

Separation and determination of trace metals in concentrated salt solutions using chelation ion chromatography

O.J. Challenger, S.J. Hill and P. Jones*

Department of Environmental Sciences, University of Plymouth, Drake Circus, Plymouth PL4 8AA (UK)

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ABSTRACT

A high-performance ion chromatography system using chelating dye coated columns for the determination of trace metals in high-ionic-strength media is described. All the preconcentration and separation studies of metal ions were carried out using a single chelating column. Spectrophotometric detection using 4-(2-pyridylazo)resorcinol and Pyrocatechol Violet post-column reagent was employed to investigate divalent and trivalent metal ions. A number of metal ion determinations in 1 M laboratory salt solutions, concentrated brines and sea waters were achieved under isocratic and step gradient elution conditions, where up to nine metal ions could be separated in a single injection. Standard addition was used for calibration and good linearity was obtained in the low $\mu\text{g l}^{-1}$ range.

INTRODUCTION

Present ion chromatography techniques for the determination of trace metals work well if the sample is relatively low in ionic strength. If the ionic strength is too high, the salt ions may "swamp" the ion-exchange sites, seriously affecting any separation. Thus, direct analysis of important samples such as concentrated brines and sea waters is extremely difficult by conventional ion chromatography. This problem can be overcome by using chelating exchange groups instead of ion exchange groups on the stationary phase substrate. Metal ion separations will then be dependent on the conditional stability constants of each metal chelate, and are much less affected by the ionic strength of the sample.

Chelating resins have been used for some time for preconcentration of metal ions. One of the first to demonstrate this for preconcentrating

trace metals from sea waters were Riley and Taylor in 1968 [1]. They used Chelex 100 which contains covalently bonded chelating groups to the surface of the substrate. Since then, many chelating groups have been synthesized beforehand and covalently bonded to the substrate. However, they have predominantly been used for matrix elimination and preconcentration before determination by another technique. Siriraks *et al.* [2] used a chelating column for trace metal preconcentration in trace elemental analysis in various environmental and biological samples before separation by conventional ion chromatography, but the ion chromatography system used was rather complex. Fritz *et al.* [3] prepared a number of chemically bonded chelating substrates and demonstrated their use for separation of trace metals, however efficiency was low. Toei [4] has used a covalently bonded chelating column employing iminodiacetic acid functional groups for the analytical separation of magnesium and calcium in sea water with high efficiency. A recent review highlights many

* Corresponding author.

bonded chelating polymers suitable for trace metal separation and preconcentration of environmental samples [5].

An alternative approach to chemical bonding is to coat the substrate with a chelating dye. This avoids the need to synthesise and bond the chelating group onto the substrate, which can be a very time-consuming and difficult procedure. Most chelation exchange coatings have been on anion exchange resins with very few on neutral resins as shown in a review of this area by Marina *et al.* [6]. Again the majority of these coated resins have been used for preconcentration and matrix elimination. For example, recently a Xylenol Orange column coated onto Dowex 1-X8 anion-exchange resin has been used as a preconcentration column as part of an automated HPLC system for trace metal determinations in concentrated brines [7]. However, little work has been carried out using coated chelating columns to investigate trace metal separations on high performance grade substrates. Jones and Schwedt [8] investigated a dyestuff-coated HPLC resin for chelation exchange separation of metal ions. Although a range of chelating dyes were initially examined for their depth of coating and chemical stability, Chrome Azurol S was chosen for further study and coated onto a neutral Benson BPI-10 resin. Separations of divalent and trivalent metals in 1 M potassium nitrate was achieved, though the efficiency was relatively low.

Recently, we have reported [9] a more detailed investigation into dyestuff-coated columns using a range of chelating dyes coated onto a number of resins of varying particle size. The chelating performance was found to vary markedly depending on the type of substrate and chelating dye employed. Xylenol Orange was then chosen to coat onto a neutral small-particle-size HPLC-grade resin, and a separation of all four alkaline earth metals in 1 M potassium nitrate was achieved. Further work using these columns enabled separations of other divalent metals, and separations from high concentrations of alkaline earth metals using gradient elution [10].

This paper reports on further developments in combined preconcentration and high-perform-

ance separations of trace metals in various high-ionic-strength matrices, using a single dye-coated HPLC grade chelation exchange column. The application of this column for the determination of trace metals in concentrated brines and sea waters is also reported.

EXPERIMENTAL

Instrumentation

The chelation ion chromatography post-column reaction system employed is shown in Fig. 1. Two injection valves were used to enable either preconcentration or a direct injection onto the column.

The instrumentation used consisted of two ConstaMetric Model III pumps (Laboratory Data Control, Riviera Beach, FL, USA) for the eluent and post-column reagent. Injector 1 was a stainless-steel injector with 100- μ l sample loop (Rheodyne, Cotati, CA, USA) and used for direct injections. The preconcentration system was composed of entirely inert materials which comprised an Eldex Labs. (Menlo Park, CA, USA) Model AA pump with PTFE-lined pump heads and check valves, and titanium injector (number 2) (Valco, Schenkon, Switzerland). All connecting tubing and junctions were composed of PTFE. The UV-visible detector was a Spectroflow Monitor SF770 (Schoeffel, Westwood, NJ, USA).

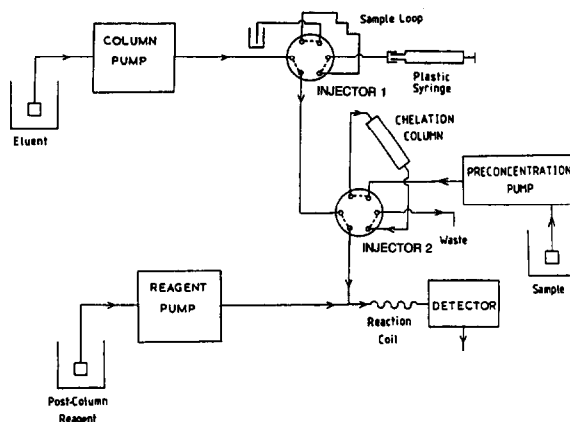


Fig. 1. Chelation ion chromatography post-column reaction system.

Chelating columns

Two dye-coated columns were investigated. These were Xylenol Orange (5,5'-bis-NN-bis(carboxymethyl)aminomethyl-4'-hydroxy-3,3'-dimethylfuchstone-2''-sulphonic acid (tetrasodium salt)] (BDH, Poole, UK), and Chrome Azurol S [2'',6''-Dichloro-4'-hydroxy-3,3'-dimethyl-3''-sulphofuchstone-5,5-dicarboxylic acid (Trisodium salt), (Sigma, St. Louis, MO, USA) coated onto 8 μm , 100 Å polystyrene-divinylbenzene neutral PLRP-S resin (Polymer Labs., Church Stretton, UK). These columns were 10 cm \times 4.6 mm I.D., metal free and inert, being made of poly ether ether ketone (PEEK), (Alltech, Carnforth, UK). These columns were coated by pumping a 0.2% solution of the dye through a packed PLRP-S column.

Materials

All chemicals were obtained from BDH except 4-(2-pyridylazo)resorcinol (PAR), ZnEDTA and sodium sulphate which were obtained from Fluka (Buchs, Switzerland). Metal stock solutions were Spectrosol atomic absorption standards obtained from BDH. All reagents and working standards were prepared using distilled deionized water obtained from a Milli-Q system (Millipore, Bedford, MA, USA).

To reduce the levels of metal impurities, the eluents and buffers were pumped through a Xylenol Orange coated XAD-2 (BDH) chelating column (10 cm \times 4.6 mm I.D.). This off-line clean up process considerably reduced levels of metal ions which are likely to build up on the analytical column during preconcentration and step gradient elution processes.

Eluents and post-column reagents

Divalent metal ion determinations. The eluent used in all cases was 1 M potassium nitrate containing 0.05 M lactic acid, adjusted to the appropriate pH with dilute nitric acid or dilute ammonia. The post-column reagent employed was $1.2 \cdot 10^{-4}$ M PAR– $2 \cdot 10^{-4}$ M ZnEDTA in 2 M ammonia for all samples except sea water where $1.2 \cdot 10^{-4}$ M PAR in 2 M ammonia without the ZnEDTA was used. Absorbance was monitored at 490 nm.

Trivalent metal ion determinations. The eluent used here was 1 M potassium nitrate, and the post-column reagent employed was 0.004% Pyrocatechol Violet in 0.5 M hexamine adjusted to pH 6. Absorbance was monitored at 580 nm.

Samples and sample treatment

Samples. Sodium chloride and potassium chloride brines were obtained from ICI Chemicals and Polymers, Runcorn, UK. The sea water sample was obtained from Plymouth Sound. Laboratory chemicals were made up as 1 M solutions. A pH meter was used to monitor all pH adjustments as detailed below. Blank determinations showed negligible contamination from the small volumes of acid or alkali used to adjust the pH.

Sample analysis

Direct injection. The pH of the sample was adjusted to the same pH as the eluent using dilute nitric acid or dilute ammonia before injection. A 100- μl volume of sample was then injected using injector 1.

Preconcentration. The sample was adjusted to an appropriate pH using dilute nitric acid or dilute ammonia, depending on the metals of interest. Before preconcentration it was necessary to equilibrate the column to the same pH as the sample by pumping 10 ml of the appropriate buffer (0.1 M borate for pH 10 or pH 11, and 0.1 M hexamine for pH 6). This was followed by 10 ml of the sample, and finally 3 ml of distilled deionized water. This was all carried out with the potassium nitrate eluent bypassing the column as shown in Fig. 1. The gradient program was initiated by switching the titanium injector to allow the potassium nitrate eluent to pass through the preconcentration column. The pH of the 1 M potassium nitrate eluent was then changed in a series of steps at specified times as described in the Results and Discussion section.

RESULTS AND DISCUSSION

The stability of the columns after coating proved to be very good. There was an initial bleed of the dye during the cleaning process directly after coating the column, but only a

large sudden change in ionic strength would produce any further slight bleeding of the dye. To illustrate the different chelating strengths of the two dyes, the pH required to completely retain various metal ions on small particle size coated columns was investigated. Initial studies showed that these two columns were distinctly different (Table I), the Chrome Azurol S showing much weaker chelation than Xylenol Orange, not retaining alkaline earth metals until pH 11 or above.

Since pH is a major controlling factor on chelating strength, various groups of metal ions can be selectively eluted in the order of increasing stability constants. However, under isocratic conditions the peaks become quite broad after a relatively short time and therefore only three or four metal species can reasonably be determined this way. To separate a greater number of metals a pH gradient is necessary. Peak compression occurs and even the last eluting peaks are relatively sharp. We found that step gradients gave better results than a continuous gradient, though in some cases this caused steps in the chromatogram baseline. An example of a nine metal separation on a Xylenol Orange coated column using three step gradients is shown in Fig. 2. The metal mixture was directly injected at pH 10

TABLE I

MINIMUM pH REQUIRED FOR COMPLETE RETENTION OF 5 mg l⁻¹ METAL STANDARDS (10 mg l⁻¹ FOR BARIUM), ON SMALL-PARTICLE-SIZE DYE-COATED COLUMNS, USING 1 M POTASSIUM NITRATE MOBILE PHASE

Standard	Xylenol Orange-coated PLRP-S	Chrome Azurol S-coated PLRP-S
Ba ²⁺	10	>11
Mg ²⁺	9	11
Sr ²⁺	9	>11
Ca ²⁺	8	>11
Mn ²⁺	6	8
Co ²⁺	4	7
Zn ²⁺	4	7
Cd ²⁺	5	7
Pb ²⁺	4	6
Ni ²⁺	3	6
Cu ²⁺	2	5

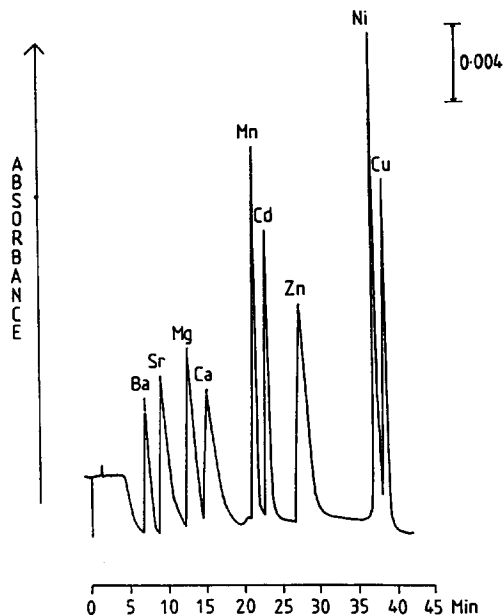


Fig. 2. Chromatogram showing separation of nine metals on a Xylenol Orange-coated PLRP-S dye-coated column, using three step gradients. Sample conditions were direct injection of 100 μ l of 1 M KNO₃ containing 0.05 M lactic acid adjusted to pH 10, spiked with the following concentrations of metal ions: 5 mg l⁻¹ Mg²⁺, Ca²⁺, Mn²⁺, Ni²⁺, Cu²⁺, 10 mg l⁻¹ Cd²⁺ and Zn²⁺, and 20 mg l⁻¹ Ba²⁺ and Sr²⁺.

where every metal would be retained on the column. By stepping the eluent to pH 6.5 the alkaline earth metals were eluted, then a change to pH 3 after 15 min eluted manganese, cadmium and zinc, and a final step to pH 0.5 after 30 min to elute nickel and copper which form the strongest chelates.

Preconcentration and separation of trace metals

As described above, many metal ions can be separated in a single injection using pH step gradients. However, in order to investigate samples containing metals at low parts per billion levels, a preconcentration step was needed prior to the analytical separation. In the following work the preconcentration and separation is carried out on the same column. Because of the much lower concentration of metals, it is important that the preconcentration system is composed of inert materials as described in the Experimental section. No observable contamination was found from the steel pumps pumping 1

M potassium nitrate eluent, even in acidic media. However, the major contamination occurred with impurities in the potassium nitrate itself and the buffer solutions. This necessitated clean-up with a Xylenol Orange-coated XAD-2 column as described in the Experimental. In all cases blank runs were carried out using the same step gradient program, but omitting the sample. All quantitative data was blank corrected if necessary.

Concentrated brines

Actual industrial samples of concentrated sodium and potassium chloride brines used in the chloralkali industry, obtained from ICI, were analyzed for trace metal content using the Xylenol Orange column. The actual concentrations of these samples determined by titration was 2.4 M for KCl and 5.1 M for NaCl brine.

Fig. 3 shows a typical separation of alkaline earth metals in KCl brine, using a single-step gradient from pH 11 to pH 6. Some degree of selectivity is possible by changing the starting pH of the gradient. Thus, by starting at a lower pH the separation of some transition metals is possible while the alkaline earth metals pass straight

through on the solvent front. A calibration series for alkaline earth and some transition metals in KCl brine was carried out by the method of standard addition. Good linear results were obtained with the correlation coefficient, r , ranging from 0.991 to 0.999.

If the full range of metal species need to be studied in a single determination then a more complex step gradient programme can be used. The chromatogram in Fig. 4 shows the separation of nine metals in 2.4 M KCl brine achieved with a three-step gradient. A step gradient from pH 10 to pH 6 eluted the alkaline earth metals, followed by a step to pH 3 after 7 min to elute manganese, cadmium and zinc, then a final step to pH 0.7 after 15 min to elute nickel and copper.

A calibration series for alkaline earth metals in saturated NaCl brine (5.1 M) was also carried out and the results compared to those obtained for KCl brine (Table II). It can be seen that the KCl brine contains higher levels of calcium, but the NaCl brine as expected, contains much higher levels of strontium, due to the high levels naturally occurring in rock salt. For comparison a separation of alkaline earth metals in a NaCl brine sample using the same step gradient as KCl, is shown in Fig. 5.

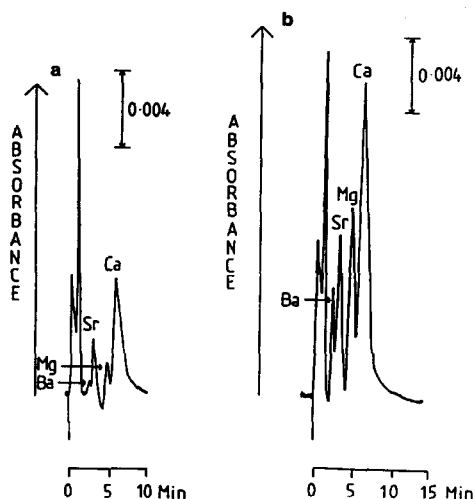


Fig. 3. Chromatograms showing pre-concentration and separation of alkaline earth metals in KCl brine using the Xylenol Orange coated column. (a) KCl brine sample, (b) KCl brine spiked with $25 \mu\text{g l}^{-1} \text{Mg}^{2+}$, $50 \mu\text{g l}^{-1} \text{Ca}^{2+}$, Sr^{2+} and Ba^{2+} . Sample volumes were 10 ml adjusted to pH 11.

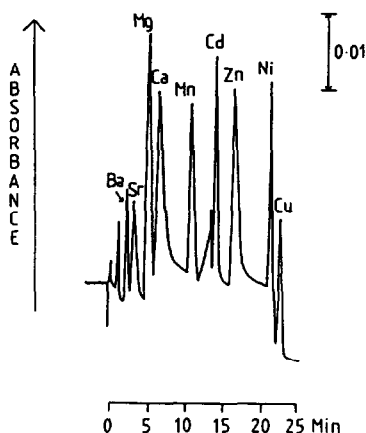


Fig. 4. Chromatogram showing pre-concentration and separation of nine metal ions in 2.4 M KCl brine using the Xylenol Orange-coated column with a three-step gradient. Spiked metal concentrations were $50 \mu\text{g l}^{-1} \text{Mg}^{2+}$, Ca^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and $0.1 \text{mg l}^{-1} \text{Sr}^{2+}$, Ba^{2+} , Mn^{2+} and Cd^{2+} . Sample volume was 10 ml adjusted to pH 10.

TABLE II
CONCENTRATION OF TRACE METALS IN KCl AND NaCl BRINES

ND = Not determined. Reproducibilities were determined on samples spiked at the midpoint of each calibration range. The relative standard deviations on six replicates all ranged between 2 and 5%.

	Concentration ($\mu\text{g l}^{-1}$)		Approx. detection limit ^a
	NaCl	KCl	
Mg ²⁺	3	1	0.5
Ca ²⁺	6	18	2
Sr ²⁺	95	28	4
Ba ²⁺	9	3	2
Mn ²⁺	ND	8	0.5
Zn ²⁺	ND	17	1
Ni ²⁺	ND	4	2
Cu ²⁺	ND	<1	1

^a Detection limits are for a 10-ml preconcentration volume and for 2 \times baseline noise level.

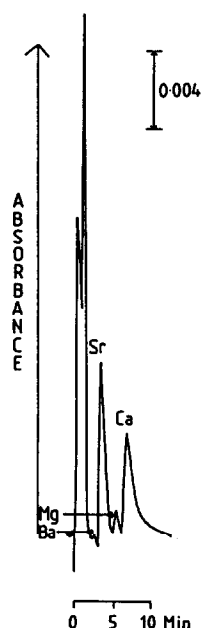


Fig. 5. Chromatogram showing preconcentration and separation of alkaline earth metals in a saturated (5.1 M) NaCl brine sample using the Xylenol Orange-coated column. Sample volume was 10 ml adjusted to pH 11.

Impurities in laboratory chemicals

The successful use of these columns in the determination of trace metals in concentrated brines encouraged further work with other matrices. One such area is the investigation of trace metal impurity levels in laboratory reagents. Three laboratory chemicals were selected, these were potassium nitrate, sodium sulphate and caesium iodide. These were made up as 1 M solutions for analysis. Using a step gradient from pH 6 to pH 3.7, then pH 2 after 1 min and pH 0.7 after 6 min, six metal species could be separated, namely manganese, cadmium, zinc, lead, nickel and copper. A typical example of the separation achieved by this gradient programme on a spiked sample is shown in Fig. 6 and Fig. 7 shows the actual trace metal impurity profiles obtained for the three laboratory chemicals. It can be seen that the potassium nitrate used as our eluent contains relatively high levels of zinc, and shows the necessity for clean-up of this reagent as described in the experimental section. There were some problems in quantifying copper in caesium iodide, probably due to

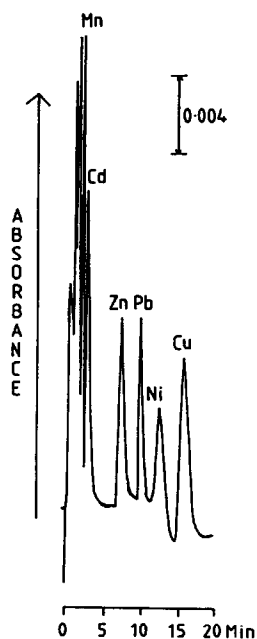


Fig. 6. Chromatogram showing preconcentration and separation of trace metals in 1 M Na₂SO₄ sample spiked with 10 $\mu\text{g l}^{-1}$ Mn²⁺, 25 $\mu\text{g l}^{-1}$ Zn²⁺ and 0.1 mg l⁻¹ Cd²⁺, Pb²⁺, Ni²⁺ and Cu²⁺. Sample volume was 10 ml adjusted to pH 6.

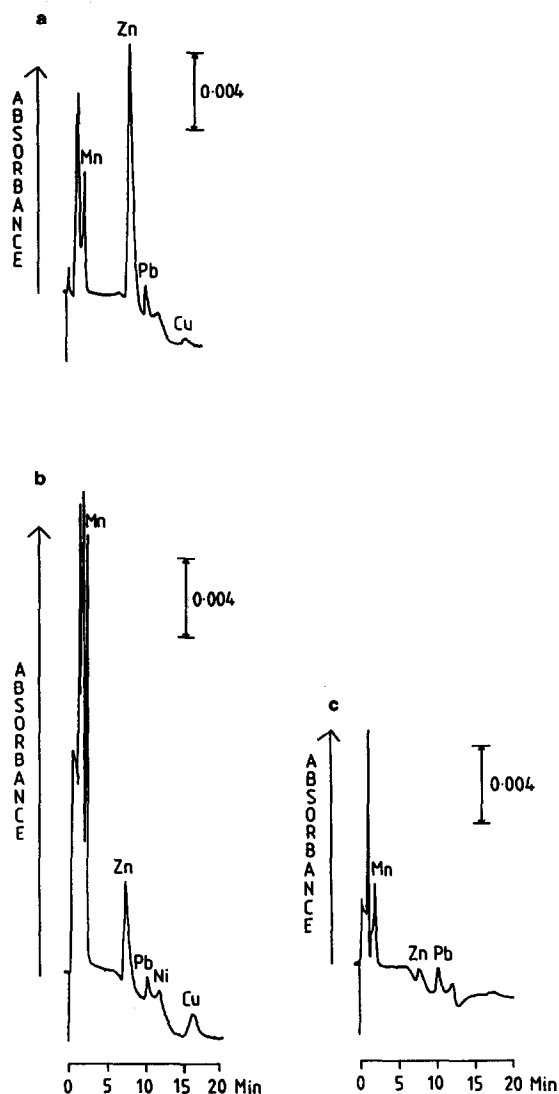


Fig. 7. Chromatograms showing preconcentration and separation of trace metal ions in laboratory chemical samples using the Xylenol Orange-coated column. (a) 1 M KNO_3 sample, (b) 1 M Na_2SO_4 sample and (c) 1 M CsI sample. Sample volumes were 10 ml adjusted to pH 6.

interference of iodide which is known to reduce Cu^{2+} to Cu^+ . Approximate impurity levels in all three chemicals are shown in Table III.

Analysis of trace metals in sea waters

The Chrome Azurol S-coated column although more suitable for sea waters because of its weak affinity for calcium and magnesium, was not as efficient as the Xylenol Orange-coated column

TABLE III

APPROXIMATE IMPURITY LEVELS IN THREE LABORATORY CHEMICALS

X = Not quantified (see text).

	Concentration ($\mu\text{g l}^{-1}$)		
	1 M KNO_3	1 M Na_2SO_4	1 M CsI
Mn^{2+}	5	28	4
Cd^{2+}	—	—	—
Zn^{2+}	60	21	2
Pb^{2+}	10	10	15
Ni^{2+}	—	5	—
Cu^{2+}	3	12	X

and could not separate all of the metals investigated. However, it was still possible to use the Xylenol Orange-coated column by adjusting the sea water to pH 6 when most of the magnesium and calcium present will not be retained. Also by using PAR alone, which does not react well with alkaline earth metals, as the post-column reagent, the magnesium/calcium peak can be further reduced.

Sea water from Plymouth Sound, filtered before use to remove particulate matter, was investigated for traces of cadmium, zinc, lead, nickel and copper. This separation was achieved with a step gradient from pH 6 to pH 3.7, then to pH 2 after 5 min and pH 0.7 after 10 min. Fig. 8a shows Plymouth Sound sea water, whilst Fig. 8b shows a spiked sample. A large peak due to magnesium and calcium still occurs at the solvent front as PAR does react slightly with these ions [11]. Zinc and copper were shown to be present at $1 \mu\text{g l}^{-1}$ and $3 \mu\text{g l}^{-1}$, respectively, with a slight hint that lead may be present in the sea water. Higher preconcentration volumes will be needed to quantify this. The level of copper present is significantly higher than would normally be expected as several rivers feeding into Plymouth Sound are enriched with copper due to the local geology.

Trivalent metal ion separation

The work so far demonstrates the suitability of the chelation chromatography approach for the determination of divalent metal ions. However,

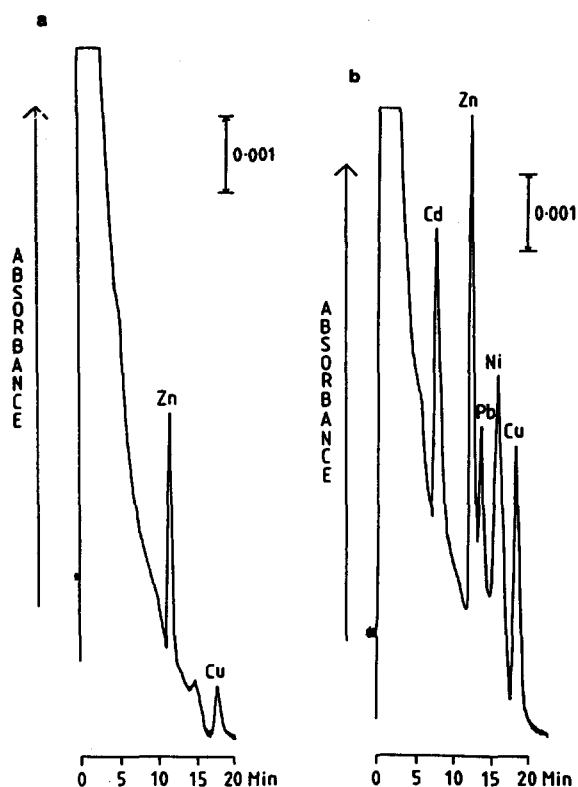


Fig. 8. Chromatograms of trace metals in Plymouth Sound sea water preconcentrated and separated using the Xylenol Orange-coated column. (a) Plymouth Sound sea water showing Zn^{2+} ($1 \mu g l^{-1}$) and Cu^{2+} ($3 \mu g l^{-1}$) present in the sample, (b) Plymouth Sound sea water spiked with $5 \mu g l^{-1}$ Zn^{2+} , $20 \mu g l^{-1}$ Cu^{2+} and $50 \mu g l^{-1}$ Cd^{2+} , Pb^{2+} and Ni^{2+} . Sample volumes were 10 ml adjusted to pH 6.

trivalent metal ions in general form much stronger chelates than divalent metal ions. The Xylenol Orange-coated column would require much more acidic eluents for desorption, therefore it was decided to investigate these ions using the weaker chelating Chrome Azurol S column.

Fig. 9 shows an isocratic separation of aluminium, gallium and indium in 1 M potassium nitrate achieved at pH 2.2. Because the exchange kinetics are slow, the column was operated at an elevated temperature of 60°C. The separation profile is similar to previous work [8], but the elution order is different, gallium eluting before indium. Further studies are underway including other trivalent metal ions such as iron and bismuth.

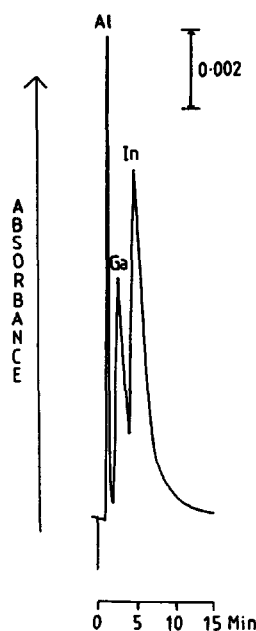


Fig. 9. Chromatogram showing isocratic separation of $2 mg l^{-1}$ Al^{3+} , $10 mg l^{-1}$ Ga^{3+} and $20 mg l^{-1}$ In^{3+} in 1 M KNO_3 , at pH 2.2, using the Chrome Azurol S-coated column at 60°C. Direct injection of 100 μl sample.

CONCLUSIONS

This work shows that chelation ion chromatography using dye-coated columns shows clear potential for the determination of trace metals in high-ionic-strength media. They give high efficiencies and can be used to separate selective groups of metal ions, or a larger range using a series of step gradients.

Combined preconcentration and separation of trace metals in various high-ionic-strength media including concentrated brines, sea waters and laboratory chemicals can be achieved using a single chelating column. A separation of nine metal ions in 1 M potassium nitrate and concentrated KCl brine has also been successfully achieved.

These chelating dye-coated columns are much easier to prepare than chemically bonded chelating columns, and so far the Xylenol Orange-coated column has proved to be very stable, having been used for over 1.5 years without any apparent loss of efficiency.

Chelation ion chromatography can only de-

velop further in the future as a relatively simple and inexpensive method of directly determining trace metals in various high-ionic-strength media.

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