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New strategies for determination of transition metals by complexation ion-exchange chromatography and post column reaction

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Abstract

A method for the simultaneous determination of metals (Fe^{3+} , Fe^{2+} , Cu, Ni, Zn, Co, Cd, Mn and Pb) at $\mu\text{g/l}$ levels in environmental matrices is demonstrated. The metals are separated by ion chromatography on a mixed-bead ion-exchange column (IonPac CS5A) and detected by post-column reaction and spectrophotometric detection. The use of a gradient program (based on oxalic acid–hydrochloric acid–sodium chloride and sodium nitrate eluents) allows the separation of nine metals in a single run. The direct injection of a large volume of samples lowers the detection limits to below and/or few $\mu\text{g/l}$. The chromatographic conditions and colour-development reaction were optimised. Two post-column reagents, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) and 4-(2-pyridylazo) resorcinol, were tested and detection limits were compared. The use of 5-Br-PADAP increased the sensibility for Cu, Cd, Zn and Mn. For the proposed method, linearity, reproducibility, detection limits and interference due to alkaline-earth metals (noticeably Mg and Ca) were discussed. Under the suggested chromatographic conditions Mg^{2+} and Ca^{2+} up to 0.2 g/l do not interfere with separation and quantitative analysis of the metals. The calibration graphs were linear ($r^2 > 0.986$) in the range 5–5000 $\mu\text{g/l}$. The application of the method to the determination of metals in coastal marine sediments is shown. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Complexation; Marine sediments; Environmental analysis; Metal cations

1. Introduction

The use of ion chromatography (IC) offers several advantages for the determination of metals, including the ability for oxidation state speciation (i.e.: $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Cr}^{3+}/\text{Cr}^{6+}$, $\text{Sn}^{2+}/\text{Sn}^{4+}$, etc.) and multielement capability in a single analysis. Thus, IC is a useful tool for bioavailability studies of toxic metals (i.e.: Pb^{2+} , Cd^{2+}) and their effect on the environment. Conversely, the low concentration ($\mu\text{g/l}$) of

metals and the relatively high concentrations of alkali and alkaline-earth metals in environmental samples represents a limitation in the use of IC for direct metal analysis. In order to deal with this problem, significant work has been done utilising matrix elimination and/or a preconcentration step in order to minimise interferences and to lower detection limits [1–8]. Most IC methods for metal separation are based on cation exchange with reversible complexation [9–19], although some studies have explored anion exchange with irreversible complexation. The bifunctional ion-exchange column

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IonPac CS5A (Dionex, Sunnyvale, CA, USA) is the most effective analytical column for heavy and transition metal separations. The common eluents used are oxalic acid (Ox) [20,21] and pyridine-2,6-dicarboxylic acid (PDCA) [20,22,23]. The selectivity of the separation is due to the different degrees of association between the metals and the chelating agent producing different net charges on the metal complexes.

PDCA was used as eluent and detection accomplished using 4-(2-pyridylazo) resorcinol (PAR) as post-column reaction agent and absorbance monitoring at 530 nm. In this case metals are separated as anionic complexes: the anion-exchange approach does offer some advantages with respect to selectivity and the analysis of complex samples [24–30]. These chromatographic conditions are not suitable for Pb^{2+} determination because of competition in complexation. The metal–PDCA complexes are more stable than corresponding metal–Ox complexes, so the sensitivity is in some case reduced.

Transition metals are separated as both cationic and anionic complexes with the oxalate chelating agent. The use of an oxalic eluent does not allow Fe determination and the detection limit for Pb^{2+} is too high for practical purposes.

The present work involves two strategies: (1) the optimisation of the composition of the two eluents (based on oxalic acid–hydrochloric acid–sodium chloride and sodium nitrate) and of the gradient program in order to modulate oxalate complexation and anion-exchange selectivity and (2) the use of a new reagent 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) for post-column reaction in order to enhance selectivity and lower the detection limits of some metals by direct injection.

Recently [31] 5-Br-PADAP was used as a novel derivatizing agent whose metal complexes showed relatively high molar absorptivities ($>10^5$) in the range 550–570 nm and it had a relatively low background absorbance [32,33]. The injection of a large sample [34,35] lowers the detection limits to less than a few $\mu\text{g}/\text{l}$, comparable to atomic absorption spectrometry (AAS) or inductively coupled plasma (ICP) techniques without any need to increase instrument complexity.

In this work, a comparison between the different sensitivities obtained using PAR or 5-Br-PADAP as

post-column reagent is made. For the suggested method, linearity, reproducibility, detection limits and interference due to alkaline-earth metals (noticeably Mg and Ca) are discussed. The method can be used for the analysis of metals in real samples such as drinking waters and wastewaters. In this paper, its application for the simultaneous determination of labile and total metals in marine sediments is shown.

2. Experimental

2.1. Instrumentation

Chromatographic analyses were performed on a metal-free high-pressure ion chromatograph, model 4500i (Dionex) which included one gradient pump GPM-2, a post-column pneumatic controller for post-column reagent addition and a VDM-2 variable wavelength absorbance detector set at 530 nm. A Rheodyne model 9126 injector was used with different volume sample loops. Trace of metals in the chromatographic system were removed by flushing all flow paths, pump and columns with 0.2 M oxalic acid for 2 h at 1 ml/min, followed by rinsing with deionized water. The 250×4 mm I.D. IonPac CS5A (Dionex) analytical column (9 μm bead diameter, ethylvinylbenzene functionalized with both quaternary ammonium and sulfonate functional groups) was used for the separation of metals. The column has a microporous 55% cross-linked resin core based on hydrophobic poly(ethylvinylbenzene–divinylbenzene) that has been agglomerated with two layers of permeable ion-exchange latex particles. The first sulphonic latex layer is attached to the surface of the structural polymer by a quaternary amine graft. The outer aminated latex layer is electrostatically bonded to the sulphonic layer. Thus, simply changing the eluent can make major selectivity changes. The 50×4 mm I.D. IonPac CG5A guard column was placed prior to the CS5A in all experiments to prevent potential fouling of the analytical column. In order to remove oxygen from columns, a solution of 0.1 M sodium sulphite was pumped through the columns for 1 h.

All measurements were made at room temperature. In all cases, injection of the sample was done at

least in triplicate. All the samples were filtered through a 0.45- μm filter. A 750- μl sample loop was chosen for all the determinations. Chromatographic conditions are summarised in Table 1. Data collection and the operation of all components in the system were controlled by DIONEX PEAKNET 5.01 chromatography software interfaced via an ACI-2 advanced computer interface to a Vectra XU 6/0200 computer (Hewlett-Packard).

2.2. Reagents and standards

All reagents were analytical grade and contained very low concentrations of trace metals. Nitric acid and hydrochloric acid were Suprapur (Merck, Darmstadt, Germany). Pyridine-2,6-dicarboxylic acid (PDCA), PAR and 5-Br-PADAP were obtained from Aldrich (Milwaukee WI, USA). Potassium hydroxide, Triton X-100, potassium sulphate, formic acid, 2-dimethylaminoethanol, ammonium hydroxide, sodium chloride, sodium nitrate and sodiumhydrogen carbonate were analytical reagent grade (Novachimica, Milan, Italy). Ultrapure water with con-

ductivity $<0.1 \mu\text{S}$ (DI water) was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). Working standard solution of metals were prepared by serial dilution of stock standard solutions of each metal containing 1000 mg/l (BDH, Poole, UK). Normal precautions for trace analysis were observed throughout.

2.3. Eluents and post-column reagents

The eluents were: (A) 28 mM oxalic acid, 45 mM NaCl, 116 mM NaNO_3 , 40 mM HCl and (B) 28 mM oxalic acid, 45 mM NaCl, 265 mM NaNO_3 , 40 mM HCl. The eluents were purged with nitrogen for 20 min before use, since the ferrous ion is easily oxidised to the ferric ion. The flow-rate was 1 ml/min. The gradient program is shown in Table 1. Two post-column reagents were used (Table 1): 5-Br-PADAP and PAR. Prior to use, the reagents must be filtered on a 0.2- μm filter. Since 5-Br-PADAP and PAR are readily oxidised they were degassed and stored under nitrogen.

Table 1
Ion chromatographic conditions

	PDCA	OxGradient		
Columns	IonPac CG5A+CS5A	IonPac CG5A+CS5A		
Eluents	7 mM PDCA	A	B	
	66 mM KOH	28 mM Oxalic acid	28 mM Oxalic acid	
	5.6 mM K_2SO_4	45 mM NaCl	45 mM NaCl	
	74 mM HCOOH	116 mM NaNO_3	265 mM NaNO_3	
Gradient program	–	40 mM HCl	40 mM HCl	
		Time	%A	%B
		0	100	0
		9	0	100
Flow-rate (ml/min)	1.0	1.0		
Injection loop (μl)	750	750		
Post-column reagent	PAR	5Br-PADAP		
	0.4 mM PAR	0.3 mM 5Br-PADAP		
	1 M 2-Dimethylaminoethanol	0.8% Triton X-100		
	0.5 M NH_4OH	0.5 M NH_4OH		
	0.3 M NaHCO_3 (pH 10.4)	0.3 M NaHCO_3 (pH 10.5)		
Flow-rate (ml/min)	0.6	0.6		
Detection	Vis 530 nm	Vis 560 nm		

3. Results and discussion

3.1. Chromatographic separation

The IonPac CS5A has cation and anion-exchange capacity, allowing metals to be separated as cations and anions on a single column. Hydrated and weakly complexed transition metals can be separated as cations on cation-exchange sites. By adding a carboxylic acid chelating agent to the eluent the net charge on the metal is reduced since the carboxylic acids are anionic in solution above their pK_a values.

The selectivity of the separation is due to the different degrees of association between the metals and the chelating agents producing different net charges on the metal complexes. If strong enough chelating agents are used in high enough concentrations, the net charge of the metal complexes can be negative and these anionic species are separated by anion exchange.

In the last few years, a PDCA eluent was used for metal separation and detection was accomplished using PAR as post-column reagent with absorbance monitoring at 530 nm.

PDCA forms strong anionic complexes ($\beta > 10^8$) with most metal ions; thus the separation of metals with PDCA on the IonPac CS5A column is an anion-exchange separation. The PDCA eluent allows

Fe(II,III) separation (Fig. 1), but the detection limits for some metals (i.e. Pb) are not satisfactory for trace analysis because the metal–PDCA complexes are very stable. A separation of transition and heavy metals can be also achieved using an oxalic acid eluent. This separation has both anion and cation-exchange components: since metals, such as Pb(II) and Cd(II), form relatively weak complexes with oxalate, they were separated by cation exchange. The other metals form stable complexes with oxalate and can be separated by anion exchange. Oxalic acid eluent does not elute the iron; therefore, the column should be periodically cleaned in order to prevent excessive accumulation of iron from samples.

In the present work new compositions of eluents, based on oxalic and hydrochloric acids, were studied. The chromatographic method allows the separation of nine metals on IonPac CS5A in one run and, in particular, both the lead determination and the Fe²⁺/Fe³⁺ speciation in the same run. Both the gradient elution and the composition of eluents were optimised. And a series of gradient programs were tested. The best conditions are summarised in Table 1.

The separation of transition metals using the oxalic acid–HCl–NaCl–NaNO₃ gradient is accomplished predominantly by anion exchange. For metals which form stable complexes with oxalic acid,

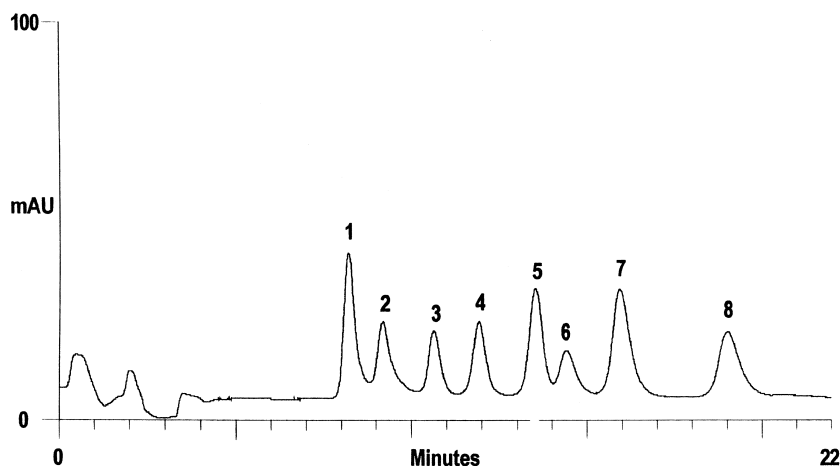


Fig. 1. Chromatogram of a standard solution of transition and heavy metals. Eluent: 7 mM PDCA, 66 mM KOH, 5.6 mM K₂SO₄, 74 mM HCOOH (pH 4.2). Post-column reagent: 0.4 mM PAR, 1 M 2-dimethylaminoethanol, 0.5 M NH₄OH, 0.3 M NaHCO₃ (pH 10.4). Peaks: 1=Fe³⁺ (50 µg/l); 2=Cu²⁺ (50 µg/l); 3=Ni²⁺ (150 µg/l); 4=Zn²⁺ (50 µg/l); 5=Co²⁺ (50 µg/l); 6=Cd²⁺ (250 µg/l); 7=Mn²⁺ (150 µg/l) and 8=Fe²⁺ (50 µg/l).

Table 2

Comparison between the order of elution and the stability constants of metal oxalate complexes; chromatographic conditions as in Table 1

Metal	Elution order	Ox ²⁻ (log β_2)
Cu(II)	1	9.5
Cd(II)	2	4.1
Ni(II)	3	6.6
Zn(II)	4	6.4
Co(II)	5	5.9
Mn(II)	6	4.4
Fe(II)	7	5.2
Fe(II)	8	18.5 (log β_3)
Pb(II)	9	6.3

mainly Cu, Ni, Zn, Co and Mn, anion-exchange retention dominates with elution order being inverse-related to the stability constant. The first row transition metals form divalent anionic complexes with oxalate, $M(\text{Ox})_2^{2-}$. Fe(III) forms a trivalent complex with oxalate, $\text{Fe}(\text{Ox})_3^{3-}$ and elutes later than most of the first row transition metals, but faster than expected from β value of stability constant. Chloride is a weak ligand compared to oxalate and thus has little affect on the chromatography, but its presence in the eluent system is fundamental for the elution of iron, due probably to a mixed oxalate–chloride complexation of iron species.

The retention of Pb with the oxalate eluent is

thought to be primarily anion exchange, and the complex, $\text{Pb}(\text{Ox})_2^{2-}$ behaves as a polarizable anionic complex. Cadmium forms the least stable complex with oxalate and based on retention time, must have a relatively large hydrated radius (see Table 2 for the comparison between elution order and complexation constants with oxalate only). The nitrate is used for its eluting power as anionic eluent and has no role as a complexing agent.

Moreover, the use of NaNO_3 in the eluent reduced the tailing of the Pb^{2+} and Cd^{2+} peaks [31] and improved the peak shape. A typical chromatogram is shown in Fig. 2. The separation of metals was effected in about 15 min.

3.2. Post-column reagents and spectrophotometric detection

The post-column reagent choice is crucial for the improvement of detection limits. PAR is the most commonly used reagent in the spectrophotometric detection of transition metals, but recently 5-Br-PADAP has been used [31] because it forms stable metal complexes with metal ions. The colour development depends upon 5-Br-PADAP concentration; when it is increased, the background absorbance increases too. The presence and the concentration of a surface-active agent (usually Triton

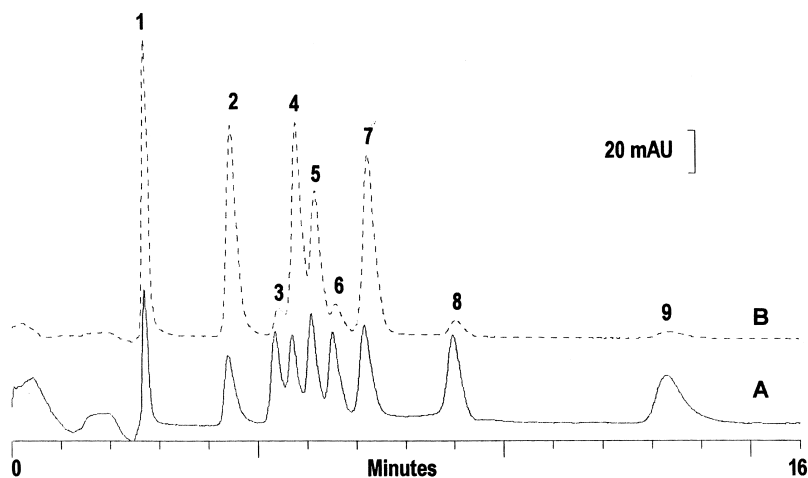


Fig. 2. Chromatogram of a standard solution of transition and heavy metals. Chromatographic conditions as in Table 1. Eluent: OxGradient. Post-column reagent: (a) PAR; (b) 5Br-PADAP. Peaks: 1= Cu^{2+} (50 $\mu\text{g}/\text{l}$); 2= Cd^{2+} (100 $\mu\text{g}/\text{l}$); 3= Ni^{2+} (50 $\mu\text{g}/\text{l}$); 4= Zn^{2+} (50 $\mu\text{g}/\text{l}$); 5= Co^{2+} (50 $\mu\text{g}/\text{l}$); 6= Fe^{2+} (100 $\mu\text{g}/\text{l}$); 7= Mn^{2+} (50 $\mu\text{g}/\text{l}$); 8= Fe^{3+} (50 $\mu\text{g}/\text{l}$); 9= Pb^{2+} (500 $\mu\text{g}/\text{l}$).

Table 3
Comparison between the different sensitivities (peak area counts) for metals using PAR and 5-Br-PADAP^a

Element	Sensitivity (peak area counts)	
	PAR	5-Br-PADAP
Cu(II)	41 114	83 337
Cd(II)	27 329	97 802
Ni(II)	33 388	8 133
Zn(II)	34 137	86 378
Co(II)	42 534	33 161
Fe(II)	21 638	19 922
Mn(II)	42 208	58 360
Fe(III)	65 034	18 972
Pb(II)	42 442	8 381

^a Chromatographic conditions as in Table 1. Eluent: OxGradient. Concentrations: Cu²⁺ (25 µg/l); Cd²⁺ (50 µg/l); Ni²⁺ (25 µg/l); Zn²⁺ (25 µg/l); Co²⁺ (25 µg/l); Fe²⁺ (50 µg/l); Mn²⁺ (25 µg/l); Fe³⁺ (25 µg/l); Pb²⁺ (250 µg/l).

X-100) is also important in order to avoid precipitation of metal complexes, which could lower sensitivity. pH also influences colour development; high pH increases the ionisation of 5-Br-PADAP, thus exploiting its complexing capabilities. When pH increases, the background absorbance also increases and provokes hydrolysis of metals. The optimum pH value for colour development was 10.5 [31] for various metals. For lead determination, the sensibility increases at pH > 10.5.

In Fig. 2 two chromatograms obtained using PAR or 5-Br-PADAP as post-column reagent are shown. In Tables 3 and 4 a comparison between sensitivity and detection limits related to use of two reagents is

Table 4
Detection limits for different metals calculated according IUPAC guidelines [36] and using PAR or 5-Br-PADAP post-column reagent; injected volume 750 µl

Element	Detection limit (µg/l)	
	PAR	5-Br-PADAP
Cu(II)	0.5	0.3
Cd(II)	2.5	0.5
Ni(II)	0.8	2.7
Zn(II)	0.6	0.3
Co(II)	0.4	0.8
Fe(II)	2.2	2.3
Mn(II)	0.6	0.4
Fe(III)	0.3	1.1
Pb(II)	8.0	39.0

shown. 5-Br-PADAP increases sensitivity for Cu, Cd, Zn and Mn, whereas it decreases remarkable sensitivity for Ni, Fe³⁺ and Pb. Therefore, the post-column choice depends upon the kind of metal to be determined. The use of a mixed reagent could represent a valid option to increase sensibility for lead. Research on this subject is still on-going.

3.3. Interferences

The selectivity of IonPac CS5A was evaluated in order to avoid the potential interference of main cationic components in real samples, i.e. alkali and alkaline-earth metals. Alkaline metals do not interfere with the determination, while Mg and Ca react with post-column reagents and elute in the chromatogram, but the sensitivity in these operating conditions is 100–500 times lower than that of transition metals. At high levels Ca and Mg can interfere with the column capacity and retention times.

3.4. Linearity and detection limits

For the considered metals the method shows a good linearity ($r^2 > 0.986$) for concentrations ranging from 5 to 5000 µg/l. The use of the large volume injection technique (750 µl) lowers the detection limits and does not have any detrimental effect on peak efficiency or asymmetry. Under these conditions, the relatively large quantity of sample injected into the eluent stream does not elute the metals that are concentrated at the head of the column. The detection limits, calculated according IUPAC suggestion [36], are summarised in Table 4.

3.5. Analysis of sediment samples

Fig. 3 shows a chromatogram of the labile bound metals extract, according to the method of Tessier et al. [37], with 1 M ammonium acetate (pH 5) from a surface marine sediment taken in Mar Piccolo of Taranto (Italy). Knowledge of the chemical speciation of metals in sediments is important in order to assess the capacity of those sediments to release metals. This method allows the Fe²⁺/Fe³⁺ speciation which is very important for the study of redox processes at water–sediment interface.

Fig. 4 shows the chromatogram of total metals

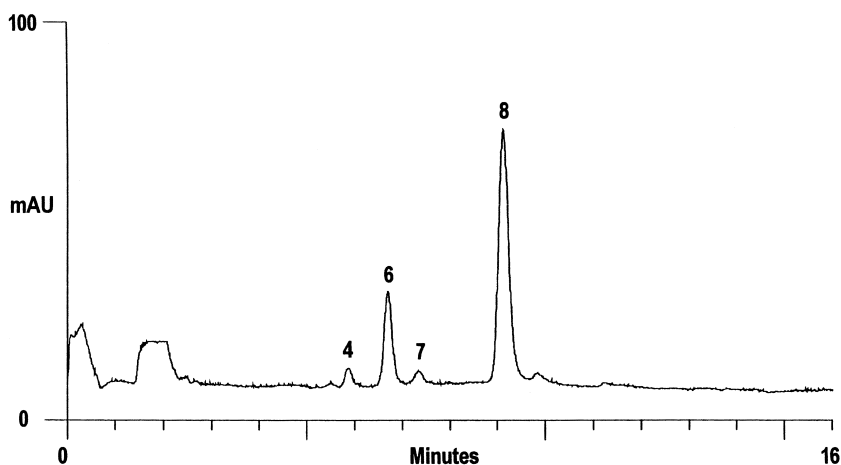


Fig. 3. Chromatogram of labile bound metals extract with ammonium acetate from a marine sediment taken in Mar Piccolo of Taranto. Chromatographic conditions as in Table 1. Eluent: OxGradient. Post-column reagent: 5-Br-PADAP. Peaks: 4= Zn^{2+} (3.15 mg/kg dry mass), 6= Fe^{2+} (68.02 mg/kg dry mass), 7= Mn^{2+} (2.52 mg/kg dry mass), 8= Fe^{3+} (40.52 mg/kg dry mass).

from a certified marine sediment obtained from International Atomic Energy Agency Laboratory in Monaco (IAEA-356). A 0.1-g amount of sediment was transferred into a PTFE vessel and digested with 5 ml of concentrated HNO_3 and 5 ml of concentrated HCl in a microwave oven system (CEM, USA, model MSD 2000). The digested sample was diluted to 50 ml with deionized water, filtered and analysed by direct injection. The quantitative analysis was

effected by standard addition method. Found concentrations (Table 5) are in good agreement with certified values.

4. Conclusions

The IonPac CS5A with a new eluent system allows the simple and efficient determination of trace

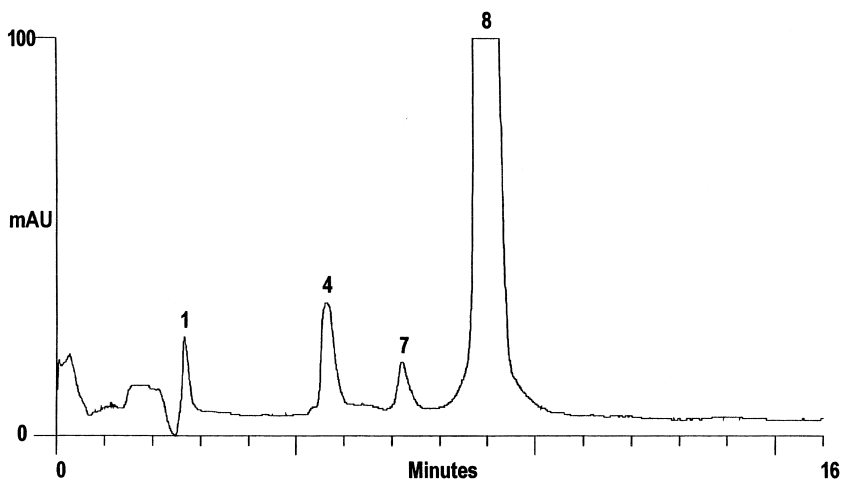


Fig. 4. Chromatogram of metals from certified marine sediment. Chromatographic conditions as in Table 1. Eluent: OxGradient. Post-column reagent: 5-Br-PADAP. Peaks: 1=Cu (358 mg/kg dry mass), 4= Zn^{2+} (979 mg/kg dry mass), 7= Mn^{2+} (302 mg/kg dry mass), 8= Fe^{3+} (23.73 g/kg dry mass).

Table 5

Precision and accuracy of analytical method obtained using a certified polluted marine sediment (IAEA-356)^a

Metal	Certified conc. ^b	Confidence interval ^c	Found (RSD, %)
Cu	365	351–375	358 (7.1)
Zn	977	936–1019	979 (6.4)
Mn	312	288–323	302 (5.7)
Fe	24 100	22 500–25 100	23 730 (12.4)

^a Concentrations are expressed in mg/kg dry mass ($n=5$).^b Median values.^c 95% confidence intervals of the median.

transition metals in natural waters and marine sediments. Low detection limits can be achieved using larger (750–1000 μ l) sample volumes. The use of eluents containing oxalic acid, hydrochloric acid and sodium nitrate allows a good chromatographic separation for the various metals. Detection limits are improved for cadmium but are still too high for lead using 5-Br-PADAP as post-column reagent. Therefore, the work development is concentrated on finding a new post-column reagent which may further improve sensitivity, particularly for heavy metals. At the moment, this method is very effective for analysis of labile or weakly complexed metals in marine sediments with direct injection of ammonium acetate extract and allows the study of redox processes. The method is very suitable for analysis time reduction and for lowering risks of chemical contamination of the sample.

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References

- [1] A. Siriraks, H.M. Kingston, J.M. Riviello, *Anal. Chem.* 62 (1990) 1185.
- [2] J.M. Riviello, A. Siriraks, R.M. Manabe, R. Roehl, M. Alforque, *LC·GC* 9 (1991) 704.
- [3] O.J. Challenger, S.J. Hill, P. Jones, *J. Chromatogr.* 639 (1993) 197.
- [4] L. Ebdon, A. Fisher, H. Handley, P. Jones, *J. Anal. At. Spectrom.* 8 (1993) 979.
- [5] R. Caprioli, S. Torcini, *J. Chromatogr.* 640 (1993) 365.
- [6] S. Mou, A. Siriraks, J.M. Riviello, *Sepu* 12 (1994) 166.
- [7] B. Paull, M. Foulkes, P. Jones, *Analyst (London)* 119 (1994) 937.
- [8] N. Cardellicchio, S. Cavalli, J.M. Riviello, *J. Chromatogr.* 640 (1993) 207.
- [9] S. Cavalli, J.M. Riviello, A. Woodruff, N. Advalovic, Presented at the 1996 International Ion Chromatography Symposium, University of Reading, Reading, 1996, paper No. 45.
- [10] S. Reiffenstuhel, G. Bonn, *J. Chromatogr.* 482 (1989) 289.
- [11] X. Cui, F. Dong, *Sepu* 7 (1989) 293.
- [12] J. Hradil, F. Svec, A.A. Aratskova, L.D. Belyakova, V.I. Orlov, *J. Chromatogr.* 509 (1990) 369.
- [13] K.A. Ruth, R.W. Shaw, *J. Chromatogr.* 546 (1991) 243.
- [14] V.I. Orlov, A.A. Aratskova, A.R. Timerbaev, O.M. Petrukhin, *Zh. Anal. Khim.* 47 (1992) 686.
- [15] M.D.H. Amey, D.A. Bridle, *J. Chromatogr.* 640 (1993) 323.
- [16] P. Alumaa, J. Pentsuk, *Chromatographia* 38 (1994) 566.
- [17] X.S. Zhang, X.P. Jiang, *J. Chromatogr. A* 671 (1994) 23.
- [18] J. Carnevale, P.E. Jackson, *J. Chromatogr. A* 671 (1994) 115.
- [19] S. Zappoli, C. Bottura, *Anal. Chem.* 66 (1994) 3492.
- [20] P.L. Buldini, S. Cavalli, A. Mevoli, E. Milella, *J. Chromatogr. A* 739 (1996) 131.
- [21] A.W. Al-Shawi, R. Dahl, Presented at the 1996 International Ion Chromatography Symposium, The University of Reading, Reading, 1996, paper No. 59.
- [22] J. Riviello, A. Woodruff, C. Pohl, Presented at the PittCon 1996, paper No. 1193.
- [23] K.A. Ruth, R.W. Shaw, *J. Chromatogr.* 546 (1991) 243.
- [24] R.D. Rocklin, *Anal. Chem.* 56 (1984) 1959.
- [25] T. Tanaka, *Fresenius' Z. Anal. Chem.* 320 (1985) 125.
- [26] F.I. Brouček, R.A. Demetrasvili, O.V. Orlova, *Izv. Akad. Nauk. Gruz. SSR. Ser. Khim.* 14 (1988) 232.
- [27] O.N. Obrezkov, V.I. Slyamin, O.A. Shpigun, *Anal. Sci.* 6 (1990) 617.
- [28] Z. Lei, S. Tian, J. Chen, *Gaodeng Xuexiao Huaxue Xuebao* 10 (1989) 156.
- [29] H. Siren, M.L. Riekkola, *Mikrochim. Acta* 2 (1989) 77.
- [30] E.M. Basova, T.A. Bol'shova, E.N. Shapolova, V.M. Ivanov, *Zh. Anal. Khim.* 45 (1990) 1947.
- [31] H. Lu, S. Mou, Y. Yan, S. Tong, J.M. Riviello, *J. Chromatogr. A* 800 (1998) 247.

- [32] W. Jim, *Phys. Testing Chem. Anal. B, Chem. Anal.* 31 (1995) 53.
- [33] Y.X. Yuan, H.Q. Liu, Y.J. Whang, *Anal. Chem. (Chinese)* 19 (4) (1991) 460.
- [34] N. Cardellicchio, P. Ragone, S. Cavalli, J.M. Riviello, *J. Chromatogr. A* 770 (1997) 185.
- [35] N. Cardellicchio, A. Dell'Atti, S. Giandomenico, A. Di Leo, S. Cavalli, *Ann. Chim. (Rome)* 88 (1998) 819.
- [36] G.L. Long, J.D. Winefordner, *Anal. Chem.* 55 (1983) 712A.
- [37] A. Tessier, P.G.C. Campbell, M. Bisson, *Anal. Chem.* 51 (1979) 844.