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## Preconcentration of divalent trace metals on chelating silicas followed by on-line ion chromatography

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### ABSTRACT

A novel method for the on-line preconcentration and chromatography of trace metals, *e.g.*, Mn, Co, Ni, Cu, Zn, Cd and Pb, on ethylenediamine triacetate-bonded silica is described. The preconcentrated metals were desorbed with 0.1 M nitric acid. Post-precolumn modification of the eluent was done by means of a tee mixer and a second high-performance liquid chromatographic pump. The modified eluent, consisting of tartaric acid and sodium nitrate, allows the separation of metals on a cation-exchange chromatographic column. The metals separated were detected by postcolumn reaction with 4-(2-pyridylazo)-resorcinol and measuring absorbances at 500 nm. Linear calibration graphs were obtained over the range  $3 \cdot 10^{-9}$ – $3 \cdot 10^{-6}$  M. The characteristics of this chelating silica are given and the on-line and off-line preconcentration methods were compared. Application of the method to the analysis of river water is described. The results show that the method is applicable to the determination of Co, Ni, Cu, Zn, Cd and Pb ions. It was also demonstrated that the method can be used for the determination of free metal ions and labile or moderately labile complexes.

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### INTRODUCTION

The determination of trace metal ions (concentrations less than  $10^{-7}$  M) in natural waters by ion chromatography requires a preconcentration step. The large amounts of alkali and alkaline earth metals present in such samples have to be eliminated prior to metal separation to avoid interference effects. Elimination of these cations and concentration of trace metal ions may be achieved in a single step by using chelating silicas. On-line chromatography following preconcentration would be preferable as it would minimize contamination risks and at the same time allow the attainment of high concentration factors. In a previous paper [1], on-line preconcentration of trace metals on 8-quinolinol-silica followed by ion chromatographic separation was described. Potassium cyanide solution (0.1 M) was used to desorb metals and separation by ion pairing was achieved using tetrabutylammonium ions. The disadvantages of this method are that it is restricted to the determination of Cu(II) and Ni(II) ions and it necessitates the use of a diode-array detector because the cyano complexes of these two metals do not absorb at the same wavelength.

In this work, the use of ethylenediamine triacetate (ED3A) bonded chelating silica for the preconcentration of trace metal ions, *e.g.*, Mn(II), Co(II), Ni(II), Cu(II),

Zn(II), Cd(II) and Pb(II), was evaluated. Ohshima *et al.* [2] prepared and characterized this type of silica for the preconcentration of trace elements in sea water. As desorption of metals in acidic media is not suitable for classical cation-exchange chromatography, a neutralization system incorporating a second high-performance liquid chromatographic (HPLC) pump and a tee mixer was developed. On-line and off-line preconcentration on a Vac-Elut system were compared. Finally, the applicability of ED3A-bonded silica to the preconcentration of trace metal ions in river water is discussed.

## EXPERIMENTAL

### Apparatus

*On-line chromatography.* The chromatographic equipment (Fig. 1) consisted of a Knauer metal-free electric valve, a Knauer 64 titanium pump for delivering 0.1 M nitric acid, a Knauer 64 pump with a stainless-steel microhead for neutralizing and delivering the eluent, a laboratory-made stainless-steel membrane pulse damper and a Dionex QIC preconcentration pump. Laboratory-made titanium precolumns (13 × 1.7 and 50 × 2 mm I.D.) were packed manually with ED3A-silica. The silica was placed in the precolumn with a microspatula and the precolumn was tapped to ensure that the solid was well packed. A Macherey, Nagel & Co. analytical column (30 cm × 4 mm I.D.) was packed with Nucleosil 10SA silica. Except for two Knauer tee pieces, plastic tubing was used. Postcolumn reagent was pumped under nitrogen pressure (4.5 atm) and to ensure 4-(2-pyridylazo)-resorcinol (PAR)-metal complexation a PTFE coil (3 m × 0.5 mm I.D.) was used. A Hewlett-Packard 1040 A diode-array UV-visible detector was used for detection of metal complexes.

*Off-line chromatography.* Preconcentration was achieved by using a modified metal-free Vac-Elut SPS 24 apparatus. Syringes (9 mm diameter) were packed manually with 0.5 g of ED3A-silica (height 2 cm). After eluting the metals, the sample was injected into an ion chromatographic system consisting of a Knauer 64 stainless-steel pump and a Knauer metal-free valve with a 20- $\mu$ l sample loop.

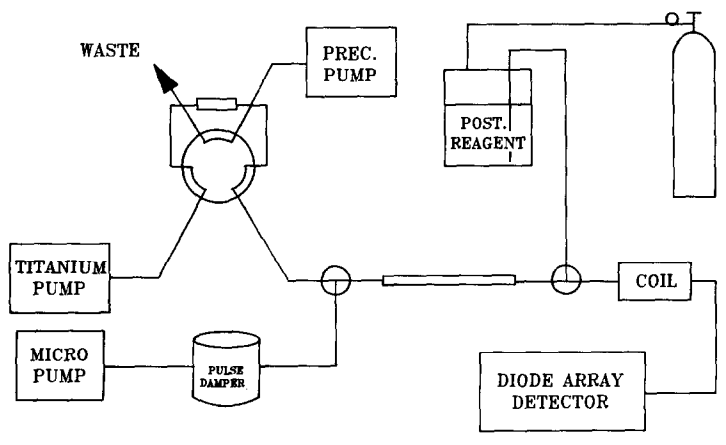


Fig. 1. Schematic representation of the chromatographic equipment.

A Stagroma analytical column (20 cm × 4 mm I.D.) was packed with Nucleosil 10SA silica. The postcolumn reactor and detector were the same as those described above.

### Reagents

*Preconcentration.* Unless stated otherwise, all chemicals were analytical-reagent grade Merck or Fluka products. All solutions were made with freshly prepared doubly distilled water. Freshly prepared 0.1 M sodium acetate–acetic acid buffer (pH 5) was used for conditioning the precolumn. It was obtained by diluting a stock solution of 5 M acetate buffer (pH 5.4) prepared as follows: 26.7 g of sodium acetate (Suprapur, Merck) were dissolved in 90 ml of water, the pH was adjusted to 5.4 with concentrated acetic acid (Suprapur, Merck) and the solution was diluted to 100 ml with water. A 1-ml volume of this 5 M buffer solution was also added to 50-ml samples prior to preconcentration.

ED3A–silica was synthesized according to the procedure described by Ohshima *et al.* [2]. A 15-g amount of silica (Polygosil 100, 40–63  $\mu\text{m}$ ; Macherey, Nagel & Co.) was washed with 150 ml of concentrated  $\text{H}_2\text{SO}_4$ – $\text{HNO}_3$  (9:1) and rinsed with demineralized water until the washings were neutral. A 5% aqueous solution of sodium N-(trimethoxysilylpropyl)ethylenediamine triacetate (Petrarch Systems) was prepared and 60 ml of this solution were added to the silica, stirred for 3 h and filtered. The solid was washed with HCl (0.2 M), demineralized water, methanol and finally diethyl ether. The chelated silica thus prepared was dried under vacuum. The loading capacity (120  $\mu\text{mol/g}$ ) of the bonded silica was determined by measuring the difference in the copper(II) ion concentration before ( $5 \cdot 10^{-3}$  M in acetate buffer, pH 5) and after contact with the bonded silica.

*Eluent for on-line chromatography.* Nitric acid (0.1 M) (Suprapur, Merck) was used for desorbing the metals from the precolumn (titanium pump). The eluent was modified before the inlet into the chromatographic column by pumping 0.5 M tartaric acid at pH 4.2 (Biochemica Microselect, Fluka), the pH being adjusted with NaOH. A few drops of pentachlorophenol solution (5 mg/l in 98% ethanol) were added to the tartrate solution to prevent bacterial growth.

*Eluent for off-line chromatography.* Nitric acid (1 M) (Suprapur, Merck) was used as eluent for desorbing metals. Tartaric acid (0.1 M) (Biochemica Microselect, Fluka) at pH 3 was used as the chromatographic eluent [3].

*Postcolumn reagent.* A solution containing  $5 \cdot 10^{-4}$  M PAR and  $5 \cdot 10^{-5}$  M Zn-EDTA in 2 M ammonia solution (pH 11) was used as the post-derivatizing reagent [3,4].

### Procedures

*On-line method.* A 20-ml (or 50-ml) volume of sample solution containing the metal ions and acetate buffer was pumped into the chelating silica precolumn (flow-rate 5 ml/min), where the metals were preconcentrated. The precolumn was rinsed with 5 ml of water. The metals retained were desorbed with nitric acid by using the titanium pump (flow-rate 1.2 ml/min, pressure 100 atm). Then, before the analytical column, the acidic solution was neutralized with tartrate buffer delivered by the micro pump (flow-rate 0.24 ml/min). During the desorption process, the precolumn and the analytical column were linked. The metals, after separation on the analytical column, were derivatized with the PAR–Zn-EDTA solution (flow-rate

0.7 ml/min) and detected at 500 nm. The precolumn was disconnected from the analytical column 1.5 min after passing the eluent. While separation was proceeding, clean-up and conditioning of the precolumn were carried out by washing it with 5 ml of 1 *M* nitric acid followed by 10 ml of 0.1 *M* acetate buffer using the preconcentration pump. A new sample may be preconcentrated while the separation of the previous sample is under way.

*Off-line method.* The syringe containing the chelating silica was first cleaned and conditioned by passing 10 ml of 1 *M* nitric acid followed by 20 ml of water. A 200-ml volume of the solution containing the elements of interest and acetate buffer was preconcentrated. The metals were desorbed with 2 ml of 1 *M* nitric acid, collected in a plastic tube and injected directly into the ion chromatograph having a 20- $\mu$ l sample loop.

## RESULTS AND DISCUSSION

### *Characteristics of ED3A-silica*

Maximum sample volumes that may be concentrated with the precolumns and syringes used in this work were determined under the experimental conditions described by Ohshima *et al.* [2], *i.e.*, using 0.1 *M* acetate buffer (pH 5), and the results are given in Table I. Acetate buffer is essential for the elimination of calcium ions present in excess in natural waters. In fact, in the absence of acetate ions, *ca.* 50% of the calcium present was retained by silica whereas in its presence, at pH 5, less than 1% was retained. Attempts were made to improve calcium elimination by varying the pH of the solution. As can be seen from Table II, the measured signals decrease with decreasing

TABLE I  
BREAKTHROUGH VOLUMES

Metal	On-line method		Off-line method (ml)
	1.3-cm precolumn (ml)	5-cm precolumn (ml)	
Cu, Ni, Co, Zn, Cd	100	500	> 1000
Pb	50	250	600
Mn	15	75	200

TABLE II  
OFF-LINE METHOD: INFLUENCE OF pH ON METAL RETENTION ON ED3A-SILICA

Signals obtained (peak surface areas in absorbance units) by preconcentration of 200 ml of 0.1 *M* acetate buffer solutions containing  $5 \times 10^{-7}$  *M* of the various metal ions.

pH	Pb	Zn	Ni	Co	Cd	Mn	Ca	Ca preconcentrated (%)
5	1392	2054	2029	1317	1416	1227	5026	0.3
4.5	781	1916	1913	1088	1557	—	600	0.04
4	298	2158	1956	1208	1366	1179	—	0
3	167	2207	1879	1160	600	1023	—	0

pH and at pH < 4 calcium was not retained at all. However, under these conditions, the test metal ion signals also decrease, particularly that of Pb. Hence pH 5 seems to be the optimal.

The effect of major ions present in natural waters on the retention of trace metal ions was also studied. The results showed that metal retention is unaffected by the presence of up to 0.5 M Na<sup>+</sup> and 10<sup>-3</sup> M Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup>.

Despite drastic treatment of ED3A-silica with acid (1 M HNO<sub>3</sub>), it degrades very slowly. On-line experiments revealed that after nineteen preconcentration-elution cycles, a decrease of 6% in the capacity had occurred.

#### *Off-line method*

*Limitations.* This method is less attractive for several reasons. First, 2 ml of 1 M HNO<sub>3</sub> are required for the desorption of metals retained on the syringe. A preconcentration factor of 100 is only achieved with a 200-ml sample volume. In the ion chromatograph, injection of sample volumes greater than 20 μl was found to perturb the chromatographic separation markedly owing to the presence of a high concentration of HNO<sub>3</sub>, hence limiting the maximum injection volume to 20 μl. Neutralizing the acid or substituting HCl for HNO<sub>3</sub> did not produce any improvement in the results.

Another drawback of the method is that the analytical column decomposes with increasing number of 1 M acid injections. The Cu(II) peak vanishes rapidly. Hence the determination of copper by this method is virtually impossible. Moreover, contrary to Yan and Schwedt's observations [3], complete chromatographic separation of Ca<sup>2+</sup> and Mn<sup>2+</sup> could not be achieved.

*Reproducibility and sensitivity.* The results of four replicate measurements made using 200-ml samples containing 10<sup>-6</sup> M test metal ions are given in Table III. A comparison with the on-line method showed that the reproducibility is slightly poorer. The limit of detection was 10<sup>-8</sup> M for a 200-ml sample volume. Linear calibration graphs were obtained over the range 3 · 10<sup>-8</sup>-3 · 10<sup>-5</sup> M for all metals except copper, for reasons mentioned earlier.

TABLE III

#### REPRODUCIBILITY

On-line method, 20 ml of 10<sup>-7</sup> M metal solutions (five replicates); off-line method, 200 ml of 10<sup>-6</sup> M metal solutions (four replicates).

Metal	Relative standard deviation (%)	
	On-line	Off-line
Cu	2.9	—
Pb	1.6	3.4
Zn	0.9	5.0
Ni	4.3	4.5
Co	0.6	5.9
Cd	1.0	4.5
Mn	2.2	3.2

### *On-line method*

*Desorption of metals.* For Mn, Co, Zn, Cd and Pb, less than 0.5 ml of 0.1 M HNO<sub>3</sub> was required to desorb quantitatively 2-ml samples containing 10<sup>-5</sup> M of the individual metal of interest. It should be pointed out that these determinations were made without the analytical column. HNO<sub>3</sub> (0.5 M) had to be used for the more strongly retained Cu and Ni ions. However, the signals obtained for these two metals by using 0.1 M HNO<sub>3</sub> were found to be proportional to the amount of metal preconcentrated.

*Eluent modification.* The conditions used for eluting the metals from the precolumn (0.1 M HNO<sub>3</sub>) are not suitable for direct loading on an analytical column as the relatively high acid concentration does not allow metal separations. Therefore, the acid must be neutralized before performing the chromatographic separation. The high ionic strength of the neutralized eluent hampers the chromatographic separation of metal ions on low-capacity ion-exchangers such as that used by Sevenich and Fritz [5]. Consequently, a high-capacity cation-exchanger was used and metal separations were carried out using Yan and Schwedt's procedure [3]. (0.1 M tartrate, pH 3). By lowering the concentration of the tartrate and using a 30-cm column, it was found that well resolved peaks such as those reported by Yan and Schwedt were obtained for all the metals except Mn(II), which was co-eluted with calcium ions. Attempts to improve the resolution of these two metal ions using complexing agents such as citrate and phthalate did not alter the results. The final concentrations of the eluent components were 0.083 M NaNO<sub>3</sub> and 0.083 M tartrate (pH 3).

More concentrated nitric acid was tried in order to facilitate the desorption of copper and nickel, but the chromatographic separation under these conditions was poor.

*Materials.* The materials used in designing the apparatus play an important role. The preconcentration part of the system should be made of titanium or plastic. Titanium and plastic precolumns yielded similar results, but the former material was chosen because it is more practical to use at high pressures. The HPLC pump delivering HNO<sub>3</sub> must be made of titanium, as stainless-steel is oxidized too quickly by this eluent. A stainless-steel micro pump, pulse damper and analytical column may be used without any problems, however.

*Eluent mixing.* The mixing of eluents is a very critical parameter as inhomogeneous mixing will result in splitting of peaks during chromatographic separation. The following points are very important for obtaining sharp chromatographic peaks. The motors of the two pumps should turn at the same rate. Therefore, eluent flow-rates of 0.24 and 1.2 ml/min were chosen for the microhead and for the titanium pump, respectively. The pulse damper is an essential part of the system as it regulates the flow-rates of the two pumps, which is important for homogeneous mixing of eluents. Hence an efficient pulse damper must be used. Tests with an SSI pulse damper yielded unsatisfactory results. In this work, a diaphragm-type (4.5-cm diameter) pulse damper similar to that of Latex (Germany) was used. The tee piece should not have too small an inside diameter. Initial tests with a high-pressure Upchurch mixing tee did not give good results.

*Comparison with direct injection.* The results obtained by replacing the precolumn with an injection loop and injecting 20- $\mu$ l samples containing 10<sup>-4</sup> M of test metal ions were compared with on-line preconcentration-separation of 20-ml samples

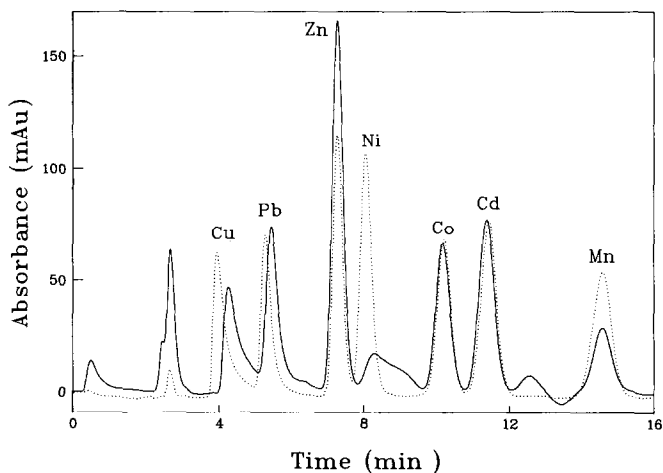


Fig 2. Comparison between on-line preconcentration and direct injection methods. Solid line: preconcentration of a 20-ml sample containing  $10^{-7} M$  of each of the test metal ions. Dashed line: injection of a 20- $\mu$ l sample containing  $10^{-4} M$  of test metal ions. Elution conditions: titanium pump, 0.1 M  $\text{HNO}_3$ , flow-rate 1.2 ml/min; micropump, 0.5 M tartaric acid (pH 4.2), flow-rate 0.24 ml/min; postcolumn reagent,  $5 \cdot 10^{-4} M$  PAR- $5 \cdot 10^{-5} M$  Zn-EDTA (pH 11), flow-rate 0.7 ml/min.

containing  $10^{-7} M$  of test metal ions (Fig. 2). Analogous results were obtained for Pb, Co and Cd. The Zn peak is larger owing to the high blank signals. The Cu peak is smaller and slightly broader owing to the difficulties in eluting it. Ni yields a broad band which does not interfere with other metals and the integrated peak was found to be proportional to the amount of Ni preconcentrated. Hence the determination of Ni is possible despite the broad band. Finally, the Mn peak is smaller owing to the small breakthrough volume. In general, preconcentration with a precolumn yields well resolved peaks similar to direct injection and concentration factors of 1000 are achieved. The recoveries of various metals calculated using the surface area and subtracting from the blank were as follows: 100% for Cu, Pb, Zn, Co and Cd, 50% for Mn and 30% for Ni.

*Reproducibility and sensitivity.* The results obtained from five replicate measurements of 20-ml samples containing  $10^{-7} M$  of various metal ions are shown in Table III. The detection limit for all the test metals was  $10^{-9} M$  for 20 ml of sample solution. Linear calibration graphs were obtained over the range  $3 \cdot 10^{-9}$ – $3 \cdot 10^{-6} M$  for Cu, Co and Cd. Analogous results were obtained for Mn by using 5-cm precolumn. The Zn and Ni calibration graphs were linear over the range  $10^{-8}$ – $3 \cdot 10^{-6} M$  owing to the high background levels. For Pb, linearity was observed over a narrow range,  $3 \cdot 10^{-9}$ – $3 \cdot 10^{-7} M$ , because of the low Zn-EDTA concentration employed in the postcolumn reagent. Zn-EDTA is usually added to the reagent to improve the detection of Pb by a substitution reaction [3,4]. However, the background absorption of the postcolumn reagent increases proportionally with the amount of Zn-EDTA added. Therefore, the minimum Zn-EDTA concentration required for detection of Pb was used to reduce the background signal. In any case, the  $\text{Pb}^{2+}$  concentration in natural water rarely exceeds  $3 \cdot 10^{-7} M$ .

*Stability of the analytical column.* Slow decomposition of the analytical column is indicated by a decrease in retention times. However, retention times similar to those obtained with the freshly prepared column can be achieved by lowering the tartrate concentration. For instance, over a period of 2 weeks of continuous usage, the tartrate concentration was lowered from 0.5 to 0.48 *M*. All attempts to regenerate the column failed.

The copper peaks decreased slightly with increased number of runs and eventually disappeared. The column can be regenerated by the following procedure, however: every 3 days, the column should be flushed with 100 ml of 0.05 *M* tetramethylammonium hydroxide (pH 9) in 50% acetonitrile followed by 20 ml of acetonitrile and 20 ml of water.

*Analytical application: determination of trace metals in river water.* As natural aquatic systems are much more complex than the synthetic systems, it was ensured that on-line preconcentration and separation of metal ions was not affected by matrix effects. This was done by spiking a river Arve (Geneva, Switzerland) water sample, which had been filtered through a 0.2- $\mu\text{m}$  filter, with  $10^{-7}$  *M* metal ions. Samples of 50 ml were immediately preconcentrated and metal ions separated as described earlier (Fig. 3C). A comparison with a standard solution containing  $10^{-7}$  *M* of test metal ions (Fig. 2) showed that no matrix effect is observed except that Mn is masked by calcium ions.

Experiments were done to establish whether this method gives the total metal concentration or allows speciation studies to be made. In this instance the spiked river water sample was left to stand for 90 min with stirring and then on-line preconcentration followed by chromatographic separation was carried out. The peak height of all the metals except Ni decreased, the decrease being marked for Pb (*ca.* 29%; see Table IV), indicating the formation of inert complexes which cannot be analysed by this method.

In order to obtain an idea of the proportion of metal ions transported by the suspended matter of river water, experiments were repeated with unfiltered river water

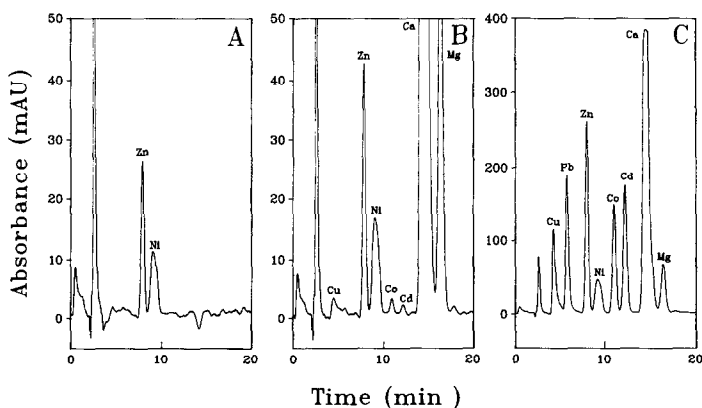


Fig. 3. Analysis of river Arve water by the on-line method. (A) Blank; (B) 50 ml of 0.2- $\mu\text{m}$  filtered river water; (C) 50 ml of 0.2- $\mu\text{m}$  filtered river water, spiked with  $10^{-7}$  *M* of each of the test metal ions. Conditions as in Fig. 2.



TABLE IV  
ANALYSIS OF RIVER ARVE WATER

Metal	Metal concentration found ( $M$ ) <sup>a</sup>			
	Filtered	Filtered and $10^{-7} M$ spiked	Filtered, $10^{-7} M$ spiked and agitated	$10^{-7} M$ spiked unfiltered
Cu	$2.4 \cdot 10^{-9}$	$9.0 \cdot 10^{-8}$ (-12)	$8.1 \cdot 10^{-8}$ (-21)	$4.1 \cdot 10^{-8}$ (-60)
Pb	—	$1.0 \cdot 10^{-7}$	$7.1 \cdot 10^{-8}$ (-29)	— (-100)
Zn	$7.8 \cdot 10^{-9}$	$1.2 \cdot 10^{-7}$ (+6.5)	$1.1 \cdot 10^{-7}$	$1.1 \cdot 10^{-8}$ (-89)
Ni	$2.2 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-7}$ (-16)
Co	$1.7 \cdot 10^{-9}$	$1.0 \cdot 10^{-7}$	$9.8 \cdot 10^{-8}$ (-3.6)	$5.4 \cdot 10^{-8}$ (-37)
Cd	$1.2 \cdot 10^{-9}$	$1.0 \cdot 10^{-7}$	$9.6 \cdot 10^{-8}$ (-4.9)	$1.9 \cdot 10^{-8}$ (-81)

<sup>a</sup> Values in parentheses represent the percentage excess or loss in the measured metal ion concentration.

spiked with  $10^{-7} M$  of each of the metal ions of interest. Solutions were stirred for 2 h, filtered through  $0.2\text{-}\mu\text{m}$  filters, preconcentrated and metal ions separated chromatographically. A sharp decrease in the peak heights were observed (Table IV), indicating that most of the test ions present in water are adsorbed on the suspended particles of sediments.

Finally, the proposed method was tested to ascertain its applicability to the determination of trace metal ions in natural waters. River Arve water was filtered through a  $0.2\text{-}\mu\text{m}$  filter and a 50-ml volume was preconcentrated and analysed by chromatography (Fig. 3b). The chromatogram of the blank is shown in Fig. 3a for comparison purposes. It can be seen that with the exception of Ni and Zn, all the other metal ions are present at close to the detection limits of the method. Trace amounts of Cu, Pb, Co and Cd could not be detected by the off-line method.

## CONCLUSION

ED3A-silica can be used for the determination of trace amounts of free divalent metal ions and labile or moderately labile complexes. The on-line method allows the determination of Cu, Pb, Zn, Ni, Co and Cd at  $3 \cdot 10^{-9} M$  concentration levels (20-ml sample volume) in natural water. The off-line method, on the other hand, can be used for the determination of Pb, Zn, Ni, Co and Cd at  $3 \cdot 10^{-8} M$  levels (200-ml sample volumes). By using larger sample volumes, the sensitivity levels can be extended at the expense of the analysis time. These two methods are also applicable to other silicas such as 8-quinolinol-silica [6].

A search for chelating silica from which metal ions can be readily eluted is in progress. This will make possible the use of a single pump and consequently simplify the apparatus and manipulation. Finally, as trace metals in natural waters are present at levels close to the detection limits, there is a need for postcolumn reagents that are as universal as but more sensitive than PAR.

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