | 22 | 1003 | <2.7 | 14.8 (0.9) | n.d. | <1.8 | 8.1 (0.5) | 6.2 (0.2) |
| P-155 | 7.5 | 25 | 684 | 4.9 (0.3) | 12.2 (0.8) | <1.1 | <1.8 | 5.6 (0.3) | <0.9 |
| P-723 | 6.9 | 24 | 1181 | n.d. | <0.6 | n.d. | 4.8 (0.4) | 47 (3) | 5.1 (0.2) |

^a Salinity is expressed as the content of total dissolved solids (TDS); numbers in parenthesis are the standard deviation values (± 1 SD) of analyses (for $n = 3$ injections); n.d., not detected; < LOD, metal traces below the limit of detection.

3.4. Determination of heavy metals in groundwater samples

Fifteen groundwater samples from local and regional aquifers surrounding a coal-fired power plant were collected. In-situ measurements of pH, temperature, and salinity (expressed as total dissolved solids, TDS in mg/l) were also performed (Table 4). Most of these water samples showed low to moderate salinities with neutral pH values. Such geochemical features enable us to classify these waters as fresh waters. After collection of water samples, they were acidified, filtered, and subsequently injected to the chromatographic system in triplicate.

Examples on the application of the IC procedure using an Ionpac CS5 column for measuring major

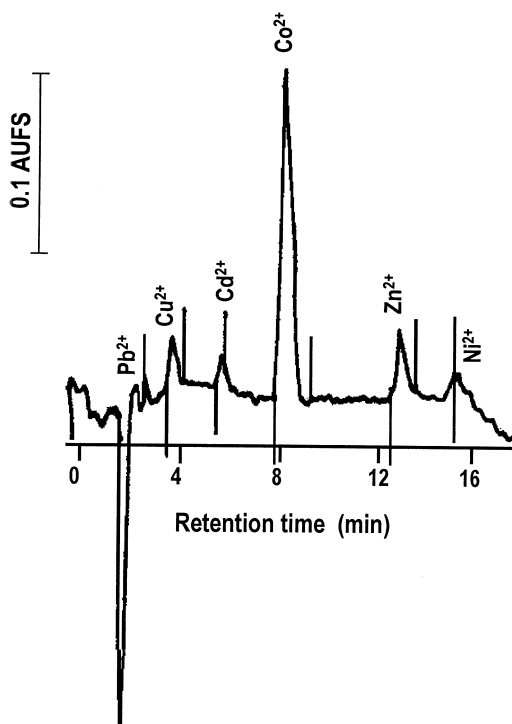


Fig. 4. Ion chromatogram of heavy metals corresponding to the IC analysis of the groundwater sample (N-25). Eluent (E): 50 mM oxalic acid–95 mM lithium hydroxide; a detector sensitivity of 0.1 AUFS and a post-column reagent of 0.2 mM PAR, 3 M ammonium hydroxide, and 1 M acetic acid. Peaks: Pb^{2+} (<1.8 $\mu\text{g/l}$), Cu^{2+} (<1.1 $\mu\text{g/l}$), Cd^{2+} (<2.7 $\mu\text{g/l}$), Co^{2+} (112 $\mu\text{g/l}$), Zn^{2+} (7.8 $\mu\text{g/l}$), and Ni^{2+} (<1.3 $\mu\text{g/l}$). For the remaining chromatographic operating conditions see Table 1.

metal ions in groundwater samples N-25 and H-2 are presented in Figs. 4 and 5, respectively. Fig. 4 shows an efficient separation of all metal ions including an acceptable sensitivity for detecting them at trace levels. In this figure, peaks of Co^{2+} and Zn^{2+} , which in fact presented the lowest detection limits, were successfully quantified by means of the corresponding calibration curves. The quantification of the remaining peaks (Pb^{2+} , Cu^{2+} , Cd^{2+} , and Ni^{2+}) was largely limited by the integration capability of the equipment software because it was possibly affected by local variations of power supply in the laboratory. In view of such a limitation, the concentrations of all these ions were reported below the individual LOD values (Table 4). An efficient separation and a much better sensitivity for all the five metal ions contained in water sample H-2 is shown in Fig. 5. Peak areas of Co^{2+} , Zn^{2+} , Cu^{2+} , and Pb^{2+} were quantified because of their high sensitivity and using their corresponding standard calibration curves, whereas the concentration of the Cd^{2+} and Ni^{2+} peaks were reported below their individual LODs. A summary of the quantification results for all groundwater samples is presented in Table 4. Standard deviation (± 1 SD)

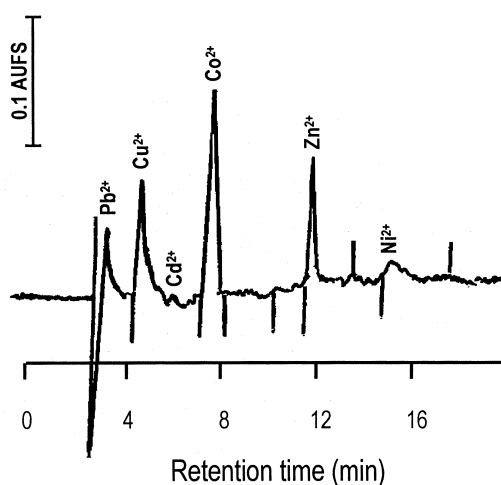


Fig. 5. Ion chromatogram of heavy metals corresponding to the IC analysis of the groundwater sample (H-2). Eluent (E): 50 mM oxalic acid–95 mM lithium hydroxide; a detector sensitivity of 0.1 AUFS and a post-column reagent of 0.2 mM PAR, 3 M ammonium hydroxide, and 1 M acetic acid. Peaks: Pb^{2+} (5.6 $\mu\text{g/l}$), Cu^{2+} (9.0 $\mu\text{g/l}$), Cd^{2+} (<2.7 $\mu\text{g/l}$), Co^{2+} (16 $\mu\text{g/l}$), Zn^{2+} (7.0 $\mu\text{g/l}$), and Ni^{2+} (<1.3 $\mu\text{g/l}$). For the rest of chromatographic operating conditions see Table 1.

values related to the triplicate analyses are also reported in the same table. Since trace amounts of some heavy metals were detected during the IC analyses, they were reported as less than the limit of detection.

3.4.1. Interferences

The low content of alkali and alkaline earth metals in the groundwater samples did not produce any interference or matrix problem. Such a chemical feature was confirmed with the low values of salinity and pH measured in the samples. However, if high concentrations of alkali and alkaline earth metals might have been detected in these samples, the excess of these interfering elements should be previously separated or removed by chemical treatments [20].

4. Conclusions

A simple and accurate IC procedure for an efficient separation and quantification of heavy metals at trace levels under isocratic eluent flow-rate conditions was reported. Three separation column systems (based on anionic, cationic, and bifunctional mixed-bed exchanges) were extensively evaluated.

The Ionpac CS5 analytical column enabled a better and efficient detection for analyzing heavy metals at trace levels in groundwater samples. The LOD's for the metal ions ranged from 0.6 to 2.7 $\mu\text{g/l}$ for the 50 mM oxalic acid–95 mM lithium hydroxide eluent and from 0.9 to 1.3 $\mu\text{g/l}$ for the 6 mM pyridine, 2,6-dicarboxylic acid eluent.

Even though the HPIC-CS2 cationic column provided satisfactory separation, it was not suitable for trace analysis of metal ions due to its high detection limits. However, its sensitivity could be improved if the eluent pH is modified by adding citric acid to the eluent mixture. Finally, the use of the HPIC-AS4 anionic column for analyzing heavy metal at trace levels was not satisfactory due to both a very poor sensitivity and the higher LODs found. In fact, this column behavior should be expected technically since it is actually recommended for detecting anions in water samples.

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