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# Determination of cadmium and lead at $\mu$g/l levels in aqueous matrices by chelation ion chromatography

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## ABSTRACT

A method for the simultaneous determination of $\mu$g/l or sub-$\mu$g/l levels of cadmium and lead in sea water by chelation ion chromatography is demonstrated. The method consists in the preconcentration of a sea-water sample containing cadmium and lead on an iminodiacetate chelating resin; alkali and alkaline earth metals are removed from the resin with an ammonium acetate buffer, the metals are eluted and separated by cation-exchange chromatography, followed by postcolumn derivatization with 4-(2-pyridylazo)resorcinol and spectrophotometric detection at 520 nm. The concentration and separation steps are automated. The detection limit, when concentrating 200 ml of sea water, was found to be 2 ng for cadmium and 6 ng for lead. Relative standard deviations of 4.5% and 6.8% for 10 $\mu$g/l of cadmium and lead, respectively, were obtained. Transition metals (Fe, Co, Ni, Zn, Cu, Mn) do not interfere in the analysis. An application of the method to the determination of cadmium and lead in sea-water samples collected in the Taranto gulf (Italy) is presented.

## INTRODUCTION

The determination of trace elements, particularly heavy metals, in real matrices has received increasing attention in recent years. The use of fertilizers, pesticides, coal and oil in combustion processes and, most significantly, the wide use of metals in a variety of industries has resulted in a significant increase of their concentration in the environment.

Among heavy metals, cadmium and lead have special importance from the ecotoxicological point of view, both for the high toxicity of their compounds and their accumulation in various organisms [1–4]. The concentrations of both metals in sea water are usually in the range of $\mu$g/l or less. Different techniques have been developed for trace level determinations of cadmium and lead in sea water; in particular, anodic stripping voltammetry (ASV) [5,6], also coupled to flow-injection analysis [7], HPLC [8] and preconcentration techniques coupled to flow-injection atomic absorption spectrometry (AAS) [9] or to inductively coupled plasma mass spectrometry (ICP-MS) [10] have been used.

Direct determination of metals is highly desirable as it entails minimum sample handling and pretreatment, thereby minimizing the risk of contamination and, more important, eliminating the reagent blank common to all chemical pretreatment methods. In sea water low concentration levels of cadmium and

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lead are associated with high concentrations of alkali and alkaline earth metals, whose presence produces interferences due to matrix effects, making direct analysis difficult. For the determination of trace metals in complex matrices it is therefore necessary to implement preconcentration followed by a separation step. This procedure is useful in order to obtain both an increase in detectability of analytes and to minimize matrix interferences.

In the preconcentration step, metals are generally complexed by chelating agents; metal complex separation can be effected by solvent extraction [11] or by precipitation [12]. The chelating agent could be in an immobilized form in a resin and packed in a chromatographic column. Metals can be released eiher by digesting the resin with acid [13] or by changing the ionic form of the resin.

The properties of iminodiacetate chelating resins such as Chelex-100 are well known [14–28]. Kingston *et al.* [24] studied the use of Chelex-100 in sea-water analysis, introducing a preliminary separation of alkali and alkaline earth elements collected on the column by stripping with 1 *M* ammonium acetate at pH 5.2. Cadmium and lead recoveries from sea water were higher than 90% at $\mu$g/l levels; the recovery values are influenced by pH and they are quantitative only in the narrow pH range 4.7–5.5. Using these resins, preconcentration methods and the separation of the saline matrix were reliable [29–31] and allowed enrichment factors of $>100$ [32].

Chelex-100 resin has been used in the batch mode for preconcentration and matrix elimination prior to graphite furnace AAS [24,29], ICP atomic emission spectrometry (AES) [32,33] and neutron activation analysis [31]. Recently, different workers have implemented an automated on-line column preconcentration for flow-injection AAS [34–36]. Many attempts to improve metal retention on Chelex-100 chelating resin have been made by decreasing the flow-rate [15], adjusting the resin size and packing in different acidic and basic solutions [24] and lowering the ammonium acetate concentration to avoid metal loss during the matrix elimination step [35]. The slight improvements observed were not considered adequate to enhance the accuracy of analysis. Characteristically, the resin volume changes substantially in acidic and basic solutions owing to its low cross-linked (gel-type) microporous poly(styrene–divinylbenzene) (PS–DVB) supporting polymer. It was concluded that the low recovery of metal ions from Chelex-100 resin [36,37] was caused by physical degradation of the resin under pressures greater than 0.69 MPa. This causes a series of problems in the use of these columns in automatic preconcentration systems.

Recently, such problems have been solved with the development of a highly cross-linked macroporous PS–DVB-based resin with iminodiacetate functional groups [38]. This resin was used to prepare a MetPac-CC1 column, which gave the best results in automatic preconcentration systems from aqueous matrices coupled on-line to ion chromatography, ICP-AES and ICP-MS. In recent years ion-exchange chromatographic techniques have been developed for environmental application [39] and in particular in the separation and detection of metals [38,40]. Ion chromatographic techniques with spectrophotometric detection after postcolumn derivatization with a chromogenic ligand, coupled on-line with preconcentration by chelation, allowed the determination of trace levels of transition metal and lanthanides in complex matrices. For transition metals the metallochromic indicator most often used is 4-(2-pyridylazo)resorcinol (PAR) [41–43]. PAR–metal complexes show relatively high molar absortivities ($>20\,000$) in the range 500–540 nm and a relatively low background absorbance at the same wavelengths.

This paper describes an automated chelation ion-exchange chromatographic system followed by postcolumn derivatization and spectrophotometric detection for the simultaneous determination of trace levels of cadmium and lead in sea water. In particular, we discuss the preconcentration of cadmium and lead present in sea water on highly cross-linked iminodiacetate chelating resin and the use of cation-exchange chromatography for the separation of the metals. Selectivity, interferences, linear dynamic range and detection limits of the technique are also discussed.

## EXPERIMENTAL

### *Instrumentation*

A metal-free high-pressure ion chromatographic (IC) system including one gradient pump (GPM, 4500i series), two single reciprocating piston pumps

(DQP) and a pressurized postcolumn reagent delivery module (RDM) (Dionex, Sunnyvale, CA, USA) was used. The gradient pump was employed for delivering different reagents during the matrix elimination, metal elution and chelating column reconditioning steps. One DQP pump was used for sample preconcentration on a MetPac CC-1 column, and the other DQP pump, equipped with a pulse damper, was used to deliver eluent through the analytical column. Two air-activated metal-free slider valves were used for switching reagents, sample, pumps and columns. The eluent and postcolumn reagent solution were mixed with the aid of a low-dead-volume T-piece, positioned at the exit of the analytical column, followed by a packed-bed reaction coil. A VDM UV–Vis detector (Dionex) was used for metal detection. Traces of metals in the chromatographic system were removed by flushing all flow paths, pumps, valves and columns with 0.2 *M* oxalic acid for 3 h at 1 ml/min, followed by rinsing with deionized water. After column removal, the flow path was washed with 6 *M* $HNO_3$ for 3 h at 1 ml/min, followed by rinsing with deionized water. Data manipulation and the operation of all components in the system were controlled by AI-450 chromatographic software (Dionex) interfaced via an Advanced Controller Interface (ACI; Dionex) to a Model 80386-based computer (Olivetti, Ivrea, Italy).

Fig. 1 shows a flow diagram of the automated chelation ion chromatographic system. The programming of time and events for columns, valves and reagent switching is outlined in Table I.

A PAR 384 B polarographic analyser (Princeton Applied Research, Princeton, NJ, USA) equipped with a mercury electrode (Model 303 SMDE) was used for cadmium and lead determination in seawater samples by differential-pulse anodic stripping voltammetry (DPASV).

### *Reagents and standards*

Potassium chloride, potassium sulphate, potassium nitrate and oxalic acid were of analytical-reagent grade (Novachimica, Milan, Italy) and hydrochloric acid, sulphuric acid, nitric acid, ammonia solution and acetic acid were of Ultrex grade (J. T. Baker, Phillipsburg, NJ, USA). 4-(2-Pyridylazo)resorcinol (PAR) of analytical-reagent grade was obtained from Aldrich (Milwaukee, WI, USA). A 2 *M* ammonium acetate solution (pH 5.5 ± 0.1) was prepared from ultrapure acetic acid and ammonia solution. All reagents and standards were prepared daily with ultra-pure deionized water (<0.1 μS at 25°C) obtained by treating doubly distilled water in a Milli-Q system (Millipore, Milford, MA, USA). Working standard solutions were prepared by serial dilution of a stock standard solution containing 1000 mg/l of Cd(II), Pb(II), Fe(II), Mn(II), Co(II), Ni(II), Zn (II) and Cu(II) (BDH, Poole, UK).

All standard, samples and reagents were stored in polyethylene bottles cleaned and conditioned fol-

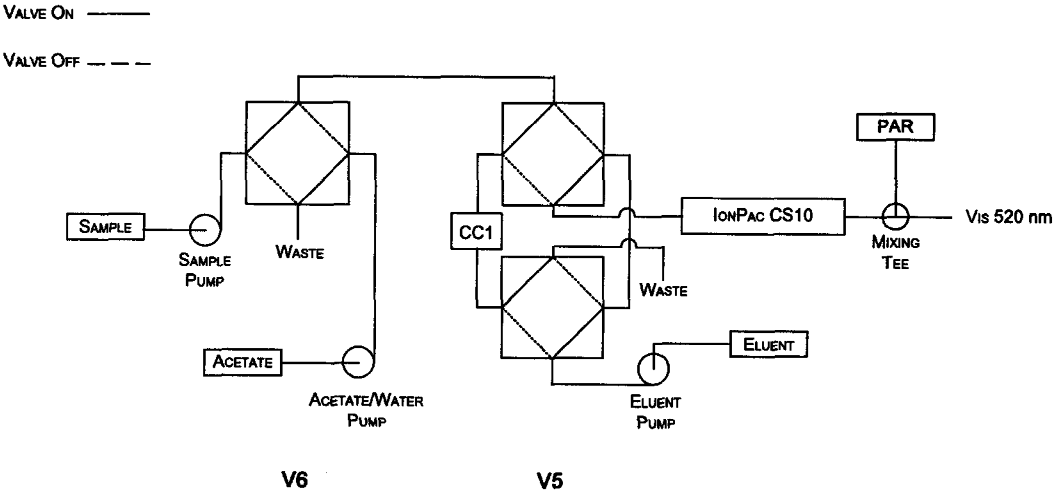

Fig. 1. Schematic flow diagram of automated chelation IC.

TABLE I

CHELATION IC PROGRAMME FOR CONCENTRATING 20-ml SEA-WATER SAMPLES

| Time (min) | Sample[a] | Acetate[b] | Water[b] | Eluent[c] | V5[d] | V6[d] | Event |
|---|---|---|---|---|---|---|---|
| 0.0 | 0 | 1 | 0 | 1 | 0 | 1 | Start MetPac conditioning |
| 2.0 | 0 | 1 | 0 | 1 | 0 | 1 | End MetPac conditioning |
| 2.1 | 0 | 0 | 1 | 1 | 0 | 1 | Start acetate elimination |
| 2.9 | 0 | 0 | 1 | 1 | 0 | 1 | End acetate elimination |
| 3.0 | 1 | 0 | 0 | 1 | 0 | 0 | Load sample on MetPac |
| 11.0 | 1 | 0 | 0 | 1 | 0 | 0 | Sample loaded |
| 11.1 | 0 | 1 | 0 | 1 | 0 | 1 | Start matrix elimination |
| 11.4 | 0 | 1 | 0 | 1 | 0 | 1 | Matrix eliminated |
| 11.5 | 0 | 0 | 0 | 1 | 1 | 1 | Injection |

[a] Flow-rate 2.5 ml/min.
[b] Flow-rate 3 ml/min.
[c] Flow-rate 1 ml/min.
[d] 1 = On; 0 = off.

lowing suggested procedures for trace element determination [44,45].

*Eluent*

The final choice for the chromatographic eluent was 0.075 *M* $H_2SO_4$–0.1 *M* HCl–0.1 *M* KCl. The eluent flow-rate was 1 ml/min.

*Postcolumn reagent*

The postcolumn reagent (PCR) solution consisted of 0.3 m*M* PAR in 1.0 *M* 2-dimethylaminoethanol–0.5 *M* ammonia solution–0.5 *M* sodium hydrogencarbonate buffer. The solution was filtered through a 0.45-μm filter before use. The chromatographic response (peak area) was found to be dependent on the PAR flow-rate. Excellent linearity was obtained in the range 0.2–0.5 ml/min. The PCR flow-rate was finally set to 0.5 ml/min. The detector wavelength was set at 520 nm.

*Columns*

Preconcentration and matrix elimination were carried out on a MetPac-CC1 (Dionex) column (50 mm × 4 mm I.D.) packed with a styrene-based macroporous 12% cross-linked iminodiacetate-functionalized chelating resin. The particle size was 20 μm and the capacity of the resin was about 0.9 mequiv. Cu(II)/g. The separations were carried out on a IonPac CS10 (Dionex) column (250 mm × 4 mm I.D.) packed with 8.5-μm solvent-compatible PS–DVB substrate agglomerated with 175-nm cation-exchange latex for a total ion-exchange capacity of 80 μequiv. per column.

*Sea-water sampling*

Surface sea-water samples (1–2 m depth) were collected using a Niskin bottle from the Taranto gulf (Ionian Sea, Italy). Samples were filtered immediately after collection by vacuum filtration through glass-fibre filters (GF/F grade, diameter 47 mm, nominal pore size 0.7 μm) and preserved by the addition of ultra-clean concentrated hydrochloric acid (1 ml/l). The samples were immediately frozen at −4°C using polypropylene bottles for storage. Before analysis, acidified samples were buffered with 2 *M* ammonium acetate (pH 5.5).

## RESULTS AND DISCUSSION

*Chelation ion chromatography*

The complete chromatographic procedure for sample preconcentration, matrix elimination and separation can be described as follows: (1) the MetPac-CC1 column was activated with 2 *M* ammonium acetate; (2) sample buffered at pH 5.5 was loaded on to the MetPac-CC1 column; (3) alkali and alkaline-earth metals in the sample were washed off the MetPac-CC1 column with ammonium acetate;

(4) ammonium acetate remaining on the chelating column was washed off with deionized water; (5) the MetPac-CC1 column was switched to the eluent line and metals concentrated on the resin was then injected into the chromatographic system for separation; (6) after separation, PAR, added postcolumn, formed derivatives of metals that were detected by a spectrophotometric detector. A schematic diagram for automated chelation IC is shown in Fig. 1 and the chelation IC programme is described in Table I.

### *Preconcentration on MetPac-CC1 column*

MetPac-CC1 has a highly cross-linked polymeric backbone compared with the Chelex-100 resin type [38]. Because of this characteristic, both the physical and mechanical properties remain stable over a wide range of pH values and ionic strengths.

In the preconcentration of transition metals it has been demonstrated that the recovery is independent of both the flow-rate used for sample loading on to the resin and 2 *M* ammonium acetate flow-rate [38]. Usually the complete elution of Cd(II) and Pb(II) from an iminodiacetate resin such as Chelex-100 was obtained by using a strong acid ($HNO_3$) or a complexing agents such as 0.0025 *M* EDTA at pH 8 [46].

In this work the same eluent as used for the ion chromatographic separation of metals was used to elute them from chelating resin. With these restrictions it was necessary to evaluate how the acidic eluent used for separation could be used for the quantitative elution of metals from the iminodiacetate resin. The types of acids and counter ions chosen must be compatible with the following chromatographic separation.

In Fig. 2 are shown the different elution profiles of cadmium and lead from the MetPac-CC1 column obtained with different acidic solutions. The resulting chromatograms show that elution is more efficient at higher acidity. The best results, corresponding to complete elution of metals in a smaller volume, can be achieved with 0.5 *M* $HNO_3$, which was found not to be useful for the desired ion chromatographic separation. Different mixtures of sulphuric and hydrochloric acid and potassium

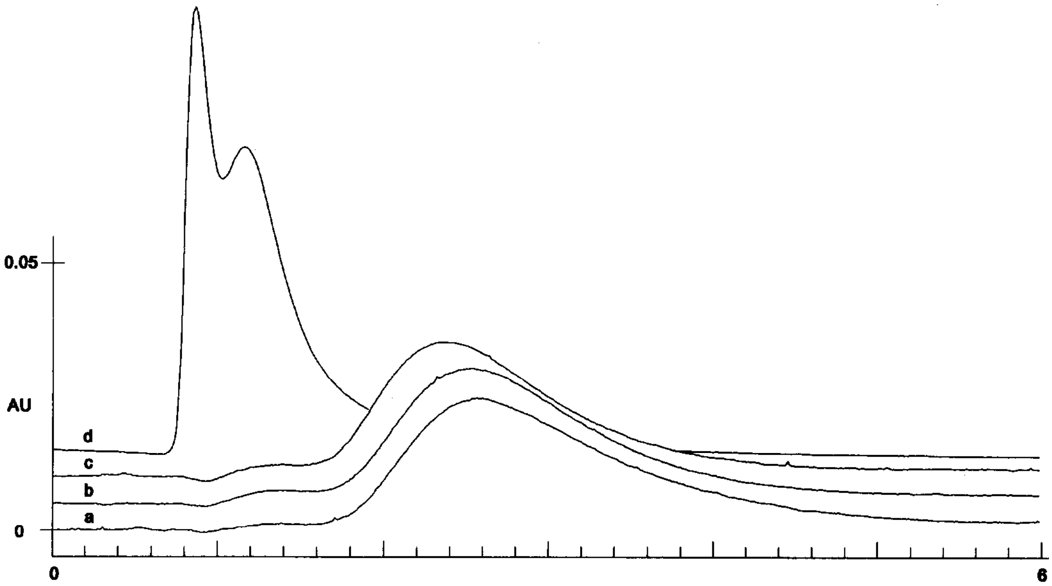

Fig. 2. Elution profile of Cd (500 ng) and Pb (500 ng) from MetPac-CC1 column using different eluents. Flow-rate, 1 ml/min; detection, absorbance (520 nm) after postcolumn derivatization with 0.3 m*M* PAR in 1.0 *M* 2-dimethylaminoethanol–0.5 *M* ammonia solution–0.5 *M* sodium hydrogencarbonate buffer. (a) 0.075 *M* $H_2SO_4$–0.05 *M* HCl–0.1 *M* KCl; (b) 0.075 *M* $H_2SO_4$–0.05 *M* HCl–0.15 *M* KCl; (c) 0.075 *M* $H_2SO_4$–0.1 *M* HCl–0.1 *M* KCl; (d) 0.5 *M* $HNO_3$–0.1 *M* KCl.

chloride elute metals in a larger volume than nitric acid, but in a volume small enough for our purposes. The elution volume for 500 ng of Cd and Pb, concentrated on the MetPac-CC1 column, using the same eluent of chromatographic separation at a flow-rate of 1 ml/min was 2.5 ml, as shown in Fig. 2.

In addition to the acidity effect, the effects of complexing agents such as chloride must also be considered. The formation of chloro–metal complexes contributes to decreasing the elution volume of cadmium and lead from the chelating resin. For the choice of the eluting solution and the successive chromatography all these effects were considered together with PAR postcolumn derivatization compatibility.

### *Matrix elimination*

It has been demonstrated previously that iminodiacetate resins can efficiently eliminate alkali and alkaline-earth metals, resulting in a great advantage in sea-water analysis. Elimination of Na, K, Mg and Ca is necessary because of interferences in chromatography and in determination by postcolumn derivatization with PAR. For the experiment, 50 ml of synthetic sea water with concentrations of 1.30 g/l of Mg and 0.41 g/l of Ca were preconcentrated on the MetPac-CC1 column, then the resin was eluted with 2 *M* ammonium acetate buffered at pH 5.5. The elution volume of alkali and alkaline-earth metals was only 1.5 ml. Changes in the flow-rate from 1 to 3 ml/min did not influence the recoveries of retained metals. With Chelex-100 a decrease in recoveries, as a function of acetate flow-rate, was observed [32].

### *Ion chromatography*

Separation of transition metals can usually be accomplished via complexation with eluent and anion or cation exchange [40]. The main problem with strong complexing eluents such as pyridine-2,6-dicarboxylic acid or oxalate is that they interfere with the metallochromic indicator used for postcolumn reaction. Also, the pH can interfere in the PAR complexation process; a higher pH increases the ionization of PAR, thus exploiting its complexing capabilities, but hydrolysis of metals could be observed along with the simultaneous disappearance of the signal, whereas on the other hand using very low pH can result in precipitation of PAR. The separation of selected groups of transition metals can be readily accomplished using cation-exchange resins. As a result of the differences in the hydrated radii of aquated metal ions within a group (*e.g.*, zinc, cadmium and mercury) and/or different rows of the Periodic Table, sulphonated cation-exchange resins have sufficient selectivity for these separations. Separations of transition metals that are in different rows or columns of the Periodic Table can usually be accomplished by cation exchange without the addition of complexing agents. A secondary equilibrium (complexation) is not required if the metal ions have different valences or different charge densities, which is often the case when the metal ions are well separated in the Periodic Table. Chromatographic separations of Cd and Pb from other transition metals performed on an IonPac CS10 cation exchanger are shown in Fig. 3. An increase in acidity lowers the retention time of the considered metals, while the separation of Cd and Pb from Fe(II) and other transition metals is sufficient.

The effect of the counter ion was investigated, because in general most transition metals show lower retention on cation exchangers as the chloride concentration increases owing to the formation of neutral or anionic complexes. Selectivity generally increases as the chloride concentration increases. For effective separation using IonPac CS10 cation-exchange resin, chloride concentrations of 0.05 *M* and above are required; in instance case cadmium and lead are separated by cation exchange while most of first-row transition elements co-elute under these conditions. Fig. 4 shows chromatograms of a standard solution containing Cd, Pb and Fe(II) analysed with different eluents; the importance of $Cl^-$ as a complexing ion on the separation of different metals can be observed. Sulphate also acts as a ligand and probably contributes to the separation.

The best compromise between total run time and selectivity was achieved with 75 m*M* $H_2SO_4$–100 m*M* HCl–100 m*M* KCl as eluent.

### *Recovery*

For the calculation of recoveries, the MetPac-CC1 column was washed with 6 ml of 0.5 *M* $HNO_3$ at 1 ml/min to eliminate any traces of metals, then rinsed with deionized water. The resin was then converted into the ammonium form by pumping 2 *M* ammonium acetate solution followed by 3 ml of

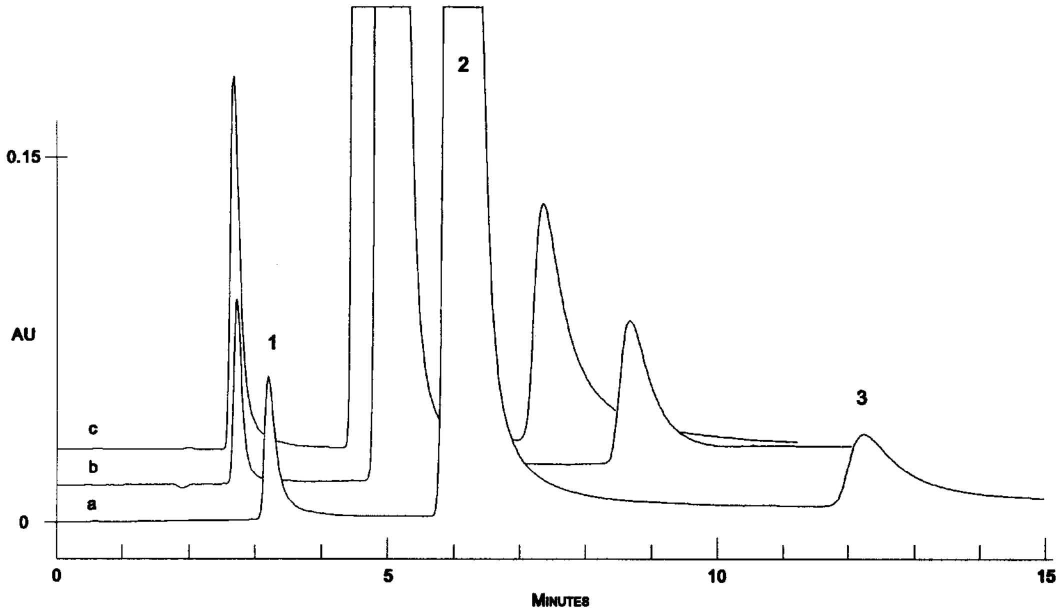

Fig. 3. Chromatogram of a standard solution (500 ng each) of metals with different eluents. Peaks: 1 = Cd; 2 = Fe(II), Ni, Cu, Zn, Co, Mn; 3 = Pb. Column, IonPac CS10; flow-rate, 1 ml/min; detection, as in Fig. 2. (a) 0.075 *M* $H_2SO_4$–0.05 *M* HCl–0.1 *M* KCl; (b) 0.075 *M* $H_2SO_4$–0.1 *M* HCl–0.1 *M* KCl; (c) 0.075 *M* $H_2SO_4$–0.125 *M* HCl–0.1 *M* KCl.

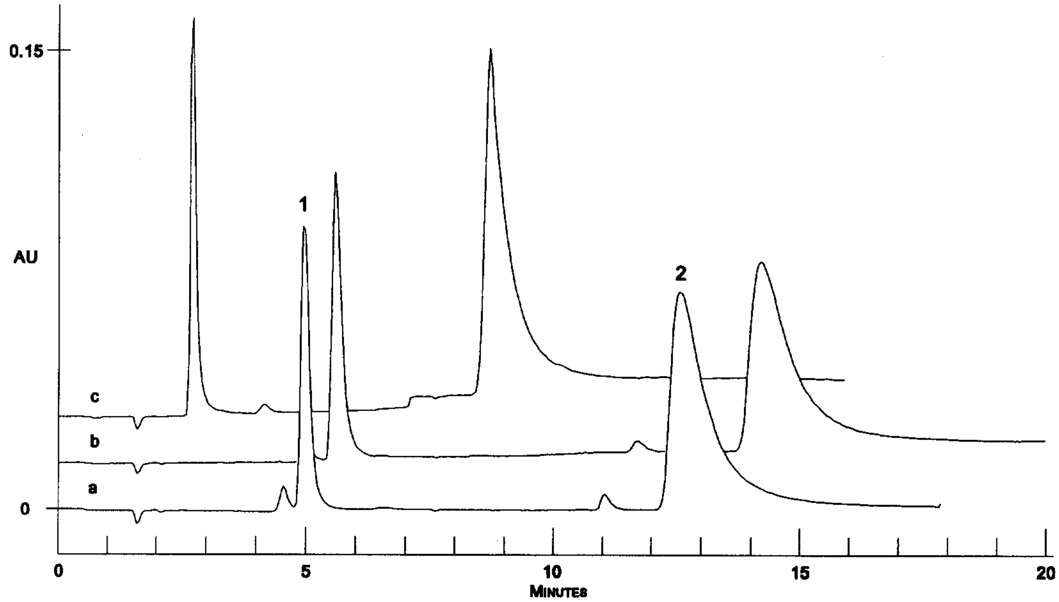

Fig. 4. Chromatogram of a standard solution (1 μg each) of metals with different counter ions in the eluent. Peaks: 1 = Cd; 2 = Pb. Column, IonPac CS10; flow-rate, 1 ml/min; detection, as in Fig. 2. (a) 0.15 *M* $H_2SO_4$–0.05 *M* $K_2SO_4$; (b) 0.15 *M* $H_2SO_4$–0.1 *M* $KNO_3$; (c) 0.15 *M* $H_2SO_4$–0.1 *M* KCl.

TABLE II

RECOVERIES OF METALS ADDED TO DEIONIZED AND SEA-WATER MATRICES

| Element | Recovery (%)[a] | | R.S.D. (%) |
|---|---|---|---|
| | Deionized water | Sea water | |
| Cd | 100 | 91 | 4.8 |
| Pb | 100 | 89 | 5.2 |

[a] Average recoveries ($n = 5$); sample size = 50 ml, concentrated.

deionized water for washing off the residual acetate. A sea-water sample adjusted to pH 5.5 with 2 *M* ammonium acetate was spiked with 10 $\mu$g/l each of Cd and Pb. The content of Cd and Pb was then confirmed by DPASV [47]. The preconcentration and matrix elimination procedure was then effected on-line by the following procedure. First 50 ml of sample were pumped through the MetPac-CC1 column at 1 ml/min. The resin was then washed by pumping 10 ml of 2 *M* ammonium acetate to eliminate alkaline-earth metals; 6 ml of eluent were pumped through the MetPac-CC1 column for elution of metals.

Table II gives the recoveries of cadmium and lead from 50 ml of sea water spiked with 5 $\mu$g/l of each metal.

### *Linearity and detection limit*

The method shows good linearity for both cadmium ($r = 0.997$) and lead ($r = 0.998$) up to 500 ng, which means that is possible to preconcentrate, *e.g.*, 20 ml of sea water with Cd and Pb concentrations ranging from 1 to 50 $\mu$g/l within the linearity of the system. Volumes of sea water up to 200 ml were preconcentrated with good linearity of response at lower metal concentrations. The detection limit (twice the standard deviation of the blank sample) was 2 ng for cadmium and 6 ng for lead.

### *Reproducibility*

The reproducibilities of the peak area and retention time were calculated by performing five replicate analyses of sea-water samples collected far from the coast of Taranto. This sea water, which usually has concentrations of Cd and Pb in the ng/l range, was fortified with 10 $\mu$g/l each of Cd and Pb.

The relative standard deviations (R.S.D.) for peak area were 4.5% and 6.8% for Cd and Pb, respectively. The R.S.D.s for retention time were

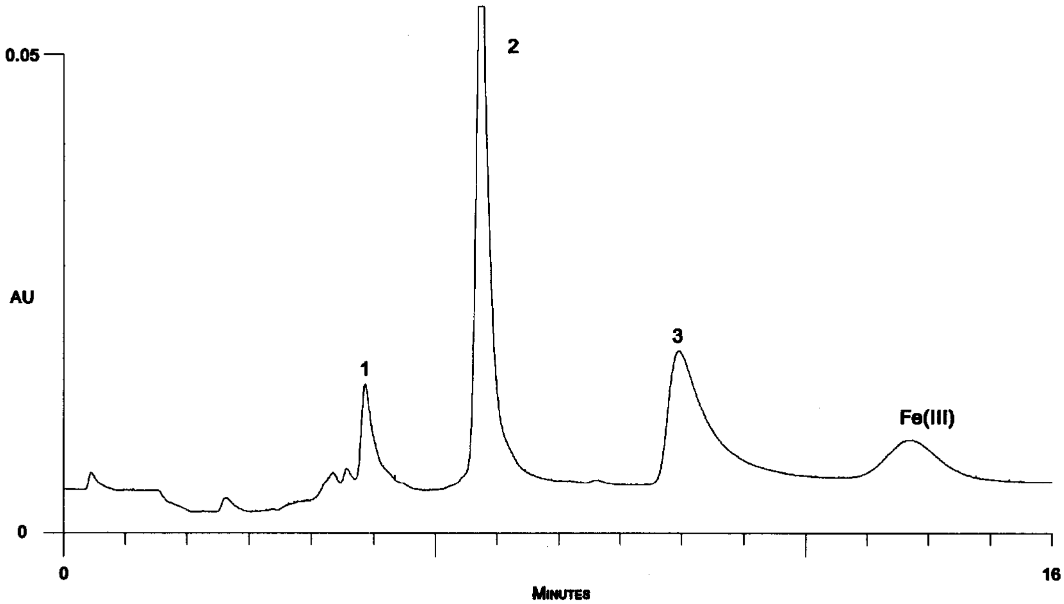

Fig. 5. Chromatogram of a standard solution. Peaks: 1 = Cd (500 ng); 2 = Fe(II), Ni, Cu, Zn, Co, Mn (50 ng each); 3 = Pb (500 ng). Column, IonPac CS10; eluent, 0.075 *M* $H_2SO_4$–0.1 *M* HCl–0.1 *M* KCl; flow-rate, 1 ml/min; detection, as in Fig. 2.

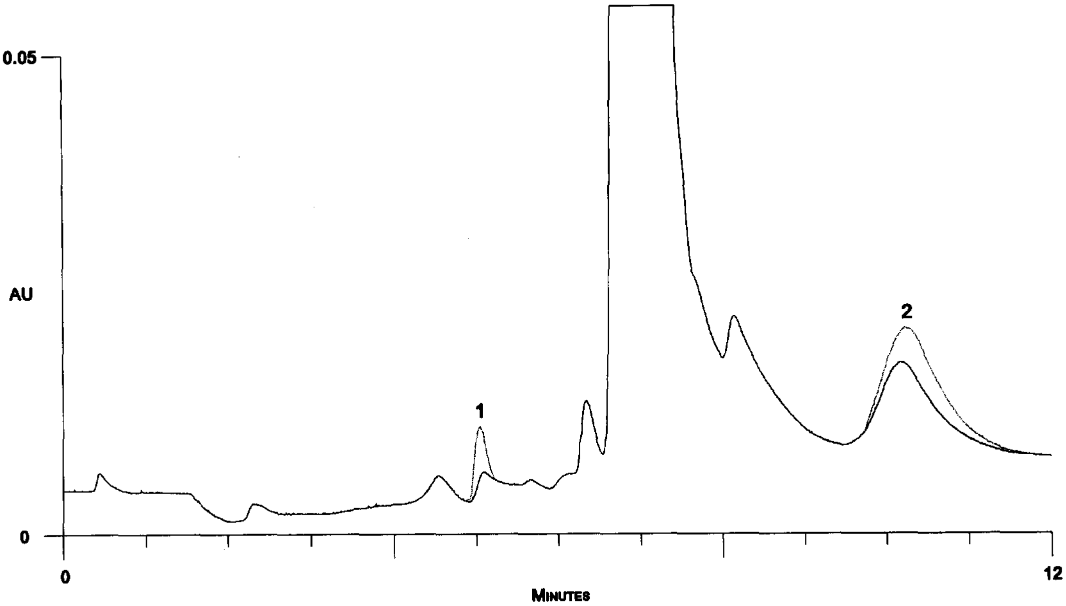

Fig. 6. Determination of metals in Taranto gulf sea water (80 ml, preconcentrated). Peaks: 1 = Cd (0.33 μg/l); 2 = Pb (2.06 μg/l). Dotted line = same sample spiked with 5 μg/l each of Cd and Pb (80 ml, preconcentrated); Cd, 5.50 μg/l; Pb, 7.46 μg/l. Conditions as in Fig. 5.

1.2% and 2.5% for Cd and Pb, respectively.

The reliability of the method was tested by analysing Taranto gulf sea-water samples, usually containing Cd and Pb in the low μg/l range, with both chelation ion chromatography and DPASV. In all instances the results were in good agreement.

### *Sea-water analysis*

*Blank.* Reagents (particularly ammonium acetate) and water were the main source of blank contamination. Major contributions to contamination arise from iron, copper and zinc. This kind of contamination can be reduced by using ultrapure reagents and water. Also, washing the flow paths with nitric and oxalic acid as described elsewhere can reduce the contamination. In any case the eventual contamination due to first-row transition metals does not interfere with cadmium and lead determination, as shown in Fig. 5.

*Sea-water samples.* For sea-water analysis it must be noted that most of the dissolved Cd and Pb can be associated with inorganic colloidal species, such as oxides, silicates, sulphides and organic materials such as humic acids [47]. Colloidal particles were not retained by the chelating resin, hence the values obtained are relative only to the "dissolved fraction" metals concentration, which is lower than the total content. A UV photo-oxidation treatment in acid, which destroys the organic matter, allows bonded metals also to be detected [29].

Fig. 6 shows the chromatogram of a sea-water sample from the Taranto gulf with trace levels of cadmium and lead; the dotted line shows the same sample spiked with 5 μg/l each of Cd and Pb. The pH of both samples was adjusted to 5.5 with 2 *M* ammonium acetate, then 80 ml of each sample were analysed. The R.S.D. for peak area were 6.4% and 7.2% for Cd and Pb, respectively. Good agreement was obtained in comparison with DPASV using the method of Batley and Florence [47].

## CONCLUSION

A simple, automated method for the determination of low concentrations of cadmium and lead in complex matrices, such as sea water, has been developed. The higher cross-linked resin used for preconcentration and matrix elimination provides reliable and reproducible analyses. The chromatographic separation of Cd and Pb by cation-exchange chromatography does not suffer from interferences from transition metals and of postcolumn derivatization with PAR is suitable for detection, without competition in complexation.

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