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# Determination of divalent trace metals in natural waters by preconcentration on N,N,N',N'-tetra(2-aminoethyl)ethylenediamine-silica followed by on-line ion chromatography

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## ABSTRACT

A method for the on-line preconcentration and chromatography of trace metals, *e.g.*, Co, Ni, Cu, Zn, Cd and Pb, on N,N,N',N'-tetra(2-aminoethyl)ethylenediamine-bonded silica is described. The preconcentrated metals were desorbed with 0.13 M tartrate, which allows direct separation on a cation-exchange chromatographic column. The metals separated were detected by postcolumn reaction with 4-(2-pyridylazo)resorcinol and measuring the absorbances at 500 nm. Linear calibration graphs were obtained over the range  $1 \cdot 10^{-8}$ – $3 \cdot 10^{-6}$  M. The synthesis and characteristics of the chelated silica are described. The method was applied to the analysis of river and interstitial sediment waters.

## INTRODUCTION

The use of ion chromatography (IC) for the determination of trace metals is attracting considerable attention because it allows multi-element analysis and, unlike anodic stripping voltammetric techniques, it is not limited to electroactive elements. However, the low level of trace metals and the presence of high levels of alkaline earth metals in natural waters hampers the direct determination of trace metals by IC. Consequently, a separation (to eliminate alkaline earth metals and interfering components present in the sample) and preconcentration step prior to IC analysis is necessary. For this purpose, chelating resins or silicas have frequently been used.

Natural waters contain organic ligands that complex with trace metals. Chelating resins or silica will retain only the labile metal fraction. Therefore, using this method and without sample pretreatment, only the free metal and moderately complexed ion concentration can be measured. However, it is very important to have a knowledge of these fractions as

they are most toxic to microorganisms. Therefore, preconcentration of metals by chelating resins or silicas followed by IC separation may be used as a complementary method to spectroscopic methods for metal ion determination.

Metals preconcentrated on the chelating silicas may be determined either (directly) by on-line chromatography or (indirectly) by off-line chromatography. The former is preferable for several reasons, *e.g.*, contamination due to sample handling is minimized, and no dilution of the preconcentrated samples will be incurred, *i.e.*, high preconcentration factors would be achieved.

Unfortunately, on-line determination is not simple owing to the difficulty in finding an eluent that is suitable for both desorbing metals retained on the chelating silica (strong acid) and separation by IC (weak acid). To date only three methods have been proposed to overcome this problem [1–3], but each of them has shortcomings.

For instance, preconcentration of metals on 8-hydroxyquinolinol-bonded silica (8Q-silica) followed by desorption of retained metals with 0.1 M KCN

allows the determination of only Cu and Ni [1]. Siriraks *et al.* [2] applied an iminodiacetate resin to the preconcentration of metals and showed that Mn, Fe(II), Co, Ni, Cu and Zn can be determined in complex matrices such as natural water and biological samples. However, their method is complicated and laborious owing to the use of two precolumns. Recently, we reported a similar method using ethylenediaminetriacetate-bonded silica (ED3A-silica) for preconcentration of metals [3]. The metals were desorbed in this instance with 0.1 M HNO<sub>3</sub> and the eluted metals were pumped into the analytical column, but before separation the acidic solution was neutralized with a tartrate buffer solution which was delivered using a second pump. Co, Ni, Cu, Zn, Cd and Pb ions were determined by this method. The necessity to use a second pump for the neutralization of the acid makes the method slightly delicate to use.

In this paper, the use of a novel silica, N,N,N',N'-tetra(2-aminoethyl)ethylenediamine (PENTEN)-bonded silica, for on-line preconcentration of transition metal ions prior to determination by IC with UV-visible detection is described. This method avoids the use of a second pump. Owing to the high acidic constants of PENTEN, the metals retained on the silica are readily desorbed using weakly acidic solutions. This allows the same eluent to be used for metal desorption and separation on the analytical column. Hence the use of PENTEN-silica for the preconcentration of metal ions simplifies the high-performance liquid chromatographic (HPLC) instrumentation, *i.e.*, any type of HPLC instrument equipped with a preconcentration unit (made of plastic or titanium) can be used for performing the analysis and, most important, the delicate step of neutralizing the eluent [3] after desorption of metals from the precolumn is avoided.

## EXPERIMENTAL

### Apparatus

The chromatographic equipment (Fig. 1) consisted of a Knauer metal-free electric valve, a Knauer Model 64 titanium pump for delivering the eluent and a Dionex QIC preconcentration pump. A laboratory-made titanium precolumn (13 × 1.7 mm I.D.) was packed manually with PENTEN-silica. A Macherey-Nagel analytical column (30 cm × 4 mm I.D.) was packed with Nucleosil 10 SA silica. Plastic

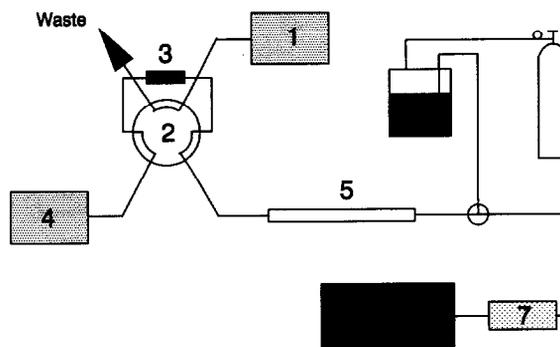


Fig. 1. Schematic diagram of the manifold used for metal analysis. 1 = Preconcentration pump; 2 = valve; 3 = precolumn; 4 = HPLC pump; 5 = analytical column; 6 = post-column reagent; 7 = reactor; 8 = detector.

tubing was used. The postcolumn reagent was pumped under nitrogen pressure (4.5 atm) and to ensure the completion of 4-(2-pyridylazo)resorcinol (PAR)-metal complexation reaction a PTFE coil (3 m × 0.5 mm I.D.) was used. A Hewlett-Packard Model 1040 A diode-array UV-visible detector was used for detection of metal complexes.

### Reagents

**Preconcentration.** Unless stated otherwise, all chemicals were of analytical-reagent grade from Merck or Fluka. All solutions were made with freshly prepared doubly distilled water. Freshly prepared 0.1 M diethanolamine buffer (pH 8.5–9) was used for conditioning the precolumn. It was obtained by diluting a 1 M stock solution. The pH of the stock solution was adjusted with HNO<sub>3</sub> (Suprapur, Merck). A 1-ml volume of this 1 M buffer solution was also added to 20 ml of acidified samples prior to preconcentration.

PENTEN was synthesized as described by Dietrich *et al.* [4]. PENTEN-bonded silica was prepared using a modification of Kudryavtsev *et al.*'s [5] method of synthesis of tetraethylenepentamine-bonded silica. A 0.03-mol (6-g) amount of  $\gamma$ -chloropropyltrimethoxysilane (Petrarch Systems) were added to 10 g of silica (Polygosyl 100, 40–63  $\mu$ m; Macherey-Nagel) in 45 ml of toluene. Water (40  $\mu$ l) and 0.2 g of *p*-toluenesulphonic acid were added to the mixture (these act as catalysts), which was then refluxed for 4 h without stirring. The solid was filtered, washed successively with hot toluene, eth-

anol and diethyl ether and dried under vacuum at 120°C; elemental analysis, C 4.07, H. 1.08%; calculated loading capacity, 1130  $\mu\text{mol/g}$ . A 2-g amount of chloropropyl-bonded silica was suspended in 10 ml of toluene, 0.004 mol (0.8 g) of bistrimethylsilylacetamide were added and the mixture was refluxed for 4 h. The solid was filtered, washed with hot toluene and diethyl ether and dried at 120°C under vacuum. Finally, to 12 ml of ethanol–water (50:50) containing 0.003 mol (2.1 g) of PENTEN  $\cdot$  6HBr (pH 9.5), 2 g of end-capped chloropropyl-bonded silica were added. The mixture was refluxed for 48 h (without stirring). The solid was filtered, washed successively with ethanol, water, 0.01 M  $\text{HNO}_3$ , water, ethanol and diethyl ether and dried at 120°C under vacuum; elemental analysis, C 6.71, H 1.59, N 1.94%; calculated loading capacity, 230  $\mu\text{mol/g}$ .

**Eluent.** The eluent used was 0.13 M tartaric acid (pH 3) [6]. The pH was 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.

**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-column derivatizing reagent [6,7].

### Procedure

A 20-ml (or 50-ml) volume of sample solution containing the metal ions [buffered with diethanolamine (pH 8.5–9) if required, for instance, with acidified solution] 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 and the metals retained were desorbed with 0.13 M tartaric acid (pH 3) delivered by means of an HPLC pump (flow-rate, 1.5 ml/min, pressure 120 atm). During the desorption step (total duration 1 min), the precolumn was linked to the analytical column. The metals, after separation on the analytical column, were derivatized with the PAR–Zn-EDTA solution and detected at 500 nm. While separation was proceeding, clean-up and conditioning of the precolumn were done by washing it with 5 ml of 0.5 M  $\text{HNO}_3$  followed by 10 ml of 0.1 M diethanolamine buffer (pH 9) using the preconcentration pump. A new sample can be preconcentrated while the separation of the previous sample is in progress.

## RESULTS AND DISCUSSION

### Characteristics of PENTEN-silica

**Conditions of preconcentration.** As the pK values of PENTEN are high, preconcentration has to be done at high pH to minimize competition by metal-complexing ligands which are present in the samples. Moreover, preconcentration of metals must be carried out at pH 9 because hydroxide ions interfere with metal preconcentration. Therefore, the chelating silica precolumn was preconditioned with diethanolamine buffer. Once the column has been conditioned, silica itself acts as an autobuffer and samples to be preconcentrated need not be buffered unless their pH values are lower than 6.5–7.

In contrast, the ionic strength of the sample solution should be adjusted to 0.1 M by adding inert electrolytes such as potassium nitrate in instances where low-ionic-strength unbuffered samples are used. This is to minimize electrostatic repulsion between similarly charged ions (metals and ligands on the surface of the silica).

**Breakthrough volumes.** Using the above-mentioned conditions, the breakthrough volumes ( $V_b$ ) for various metals were determined. The  $V_b$  values were found to be 120 and 250 ml for Pb, the least well retained metal, and Cu, the most strongly retained metal, respectively (concentration of metal ions =  $10^{-6}$  M). After 50 preconcentration–elution cycles, a ca. 20% decrease in these  $V_b$  values was observed.

**Effect of major ions on trace metal preconcentration.** The results showed that the presence of 0.5 M of  $\text{Na}^+$  and  $\text{Cl}^-$ ,  $5 \cdot 10^{-3}$  M of  $\text{Ca}^{2+}$  and  $1 \cdot 10^{-3}$  M of  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  did not affect the preconcentration of metal ions (concentration of metal ions =  $2 \cdot 10^{-7}$  M). A small fraction of  $\text{Ca}^{2+}$  (ca 1%) was found to be retained by PENTEN-silica.

**Efficiency of PENTEN-silica.** The stability constants of transition metals with PENTEN are high [8] (see Table I). However, neither the thermodynamic nor the kinetic reaction constants for these metals with PENTEN-silica are known. Metal retention depends on the latter, i.e., if the metal complexation reaction is not fast, metals will not be retained. Therefore, in order to determine the metal retention characteristics of PENTEN-silica, preconcentration of metals were done in the presence of tartrate, nitrilotriacetate (NTA) and EDTA.

The results were compared with the retention

TABLE I  
STABILITY CONSTANTS OF METALS WITH PENTEN [8]

Metal	$\log \beta_1$	Metal	$\log \beta_1$
Mn	9.37	Cu	22.44
Fe(II)	11.2	Zn	16.24
Co	15.75	Cd	16.15
Ni	19.3	Hg	29.59

characteristics of 8Q-silica and ED3A-silica reported previously [1,3]. Metal retentions were unaffected by the presence of up to  $10^{-2} M$  tartrate concentrations for all three chelating silicas.

The influence of NTA and EDTA on the retention of Cu, Pb, Zn, Ni, Co and Cd ( $2 \cdot 10^{-7} M$  in each of the metals) are shown in Fig. 2. NTA has protonation constants of 1.66, 2.95 and 10.28 [8]. Preconcentration of metals on PENTEN-silica was done at pH

8 whereas that on 8Q-silica and ED3A-silica was done at pH 5. In all three instances, the same protonated NTA species are present and the metal-NTA complexation strengths for a given metal at pH 5 and 8 are comparable. The results show that PENTEN-silica is best for the retention of  $\text{Cu}^{2+}$  owing to its high stability constant with  $\text{Cu}^{2+}$ , and also for Zn and Cd owing to the fact that their complex formation kinetics are fast. On the other hand, Ni and Co react slowly with PENTEN-silica and exhibit the same type of behaviour as observed with 8Q-silica. The striking feature of PENTEN-silica is that it shows a very poor affinity for Pb.

With EDTA, the protonation constant of 6.24 is different from that of NTA and in addition EDTA forms stronger complexes with metals than NTA. The results showed that all three chelating silicas exhibit similar behaviour towards the retention of all the target metals except  $\text{Cu}^{2+}$ , which is retained better on PENTEN-silica than the other two silicas.

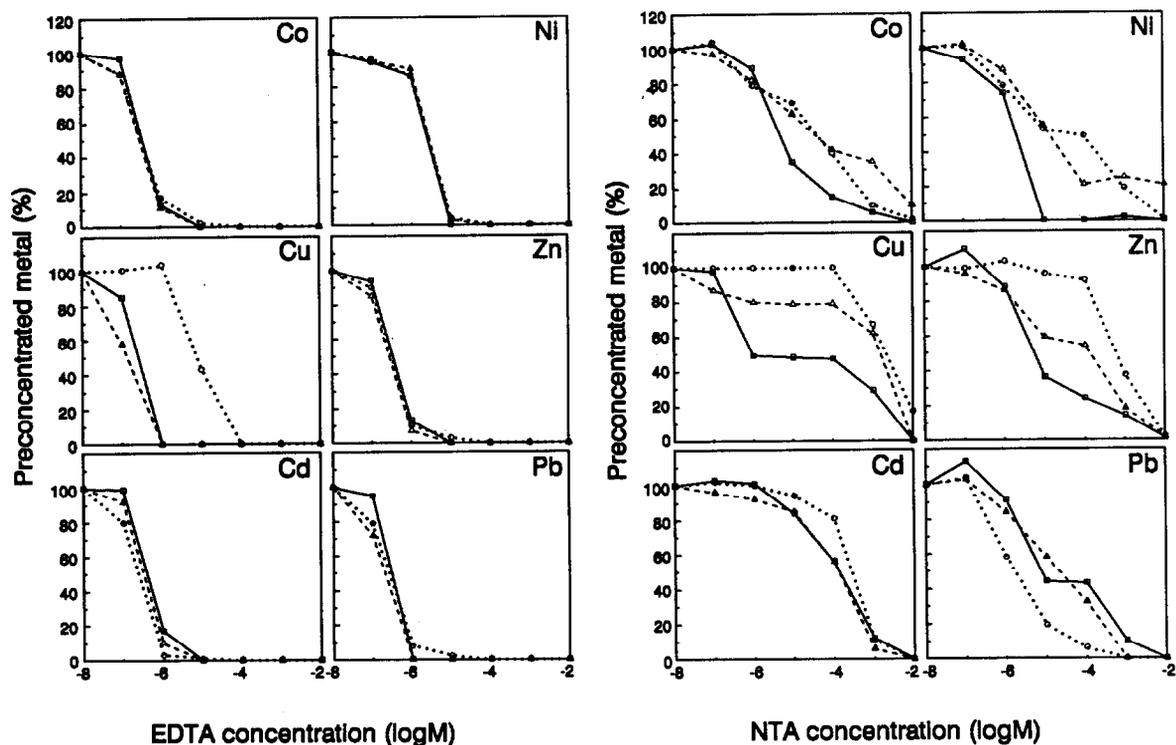


Fig. 2. Comparison between (○) PENTEN-, (△) 8Q- and (□) ED3A-silicas. Recoveries of metals with increasing concentrations of NTA and EDTA (20 ml of  $2 \cdot 10^{-7} M$  metal samples).

### Choice of buffer

The anions of the buffers may hamper the preconcentration of metals owing to problems due to precipitation or complexation. Several buffers were tested and the results showed that (1) phosphate buffer (pH 8.5–9) was not suitable as calcium ions which are present in high concentrations in natural aquatic systems form calcium phosphate precipitate; (2) ammonia is unsuitable owing to the formation of strong complexes with transition metals; (3) the low solubilities of boric acid and tris(hydroxymethyl)aminomethane (Tris) make these buffers unsuitable; and (4) diethanolamine, which is highly soluble in water and which is not a strong complexing agent, was found to be the best buffer for the preconcentration of metals. The only drawback to using this buffer is that Co(II) is oxidized to Co(III) in this medium in the presence of dissolved oxygen. In fact, an 80% decrease in the Co(II) signal was observed with Co(II) samples preconcentrated 30 min after their preparation. Co(II) therefore cannot be measured using this buffer when the sample itself is buffered (acidic sample, see above).

### On-line chromatography

Metal separations were carried out using Yan and Schwedt's chromatographic separation procedure [6]. From the results in Fig. 3, it can be seen that a 2-ml sample containing  $10^{-5} M$   $Cu^{2+}$ , preconcentrated on PENTEN-silica, can be eluted in less than 1 min by using 1.5 ml of 0.1  $M$  tartrate (pH 3). However, a 30-cm (instead of 20-cm) analytical column was used. Hence, in order to obtain acceptable retention times, a more concentrated tartrate solution (0.13  $M$ ) was used as the eluent.

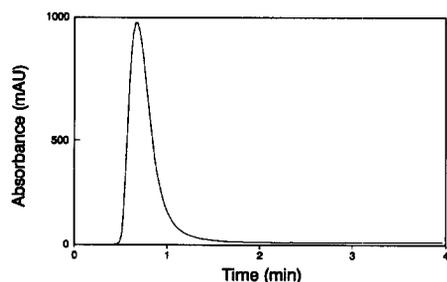


Fig. 3. Elution of preconcentrated copper (2 ml of  $10^{-5} M$   $Cu^{2+}$ ) with 0.1  $M$  tartaric acid (pH 3).

20-ml samples containing  $2 \cdot 10^{-7} M$  of test metal ions were preconcentrated, separated and detected. The results obtained were compared with the direct injection method by injecting 20- $\mu$ l samples containing  $2 \cdot 10^{-4} M$  of the test metal ions. The peak areas of the preconcentrated samples were generally found to be smaller than in the injection method. The differences in peak areas between the two methods can be as much as 50%, depending on the metal and the conditions used. A possible reason for this discrepancy is that the metal ions present are not totally preconcentrated owing to hydrolysis problems. However, this does not affect the determination of metal ions because these differences in peak areas are reproducible and the peak areas are directly proportional to the metal ion concentration.

### Precision and detection limits

The results obtained from five replicate measurements of 20-ml samples containing  $2 \cdot 10^{-7} M$  of the various metal ions are given in Table II. The day-to-day reproducibility is essentially dependent of the reproducibility of the preparation of the post-column reagent. Taking this into account, the day-to-day reproducibility is never more than 5% for each of the metals.

The detection limit for all the test metal ions was found to be  $3 \cdot 10^{-9} M$  (three times the baseline height). Linear calibration graphs were obtained over the ranges  $1 \cdot 10^{-8}$ – $3 \cdot 10^{-6} M$  for Cu, Zn, Ni, Co and Cd and  $1 \cdot 10^{-8}$ – $3 \cdot 10^{-7} M$  for Pb. The narrow linear range for Pb is due to the use of a low Zn-EDTA concentration for postcolumn reaction (see ref. 3).

TABLE II

### REPRODUCIBILITY OF THE METHOD

Relative standard deviations (R.S.D.) for five replicate measurements with 20-ml samples containing  $2.5 \cdot 10^{-7} M$  target metal ions.

Metal	R.S.D. (%)	Metal	R.S.D. (%)
Cu	1.8	Ni	3.1
Pb	3.6	Co	1.8
Zn	2.5	Cd	1.8

### Analytical applications

**Determination of trace metals in river water.** River Arve (Geneva, Switzerland) water samples were filtered through a Schleicher & Schüll 0.2- $\mu\text{m}$  filter and buffered with diethanolamine buffer. A sample of 50 ml was spiked with  $10^{-7}$  M metal ions, immediately preconcentrated on PENTEN-silica and separated as described above (Fig. 4C). The results showed that there was no matrix effect (Table III) except for the appearance of Ca, Mn and Mg at the end of the chromatogram. As can be seen from Table III, quantitative recoveries were obtained for all the target metals except Cu and Zn. Analogous results were observed in our earlier studies [3]. The lower recovery of Cu is due to the fact that a fraction of the total copper is present as an inert complex and cannot be determined by this method. For zinc, the high values for the blank make the results imprecise (Fig. 4A). The recoveries are defined as the difference between the metal found after spiking and the metal spiked (taking into account the metal already present in the sample and the blank).

A typical chromatogram of river Arve water sample preconcentrated and separated is shown in Fig. 4B. As can be seen, Cu, Zn and Ni can be determined without any problems. The concentration of free or labile lead is low and Cd is present at levels below the detection limit.

To test if the accuracy of the method is dependent on the preconcentrated volume, the measurement was repeated using a larger sample volume (100 ml). The results obtained with this sample were in good agreement with those obtained with the 50-ml sample volume (Table III).

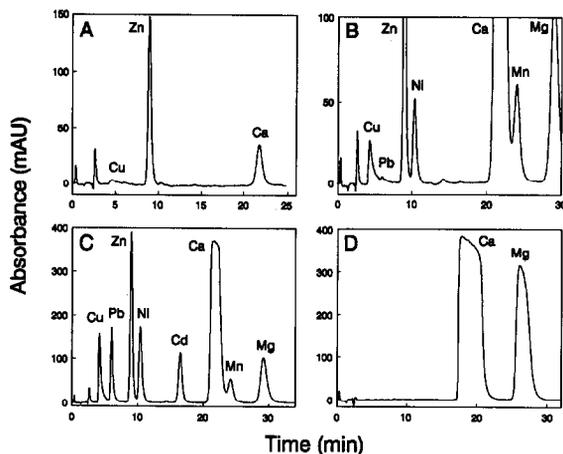


Fig. 4. Determination of trace metals in river Arve water. (A) Blank; (B) river water, 50-ml sample volume; (C) river water spiked with  $10^{-7}$  M test metal ions, 50-ml sample volume; (D) same as (B) but preconcentrated on classical high-capacity cation-exchange silica.

The effectiveness of chelating silicas for preconcentration of metals was established by comparing the results obtained with a classical high-capacity cation-exchange silica (Nucleosil 10SA, 1 mequiv./g) (Fig. 4D). The cation-exchange silica is unsuitable for preconcentration of metals in samples containing high levels of alkaline earth metals (in this instance  $1.3 \cdot 10^{-3}$  M for  $\text{Ca}^{2+}$  measured by atomic absorption spectrometry (AAS)).

**Analysis of interstitial sediment water.** Analysis of interstitial water by preconcentration of the sample on PENTEN-bonded silica followed by chromatog-

TABLE III  
ANALYSIS OF RIVER ARVE WATER

Metal	Metal concentration found (M)				
	Blank	50-ml sample	100-ml sample	$10^{-7}$ M spiked sample	Recovery (%)
Cu	$5.3 \cdot 10^{-9}$	$2.9 \cdot 10^{-8}$	$3.4 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	-12
Pb	$1.2 \cdot 10^{-9}$	$1.7 \cdot 10^{-9}$	$1.8 \cdot 10^{-9}$	$9.9 \cdot 10^{-8}$	-2
Zn	$6.8 \cdot 10^{-8}$	$3.0 \cdot 10^{-8}$	$2.8 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	-14
Ni	$1.6 \cdot 10^{-9}$	$4.7 \cdot 10^{-8}$	$4.7 \cdot 10^{-8}$	$1.5 \cdot 10^{-7}$	+3
Cd	0	0	$1.3 \cdot 10^{-9}$	$1.1 \cdot 10^{-7}$	+7

TABLE IV

## ANALYSIS OF INTERSTITIAL SEDIMENT WATERS

Comparison between IC analysis (PENTEN- and ED3A-silicas, 20-ml samples) and AAS.

Metal	Metal concentration found ( <i>M</i> )								
	Aire water			Nant d'Avril water			Nant de Châtillon water		
	PENTEN	ED3A	AAS	PENTEN	ED3A	AAS	PENTEN	ED3A	AAS
Cu	$2.0 \cdot 10^{-8}$	$1.9 \cdot 10^{-8}$	$3.0 \cdot 10^{-8}$	$1.9 \cdot 10^{-8}$	$3.5 \cdot 10^{-8}$	$5.2 \cdot 10^{-8}$	$8.6 \cdot 10^{-8}$	$8.7 \cdot 10^{-8}$	$1.9 \cdot 10^{-7}$
Pb	—	$4.5 \cdot 10^{-9}$	$4.3 \cdot 10^{-9}$	—	$7.3 \cdot 10^{-9}$	$6.5 \cdot 10^{-9}$	$3.3 \cdot 10^{-8}$	$2.9 \cdot 10^{-8}$	$3.8 \cdot 10^{-8}$
Zn	$2.2 \cdot 10^{-7}$	$1.8 \cdot 10^{-7}$	$2.8 \cdot 10^{-7}$	$2.4 \cdot 10^{-7}$	$2.5 \cdot 10^{-7}$	$3.8 \cdot 10^{-7}$	$2.1 \cdot 10^{-7}$	$2.4 \cdot 10^{-7}$	$3.1 \cdot 10^{-7}$
Ni	$9.5 \cdot 10^{-8}$	$9.4 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$	$8.2 \cdot 10^{-8}$	$9.1 \cdot 10^{-8}$	$1.1 \cdot 10^{-7}$	$4.4 \cdot 10^{-8}$	$5.7 \cdot 10^{-8}$	$4.4 \cdot 10^{-8}$
Co	$8.3 \cdot 10^{-9}$	$6.9 \cdot 10^{-9}$	$3.0 \cdot 10^{-8}$	—	$6.2 \cdot 10^{-9}$	—	—	$8.7 \cdot 10^{-9}$	—
Cd	—	—	$6.3 \cdot 10^{-10}$	—	—	$5.5 \cdot 10^{-10}$	—	—	$1.7 \cdot 10^{-9}$

raphy was compared with metal analysis by AAS (electrothermal for Cu, Pb, Ni, Co and Cd; flame for Zn) and preconcentration on ED3A-silica followed by IC [3]. Sediment samples from three polluted rivers in Geneva Canton (Switzerland), the Aire, Nant d'Avril and Nant de Châtillon, were collected. The samples were centrifuged and the supernatant interstitial water was filtered through a 0.2- $\mu$ m filter and acidified to prevent adsorption problems during their storage. The results are given in Table IV.

It can be seen that results obtained by the two chromatographic methods are comparable except that cobalt can be determined reliably only with ED3A-silica. The oxidation of Co(II) to Co(III) by diethanolamine buffer used with the PENTEN-silica hampers the determination of Co.

AAS yields either similar or higher values than IC method, because IC measures only the free and moderately complexed metals whereas AAS measures the total concentration. Reliable results for cobalt could not be obtained by AAS in this concentration range.

## CONCLUSIONS

The novel PENTEN-bonded silica allows the simple and efficient on-line preconcentration and separation of trace metals by IC. The method can be used with any standard HPLC equipment which includes an inert (plastic or titanium) preconcentra-

tion pump, switching valve, precolumn and tubing. It can be automated.

Detection limits lower than those reported here can be achieved using larger sample volumes, but at the expense of longer analysis times. Alternatively, the sensitivity of the method could be increased using a different detection system, *e.g.*, chemiluminescence [9].

The drawback of the proposed approach is that the determination of metals in biological samples containing high concentrations of phosphate or Fe(III) cannot be done owing to the precipitation of either metals as phosphates or Fe as hydroxides at pH 8.5–9.

It should be remembered that only the free and moderately labile metal fraction is measured by the use of chelating silicas. If the total concentration is required, the sample must be mineralized (*e.g.*, using UV radiation). Further, PENTEN is not a good ligand for lead. The results for the determination of lead are therefore not very useful. Finally, cobalt cannot be determined when the sample must be buffered (acidic sample).

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