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Simultaneous analysis of some transition metals at ultra-trace level by ion-exchange chromatography with on-line preconcentration

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Abstract

The quantitative analysis of six transition metals at concentrations below 1 $\mu g\ l^{-1}$ was achieved using ion-exchange chromatography with on-line preconcentration. The metal ions are selectively retained on an iminodiacetate chelating stationary phase, then desorbed and transferred to a mixed-bed ion-exchange column for separation. Both the desorption from the concentrator column and the analysis on the separator column are made possible by the use of a complexing agent in the mobile phase, namely pyridine-2,6-dicarboxylic acid, which forms stable negatively charged complexes with the metals. The detection is spectrophotometric after addition of a post-column reagent (pyridyl-azo-resorcinol).

Optimum uptake conditions (sample pH, maximum volume of preconcentration) as well as performance of the method (dynamic range, within-laboratory precision, recovery, limit of detection) were determined. It was found that recoveries would drop below 90% for preconcentration volumes larger than 25 ml and for sample pHs lower than 2.8 or higher than 3.5. Under optimum conditions, limits of detection of some tens of ng l^{-1} were achieved with precision better than 9% at the $\mu g\ l^{-1}$ level.

The accuracy was tested with a reference Canadian river water and with bottled spring and mineral waters; the results showed good agreement with the certified values. For highly mineralized waters, the influence of major cations (Na, Ca) was studied. Limitations are given and attempts to reduce the interference with calcium are discussed.

Keywords: Complex formation; Sample preparation; Trace enrichment; Water analysis; Metal ions; Transition metals

1. Introduction

In natural surface or deep waters, transition metals often occur at ultra-trace levels; their concentration scarcely exceeds some tens of $\mu g\ l^{-1}$ and often go down below 1 $\mu g\ l^{-1}$. Ion chromatography, which is a common analytical tool for these elements, is not sensitive enough for these levels.

Preconcentration of the sample with a conventional strong acid cation-exchanger drastically lacks selectivity and major cations like alkaline and alkaline-earth metals strongly interfere [1,2]. The use of chelating stationary phases reduces these interferences [3]; laboratory-made resins, such as ethylenediamine triacetate-bonded silica [4] or chelating dye-coated substrates [5,6], can concentrate metal ions from river waters, concentrated brines or sea water.

Due to their high selectivity towards transition metals and the property of the complexes to be kinetically labile, iminodiacetate (IDA)-based resins have been widely used for trace enrichment [7–10], in conjunction with spectrometric methods of analysis. In order to eliminate the remaining interferences of complex matrices, a combination of chelation and ion chromatography was developed [11–13]. The procedure requires sample loading on a chelator column, followed by a rinsing step with 2 *M*

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ammonium acetate, to selectively elute alkali and alkaline-earth metals, subsequent transfer of the metals to a high-capacity sulfonated cation-exchange column, and elimination of the residual acidity before their injection onto the separator column, which possesses both cation- and anion-exchange sites. This last step is made possible by the use of a complexing eluent containing pyridine-2,6-dicarboxylic acid (PDCA); the metals are chromatographed as their anionic chelates $M(PDCA)_2^{2-}$ on the mixed-bed resin of the analytical column [14]. The detection is spectrophotometric after introduction, in the eluent stream, of a non-selective post-column reagent, namely pyridyl-azo-resorcinol (PAR).

Although a strong acid (0.5–1 *M*) is the recommended eluent for complete desorption of the metals from the IDA resin, some workers have suggested the use of complexing reagents to accelerate their elution under moderate acidic conditions [10,15,16] and to possibly avoid the swelling of the resin, as was often observed with the Chelex 100 resin. The retention mechanism depends on the concentration of the complexing agent in the mobile phase and on the pH, from ion-exchange at low pH and ligand content, to chelation at higher pH and ligand content. PDCA was found to be of particular interest because of the enhanced ability of its dianionic form to bind transition metals in comparison to its basicity. Concentrations as low as 0.25 m*M* are sufficient to elute Zn and Co in less than 5 min with eluent pH values from 2.5 to 4.0 [15].

This paper evaluates the feasability of an IDA chelating column as an on-line concentrator column from which direct transfer onto the analytical column is realized, using an eluent containing PDCA.

2. Experimental

PDCA was purchased from Fluka and PAR was from Merck. The metal standard solutions were prepared in a class 100 laminar flow exhaust hood by dilution of Specpure standard solutions from Johnson and Matthey (1 g l^{-1}). They were acidified with HCl to pH 3, unless stated otherwise. All other chemicals were of Suprapur grade from Merck. The water used throughout these experiments was purified with a MilliQ system (Millipore).

The filters used for the calcium precipitation experiments were of Millex-HA type, 0.45 μm pore diameter (Millipore). They were rinsed with 1% HNO_3 (3 ml) and water (10 ml) successively before use. The first 10 ml of filtrate were discarded.

The chromatographic set-up consisted of an ActIon Analyser (Waters), including an inert 625 pump driven by a 600E controller unit. A Reagent Delivery Module (RDM, Waters) was connected to the flow stream at the column outlet via a T-shaped connector; the post-column reagent was delivered by nitrogen pressure. The detection was performed with a diode-array detector (Waters 990), set at 520 nm.

The configuration of the injection was either set for direct injections, using the built-in injector (Waters 125) equipped with a 100-μl loop, or for on-line preconcentration. In the latter case, the sample was taken with a DQP-1 pump (Dionex) directly from the laminar flow exhaust hood onto the concentrator column located in the loop of an automated switching valve (9010, Rheodyne). The sampling rate was 4.4 ml min^{-1}. Back-flush was used for metal desorption by the eluent.

The separator column was a CG5 (guard) + a CS5 (analytical) set of columns (Dionex). The resin bears both quaternary ammonium and sulfonate functional groups, in a pellicular layer located on the core of the beads [17,18]. The cation- and anion-exchange capacities are 0.071 and 0.033 mequiv. per ml of resin, respectively. A MFC-1 column (Dionex) was inserted upstream from the injector for eluent purification. The concentrator column was a MetPac-CC1 column (Dionex) containing a macroporous iminodiacetate chelating resin. Its capacity is 0.45 mequiv.

The analysis of the transition metals was carried out with the following optimized mobile phase: PDCA, $6 \cdot 10^{-3}$ *M*; CH_3COOH, $5 \cdot 10^{-2}$ *M*; CH_3COONa, $5 \cdot 10^{-2}$ *M*, pH 4.5, pumped at a flow-rate of 1 ml min^{-1}. The post-column reagent was delivered at a flow-rate of 0.4 ml min^{-1}. It consisted of PAR, $4 \cdot 10^{-4}$ *M* in NH_3, 3 *M*; CH_3COOH, 1 *M* (pH 9.7).

3. Results and discussion

3.1. Adjustment of the sample pH

It is widely assumed that the optimum pH range for metal uptake by iminodiacetate resins is between

5.0 and 6.0 [7–13]. This pH range is most often incompatible with that of samples conditioned for trace cation analysis, currently acidified to pH 2, to prevent precipitation of the hydroxide complexes or adsorption on the walls of the storage container. In this case, addition of a 2 *M* ammonium acetate solution (pH 5.0–5.5) either in the sample, immediately prior to its preconcentration [8–10,13], or on-line, via a mixing tee [11,12], was proposed. The main drawbacks of such pH adjustment are (1) the risk of sample contamination when using concentrated reagents and (2) increased chelation efficiency of IDA resins for alkaline-earth metals to a maximum at pH 5 in low ionic strength solutions [19,20], which is not recommended for selective uptake of transition metals.

The effect of the sample pH on the behaviour of the transition metals using the complete system was then studied in view of lowering the optimum uptake pH range.

The sample (10 ml), containing the investigated metals at a concentration of 1 $\mu g\ l^{-1}$ each, was preconcentrated on the MetPac-CC1 column and further transferred into the eluent stream to be analysed on the CS5 column. Its pH was adjusted either with HCl or with NaOH to the desired value. The concentrator column was pre-equilibrated with the mobile phase before the first injection and no further pretreatment was done before subsequent injections. Areas and retention times were compared with those obtained from direct injections of samples containing 100 $\mu g\ l^{-1}$ of the same metals (same injected amount). Fig. 1 shows the evolution of the preconcentration recoveries of each metal as a function of the sample pH.

Ni, Zn, Co and Mn follow the same trend at low pH; their uptake falls off drastically by 80% when the pH decreases from ca. 2.8 to 2.2. Cu recovery remains steady (~90%); that of Fe(III) cannot be determined at pH 2 because of an interfering peak. In this acidic region, only Cu is quantitatively retained on the MetPac-CC1 column.

Given the composition and pH of the eluent (PDCA, acetic acid–sodium acetate buffer, pH 4.5), the MetPac-CC1 chelating resin is partly in a zwitterionic form and is partly anionic before sample injection. Due to the acid–base properties of the IDA sites, hydronium ions that occur in the sample strongly compete with metal ions for the stationary

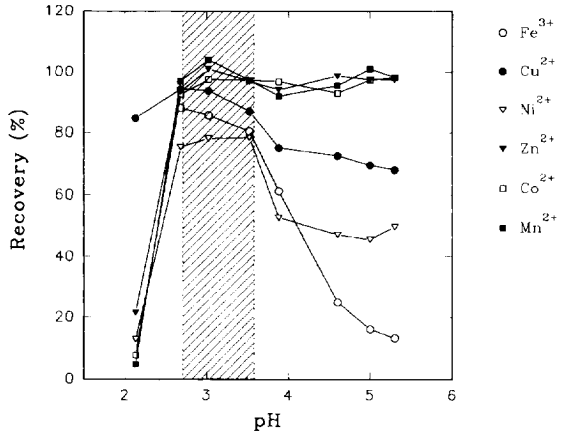

Fig. 1. Analysis of transition metals by IC with on-line preconcentration: Influence of the sample pH on metal recovery. Sample volume, 10 ml. Concentration of each metal, 1 $\mu g\ l^{-1}$.

phase and induce acidification of the IDA stationary phase. This was confirmed by subsequent analysis of the eluent of a preconcentrated sample under the same conditions. The pH increased from 2.20 (initial sample) to 2.39 (after preconcentration step), which corresponds to an H^+ uptake by the MetPac-CC1 column of 35% and represents approximatively 1% of its total capacity. Mn, Co and Zn were detected in the eluent at a concentration close to half their initial concentrations; traces of Ni and Fe were also present. All five elements were thus partially eluted from the concentrator column by the acidity of the sample matrix. This is consistent with the observed affinity of the MetPac-CC1 column towards these metals [21]:

$$Cu > Ni > Zn > Co > Mn,$$

according to the stability constant logarithms of the IDA–metal complexes [22,23]; 10.57 (Cu), 8.13 (Ni), 7.24 (Zn), 6.94 (Co) and 4.72 (Mn) ($I = 0.1$ *M*, 25°C). Fe(III) has a higher stability constant (log $K = 10.72$, $I = 0.5$ *M*, 25°C) [22] and three charges, which ensures the higher affinity of the IDA resin towards this element.

If the same experiment is conducted with a sample of initial pH 3.11, absence of metals in the eluent is observed, despite a pH increase to 4.47 in the eluent that confirms the H^+ uptake.

Direct injection of each metal on the MetPac-CC1 column confirmed the comparatively stronger preference of the IDA stationary phase for Fe(III) than for

the divalent metal ions; its retention time using the same eluent is 1.6 min while those of divalent cations are less than 0.6 min.

Some workers suggest that both complexation and ion-exchange can be involved in the retention mechanism of a metal on an iminodiacetate resin [15,16]. In the pH range 2.5–4.0, evidence for ion-exchange taking place was observed, even with partially protonated IDA moieties, but the retention behavior seems to be mainly governed by the complexing properties of IDA towards the metals, at least for the metals that form IDA complexes of higher stability (Cu, Ni). This complexing ability is attributed to the conjunction of the two carboxylic groups and the nitrogen atom.

The ability of IDA to form chelates and, consequently, the mechanism of metal retention on the IDA-based resin are strongly dependent on the pH.

At low pH values (pH<2), where the logarithm of metal–IDA conditional stability constants is low (Fig. 2), the IDA is fully protonated and electrostatic repulsion prevents the formation of the complexes.

The point of zero charge for IDA occurs at pH 2.2; IDA is in its zwitterion form, which is kinetically less reactive than any of its anionic forms. Letter and Jordan [24] found hat the carboxylate group of the zwitterion bonds first (due to the electrostatic attraction of $-COO^-$ for the positive metal ion) followed by proton loss from the amino group and final ring closure. Knowing that the bond between transition metals and oxygen is more of the ionic type while that with nitrogen is more covalent, it is assumed that ionic interactions are predominant in the formation of the complex, the protonation of the amino moiety of the IDA at such pH favouring the metal–carboxylate bond. The retention on the IDA-based resin should be governed by an ion-exchange mechanism at such a pH, if one assumes that the acid–base properties of the immobilized IDA are not significantly altered, compared to those of free IDA. The complexes are still thermodynamically very unstable at this pH (Fig. 2).

Complex stability increases with pH, due to the steric accessibility and easier formation of the tridentate chelate. For pH values higher than 2.8, all logarithms of conditional stability constants (except that of Mn–IDA) are positive. Under these conditions, the stability of metal–IDA complexes is high

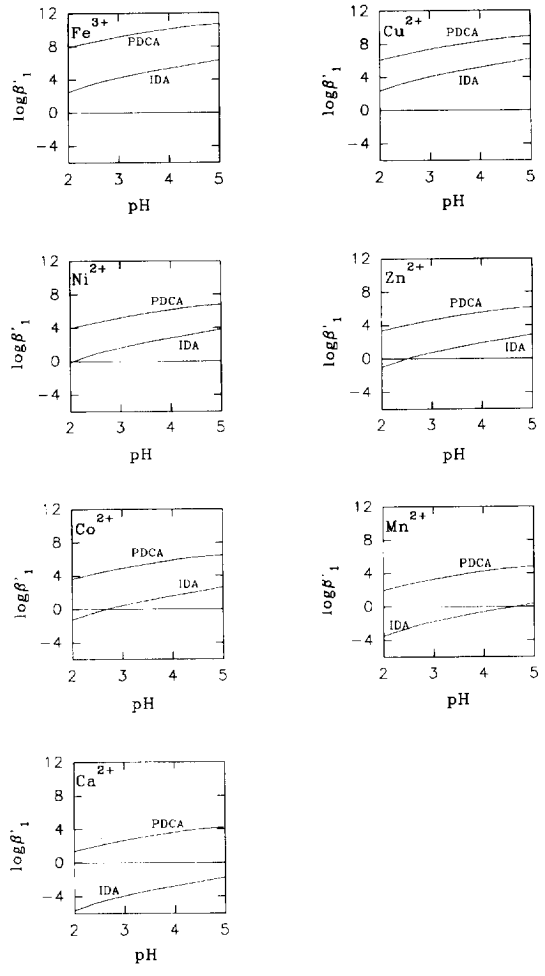

Fig. 2. pH dependence of the conditional stability constants of transition metal complexes with iminodiacetate (IDA) and pyridine-2,6-dicarboxylate (PDCA).

enough to alter the retention mechanism and favour covalent binding by chelation with the amino moiety, the covalent character being more pronounced for the last elements of the Irving-Williams series (Cu, Zn) than for the first ones (Mn). This phenomenon is delayed for Mn until pH 4.8. The complexation is rapid (the rate-determining step being possibly the ring closure to form the chelate, for discussion see [25]) and ensures reversible sorption on the IDA-based resin.

Indeed, between pH 2.8 and 3.5, all recoveries are higher than 90%, except for Ni (78%) and Fe(III) (85%). The low recovery of Ni was not due to

non-quantitative uptake during the loading phase. It may be related to slow kinetics during the desorption with the eluent phase but this hypothesis was not confirmed. Although the desorption of Fe(III) from the MetPac-CC1 column is probably quantitative at such pH, its peak shows some tailing (indicating slow kinetics) and the lower recovery of this element compared to the divalent metals was attributed to a difficult integration.

At pH values higher than 3.5, the recovery of Fe(III) drops simultaneously with the precipitation of its hydroxide; those of Cu and Ni slowly decrease while Zn, Co and Mn remain quantitatively analysed.

This decrease cannot be explained by a lower uptake recovery but, rather, by a difficult desorption from the concentrator column. Although Cu and Ni form the more stable IDA complexes (Fig. 2), the ability of PDCA to form chelates with these elements that are three to four orders of magnitude higher than that of IDA, should allow their elution from the MetPac-CC1 column during their transfer to the separator column, if only thermodynamics were to be considered. Peak broadening was observed for Ni, with an efficiency drop from 5200 (pH 3.0) to 1800 plates (pH 5.3), and, to a lesser extent, for Cu (4140 to 3840 plates, respectively), showing that the kinetics of the reaction–IDA–M + PDCA ⇒ –IDA + PDCA–M is slow.

A similar behavior was reported by Liu and Ingle [10] who observed incomplete elution of Mn, Cu and Zn from a Chelex-100 resin when using EDTA as the stripping agent.

Additional information on the adsorption–desorption mechanism of the metals can be obtained from Fig. 3, which shows the evolution of the retention times versus the pH of the sample for each investigated metal. The reference levels on the right correspond to the values obtained from direct injections on the CS5 column. At low sample pH, the elution of the metals is delayed, which confirms the protonation of the IDA sites simultaneously to the metal uptake during loading. In this case, acidification of the eluent occurs during the transfer phase, as the adsorbed H^+ are progressively replaced by the Na^+ of the eluent (by an ion-exchange mechanism). Its pH is then temporarily lowered and the PDCA, which is less dissociated, is also less efficient for both desorption from the MetPac-CC1 column and

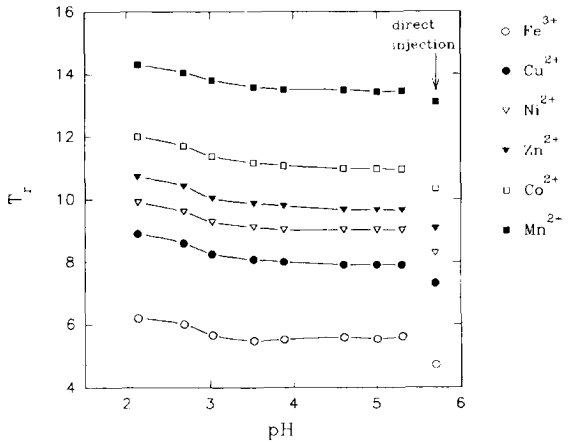

Fig. 3. Analysis of transition metals by IC with on-line preconcentration: Influence of the sample pH on the retention times. Sample volume, 10 ml. Concentration of each metal, 1 $\mu g\ l^{-1}$.

elution on the CS5 column. This phenomenon is an additional contribution to the low recovery of the transition metals at acidic pH values.

At less acidic pHs, the plateau reflects the absence of influence of the protons on the elution. The differences in retention times with direct injections on the CS5 column stand for the retention on the MetPac-CC1 column.

It can be concluded from this experiment that the best transition metal recoveries are obtained for pH≈ 3.0 with an optimum $2.8<pH<3.5$ range. Samples to be concentrated will need careful pH adjustment and control within this range.

3.2. Validation

The recovery, within-laboratory precision and limit of detection were determined for three different volumes of preconcentration; 10, 25 and 50 ml. For each transition metal, two calibration curves were established, using either the preconcentration or the direct injection mode. Recovery was derived from the slopes of the regression curves. Within-laboratory precision and limit of detection were calculated from a series of ten preconcentrated samples of a middle-range or a very low concentration, respectively. These parameters are collected in Table 1.

Fe(III), Co and Mn recoveries decrease for a preconcentration volume of 50 ml. Mn and Co,

Table 1
Characteristics of the method for 10, 25 and 50 ml preconcentration volumes

Dynamic range	Preconcentration of 10 ml 0.2–10.0 $\mu g\ l^{-1}$			Preconcentration of 25 ml 0.05–5.0 $\mu g\ l^{-1}$			Preconcentration of 50 ml 0.025–2.5 $\mu g\ l^{-1}$		
	r (%)	WLP (%)	LOD ($\mu g\ l^{-1}$)	r (%)	WLP (%)	LOD ($\mu g\ l^{-1}$)	r (%)	WLP (%)	LOD ($\mu g\ l^{-1}$)
Fe(III)	86	7.5	0.103	86	4.0	0.053	75	4.1	0.066
Cu	94	0.7	0.114	94	1.0	0.025	94	0.9	0.018
Ni	78	3.0	0.071	79	6.5	0.036	79	5.3	0.043
Zn	107	2.3	0.118	102	4.0	0.064	100	3.2	0.061
Co	97	1.1	0.060	96	1.3	0.022	85	2.0	0.012
Mn	102	4.0	0.138	103	8.6	0.042	61	9.0	0.078

r: recovery.
WLP: within-laboratory precision.
LOD: limit of detection.

towards which the chelating resin has the lowest affinities, are stripped from the MetPac-CC1 first, as the concentration volume, and thus the amount of H^+ competing for the IDA sites, increases. The recovery decrease of Fe(III) was ascribed to the increase of its peak asymmetry and width, with increasing volumes of preconcentration, indicating a difficult desorption from the IDA resin due to the temporary acidification of the eluent during the transfer phase to the separator column.

No significant improvement is observed concerning the limit of detection of these three metal ions for preconcentration volumes larger than 25 ml.

Zn and Fe(III) have a higher limit of detection than other metals, due to contaminations (Zn) and peak asymmetry [Fe(III)].

25 ml was finally chosen as the best compromise for the preconcentration volume. In this case, limits of detection are lower than 0.07 $\mu g\ l^{-1}$ for all the investigated metals.

3.3. Interferences

The effect of increasing concentrations of Na and Ca on the analysis of transition metals after on-line preconcentration was investigated. 25 ml of standard solutions of the metals of interest, spiked with the interfering cation at a given concentration, were loaded on the MetPac-CC1 column and analysed. Recoveries were deduced from the comparison of the calibration curves with those obtained by direct injection of standard solutions that were free of the interfering cation. Fig. 4 gives the evolution of the metal recovery versus the concentration of Na or Ca in the sample.

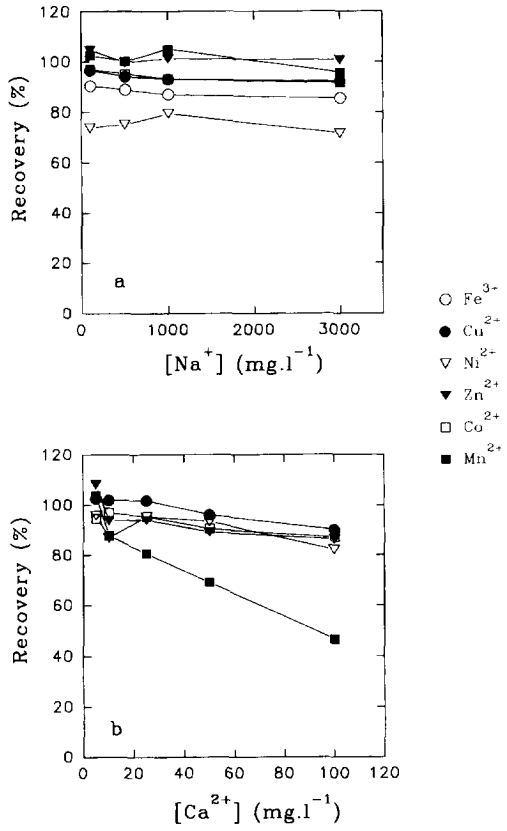

Fig. 4. Interferences: Influence of the sodium (a) or calcium (b) content in the sample on the metal uptake. Sample volume, 25 ml.

As expected, Na, for which IDA resins show very little affinity, does not induce any decrease in the metal uptake up to 3000 mg l^{-1}. Only a slight decrease of the retention time can be observed on the chromatograms at high sodium concentration.

Although IDA resins display a lower affinity for alkaline-earth metals than for transition metals, Ca gives, at the mg l^{-1} level, a detectable peak of specific shape close to that of Fe(III) (Fig. 5). For preconcentration volumes of 25 ml and a Ca concentration of 5 mg l^{-1} or higher, Fe(III) can not be quantitatively determined, due to co-elution of both species. Mn recovery remains unaffected up to Ca concentrations of 5 mg l^{-1}. The other transition metals can bear Ca contents of 100 mg l^{-1}, despite a slow decline of their recovery with increasing Ca content.

This recovery drop cannot be explained by simple saturation of the concentrator column: 25 ml of Ca (100 mg l^{-1}) corresponds to 0.125 mequiv., i.e. less than 1/3 of the total capacity of the MetPac-CC1 column. It is rather an eluting process that takes place during the loading phase. As discussed previously, Mn forms the least stable complex with IDA and, contrary to the other divalent transition metals, its mechanism of retention on the IDA resin is probably governed by ion exchange at pH 3. At this pH, Ca, for which IDA–complex formation is highly unfavoured (Fig. 2), similarly undergoes a cation-exchange process and competes more strongly with Mn than with any other metal cation involved in IDA chelates, leading to the leaching of Mn first.

As for the exchange mechanism of Ca on the analytical column, it should be noted that, under such chromatographic conditions, it is much different from that of transition metals; Ca undergoes a so-called "push–pull effect" [26–28]. While the chromatographic process of transition metals involves anion-exchange of their PDCA-chelates on the quaternary ammonium groups of the CS5 mixed-bed resin, Ca is chromatographed under its free cationic form on the sulfonate sites. Na is the competing

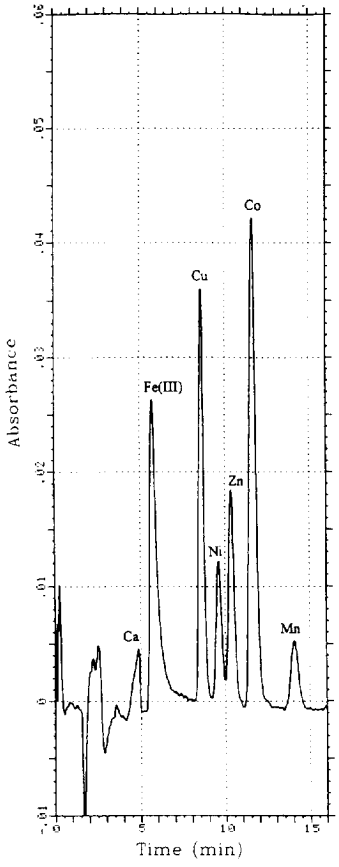

Fig. 5. Chromatogram showing the preconcentration of a standard containing 1 μg l^{-1} of each transition metal and 1 mg l^{-1} of Ca. Sample volume, 25 ml. Concentrator, MetPac-CC1. Sampling rate, 4.4 ml.min^{-1}. Separator, CG5+CS5. Mobile phase, $6 \cdot 10^{-3}$ *M* PDCA, $5 \cdot 10^{-2}$ *M* CH_3COOH, $5 \cdot 10^{-2}$ *M* CH_3COONa. Flow-rate, 1 ml min^{-1}. Post-column reagent, $4 \cdot 10^{-4}$ *M* PAR, 3 *M* NH_3, 1 *M* CH_3COOH. Flow-rate: 0.4 ml min^{-1}. Detection, $\lambda = 520$ nm.

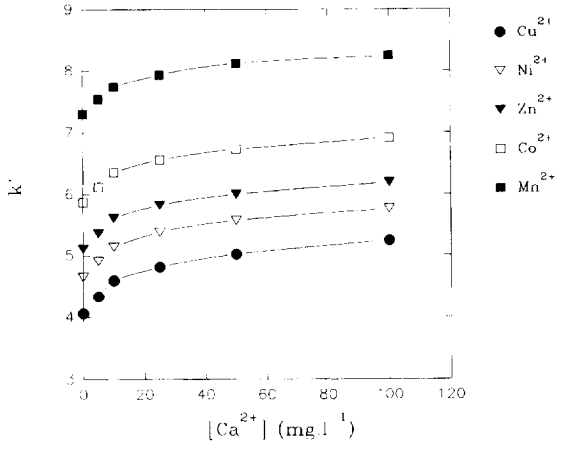

Fig. 6. Interferences: Influence of the calcium content of the sample on the retention times of the transition metals. Sample volume, 25 ml.

exchangeable cation of the eluent (pushing effect) while PDCA accelerates the elution (pulling effect), by favouring complexation in solution:

$$Ca^{2+} + PDCA^{2-} \Leftrightarrow Ca\text{–}PDCA \qquad K = 10^{5.02}$$

The observed delayed elution of the transition metals in the presence of Ca (Fig. 6) can therefore be ascribed only to the inherent decrease of the free divalent PDCA in solution during the chromatographic process on the analytical column, part of it being involved in an equilibrium with the available Ca. In a solution containing the reagents of the mobile phase used throughout these experiments and Ca, at a concentration of 100 mg l^{-1}, calculations using MINEQL software [29] show that 40% of PDCA is complexed with Ca.

Attempts to limit the interferences due to the occurrence of calcium in the samples imply that one should

— either elute the calcium retained on the IDA sites of the MetPac-CC1 column by an appropriate rinse following the loading phase

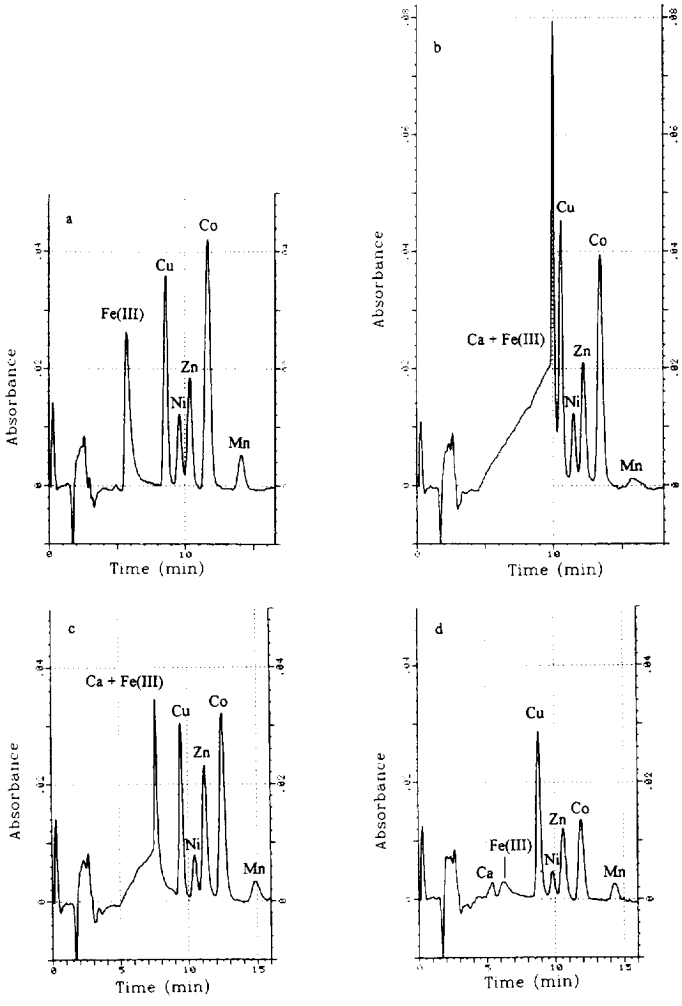

Fig. 7. Interferences: Chromatograms showing the influence of the sample treatment with sodium oxalate on the preconcentration of standards. (a) Sample, 1 $\mu g\ l^{-1}$ of each transition metal; no treatment. (b) Sample, 1 $\mu g\ l^{-1}$ of each transition metal and 1 mg l^{-1} of Ca; no treatment. (c) Sample, 1 $\mu g\ l^{-1}$ of each transition metal and 1 mg l^{-1} of Ca; addition of $2.5 \cdot 10^{-3}$ *M* $Na_2C_2O_4$ + filtration. (d) Sample, 1 $\mu g\ l^{-1}$ of each transition metal and 1 mg l^{-1} of Ca; addition of $5 \cdot 10^{-3}$ *M* $Na_2C_2O_4$ + filtration. Sample volume, 25 ml. For chromatographic conditions, see Fig. 5.

— or reduce the calcium uptake by previous addition to the sample of a ligand that selectively complexes or precipitates it.

In both cases, very high purity of the reagents is required to avoid contamination.

Some workers have successfully introduced rinse steps with 1–2 *M* ammonium acetate (pH 5.0–5.5) to remove alkali- and alkaline-earth metals from the chelator [8,9,11,13,21]. They found that, below pH 5, the transition metals were eluted by the 1 *M* ammonium acetate solution [8]. Indeed, with our configuration, a rinse with 0.3 ml of 0.4 *M* ammonium acetate, pH 5.4, induced a decrease of Fe(III), Cu, Co and Mn recoveries simultaneously to the decrease of the peak of calcium: the temporary acidification of the rinse solution by the H^+ of the resin strips off the transition metals from the column. Addition of ammonium acetate to the sample at a final concentration of 0.1–0.4 *M* prior to injection did not improve the transition metal recoveries.

Oxalate and phosphate form calcium salts of very low solubility. Addition of either of these two reagents to the sample did precipitate calcium and the filtrated samples were preconcentrated after the pH was readjusted to ca. 3. Fig. 7 compares chromatograms obtained with, or without, this special sample treatment; calcium is efficiently removed from the sample but one can observe a decrease of the analyte peaks. This is confirmed in Table 2; the recovery drops indicate that co-precipitation of the transition metals occurs and will limit the use of this method for calcium removal. Only the addition of low oxalate concentrations yield a significant increase in the recovery of Mn, without severe alteration of the other divalent transition metal uptake. Fe(III) is still not quantitatively determined with this sample treatment procedure.

Table 2
Influence of calcium precipitation from the sample on transition metal recovery. The treated samples contain 1 $\mu g\ l^{-1}$ of each transition metal and 100 mg l^{-1} of Ca. Recoveries are calculated with reference to a similar sample, free of calcium. After filtration to remove the precipitate, the pH of the filtrate is readjusted to ca. 3

Sample treatment	Recovery (%)					
	Fe(III)	Cu	Ni	Zn	Co	Mn
None		90	82	86	87	46
$Na_2C_2O_4$ $2.5\cdot10^{-3}$ *M*		83	71	cont.	75	83
$Na_2C_2O_4$ $5.0\cdot10^{-3}$ *M*		72	44	cont.	34	59
Na_2HPO_4 10^{-2} *M*	17	4	19	9	1	11

cont.: contamination assigned to the filters, despite their cleaning treatment.

Co-precipitation could be limited by introducing EDTA into the sample, prior to oxalate, in order to transform the transition metals into their stable EDTA–metal chelates. However, in this case, the limiting factor would be the ability of the IDA phase of the MetPac-CC1 column to dissociate the chelates. Flat chromatograms were obtained by preconcentration of samples containing 1 $\mu g\ l^{-1}$ (ca. $1.7\cdot10^{-8}$ *M*) of each transition metal, 50 mg l^{-1} ($1.25\cdot10^{-3}$ *M*) Ca and 10^{-5}–10^{-4} *M* EDTA, indicating that this ligand is too strong a stripping agent.

Sample treatment is therefore not recommended. Knowledge of the alkaline-earth content of the sample prior to transition metal analysis will ensure good interpretations of the results, according to the limitations given above.

3.4. Application to natural waters

The method was tested with Canadian riverine water (SLRS-3) and estuarine water (SLEW-2) reference materials for trace metals. Bottled mineral water (Volvic) and spring water (Spa) were also analysed. The reference materials were acidified on site to pH 1.6 with ultrapure HNO_3 and filtered twice before being dispatched to users. Alkali and alkaline-earth contents were not provided for SLEW-2 and were thus determined by standard suppressed conductivity ion chromatography.

Due to the high salinity of SLEW-2 (high Ca content) and the comparatively high iron concentration of SLRS-3, both water reference materials were diluted with ultrapure water and the pH was adjusted to ca. 3 with ultrapure NaOH before analysis. Volvic and Spa waters were acidified to the same final pH with ultrapure HCl.

Chromatograms are displayed in Fig. 8. The metal content, as determined by this IC method as well as certified values and confidence limits, when available, are given in Table 3. The calculated results

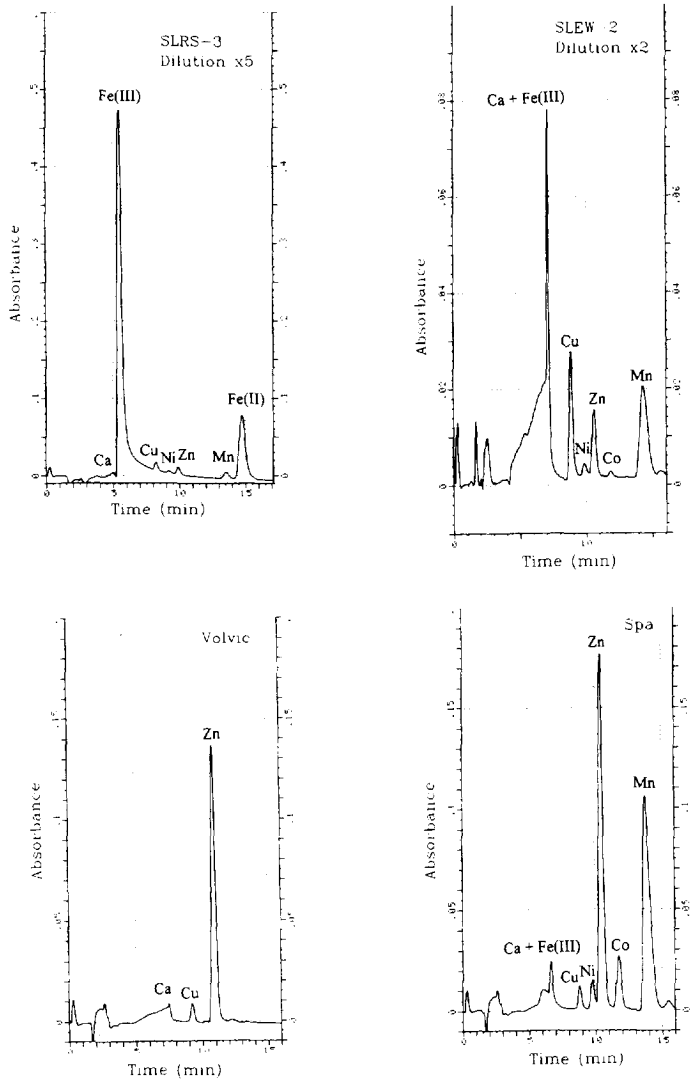

Fig. 8. Chromatograms showing the preconcentration of two Canadian water reference materials (SLRS-3 and SLEW-2, dilution factor indicated on the chromatograms) and two bottled waters (Volvic and Spa, no dilution). Sample volume, 25 ml. For chromatographic conditions, see Fig. 5.

correspond to the mean value of at least three independent injections.

As observed in Fig. 8a, iron occurs in both Fe(II) and Fe(III) oxidation states in the SLRS-3 reference material; the value for Fe content given in Table 3 corresponds to the sum of their respective contributions.

The results obtained for SLRS-3, a riverine water of low salt content, are in good agreement with the certified values, except for Ni, which seems to be underestimated. The high iron concentration did not interfere with the determination of the other transition metals.

As for SLEW-2, the high calcium concentration did not allow the quantitative analysis of Fe(III). Significantly higher Mn concentrations were obtained for greater dilutions of the sample, showing that Mn uptake was not quantitative under these conditions of preconcentration. This phenomenon, which is consistent with the already discussed in-

Table 3
Analysis of reference materials and comparison with the certified values; application to natural mineral and spring waters

	Fe ($\mu g\,l^{-1}$)	Cu ($\mu g\,l^{-1}$)	Ni ($\mu g\,l^{-1}$)	Zn ($\mu g\,l^{-1}$)	Co ($\mu g\,l^{-1}$)	Mn ($\mu g\,l^{-1}$)	Na ($mg\,l^{-1}$)	K ($mg\,l^{-1}$)	Ca ($mg\,l^{-1}$)	Mg ($mg\,l^{-1}$)
SLRS-3	97±4	1.33±0.04	0.47±0.30	1.11±0.42	LOD	3.38±0.40				
	100±2	*1.35±0.07*	*0.83±0.08*	*1.04±0.09*	*0.027±0.003*	*3.9±0.3*	*2.3±0.2*	*0.7±0.1*	*6.0±0.4*	*1.6±0.2*
SLEW-2	n.d.	1.53±0.08	0.54±0.25	1.28±0.08	n.d.	n.d.	3300	140	156	430
	2.37±0.37	*1.62±0.11*	*0.709±0.054*	*1.10±0.14*	*0.055±0.008*	*17.1±1.1*	n.a.	n.a.	n.a.	n.a.
Volvic	n.d.	0.23±0.10	LOD	9.03±0.73	LOD	LOD				
	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	*9.4*	*5.7*	*9.9*	*6.1*
Spa	0.28±0.19	0.33±0.08	1.32±0.42	11.50±0.25	0.58±0.04	23.56±0.54				
	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	*3.0*	*0.5*	*3.5*	*1.3*

LOD: Limit of detection; n.d.: not determined; n.a.: not available. Certified values in italics.

fluence of major cations, made it impossible to estimate Mn concentration in this water. The other transition metals were satisfactorily analysed.

The cobalt concentration of both water reference materials was very low, and dropped below the limit of detection when the samples were diluted for analysis.

4. Conclusion

A method derived from ion chromatography with on-line preconcentration on a chelating resin was evaluated for the quantitative analysis of traces of transition metals in natural waters. Limits of optimum conditions for metal recovery were determined. The sample pH needs particular control between pHs 2.8 and 3.5, to ensure that quantitative uptake of the metals by the concentrator column and their quantitative desorption occurs; lower pH values induce only partial uptake of the metals due to the strong competition of the hydronium ions for the IDA resin, while higher pH values lead to slower kinetics of desorption from the concentrator column. This method proved to be of particular interest for waters of low ionic strength and was successfully tested with a riverine water reference material; waters of higher salinity can also be analysed, but interferences do occur: Fe(III) co-elutes with calcium and divalent metals with low affinity for the chelator, like manganese, are not quantitatively retained under such conditions. The recovery of the other transition metals is only slightly decreased (to ca. 85%) up to a calcium concentration of 100 mg l^{-1}.

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