



ELSEVIER

Journal of Chromatography A, 770 (1997) 185–193

JOURNAL OF
CHROMATOGRAPHY A

Use of ion chromatography for the determination of transition metals in the control of sewage-treatment-plant and related waters

Nicola Cardellicchio^{a,*}, Pietro Ragone^a, Silvano Cavalli^b, John Riviello^c

^aCNR Istituto Sperimentale Talassografico, via Roma 3, 74100 Taranto, TA, Italy

^bLaboratorio Applicazioni, Dionex S.r.l., via Tulipani 5, 20090 Pieve Emanuele, MI, Italy

^cDionex Corp., 1228 Titan Way, Sunnyvale, CA 94068, USA

Abstract

Transition metals [Fe(III), Fe(II), Cu, Ni, Zn, Co, Cd, Mn] were separated using a mixed-bed ion-exchange column (Dionex IonPac CS5A). A pyridine-2,6-dicarboxylic acid eluent was used and detection was accomplished using post-column reaction with 4-(2-pyridylazo)resorcinol and absorbance monitoring at 530 nm. Under the suggested chromatographic conditions both Mg^{2+} and Ca^{2+} , up to 0.1 g/l and 0.3 g/l, respectively, do not interfere with separation quantitation. Detection limits ranged from 0.06 $\mu g/l$ for Co(II) to 0.38 $\mu g/l$ for Fe(II). The calibration graphs were linear ($r^2 > 0.986$) over two orders of magnitude (5–5000 $\mu g/l$). The selective separation of eight metals in 20 min was obtained and the method was applied to the analysis of natural and waste waters related to the maintenance of a sewage treatment plant.

Keywords: Water analysis; Transition metals; Metal cations

1. Introduction

The use of ion chromatography (IC) for the determination of metals in water samples is very diffuse. IC offers several advantages for the metals determination which include the ability for oxidation state speciation (i.e., Fe^{2+}/Fe^{3+} , Cr^{3+}/Cr^{6+} , Sn^{2+}/Sn^{4+} , etc.) and the multi-element capability in a single analysis. Thus, IC is a useful tool for bioavailability studies of metals and their effect on the environment. Conversely the low concentration ($\mu g/l$) of metals and the relatively high concentrations of alkali and alkaline-earth metals in environmental samples represent a limitation in use of IC for direct metal analysis. In order to deal with this problem, significant work has been done utilising matrix elimination and/or preconcentration in order to

minimize interference and to lower detection limits [1–8].

Most IC methods for metal separations are based on cation-exchange with reversible complexation [9–18], while fewer studies have explored anion-exchange with irreversible complexation. The anion-exchange approach does offer some advantages with respect to selectivity and for the analysis of complex samples [19–25].

This paper focuses on the development of a simple IC method for the determination of eight common metals in aqueous matrices using and a new mixed-bed ion-exchange column, the Dionex IonPac CS5A. The selectivity control is the main advantage of a mixed-bed column for transition metals separation, because a mixed-bed column allows separation of transition metals by cation, anion or cation/anion-exchange depending on the complexing agent chosen. In this case, for the intended application, the

*Corresponding author.

anion-exchange selectivity with post-column reaction (PCR) and visible absorbance detection was preferred. Linearity, reproducibility, detection limits and interference due to alkaline–earth metals (noticeably Mg and Ca) were evaluated. The influence of injection volume (up to 1 ml) on the chromatogram was studied, the injection size of the samples lowers the detection limits to less than 1 $\mu\text{g/l}$, comparable to atomic absorption spectrometry (AAS) or inductively coupled plasma–atomic emission spectrometry (ICP–AES) techniques.

The determination of transition metals in real samples, such as river water, tap water and effluents from urban waste treatment-plants, without the need for complete acid digestion of the samples is shown.

2. Experimental

2.1. Instrumentation

Chromatographic analyses were performed on a metal-free high-pressure ion chromatograph, Model 4500i (Dionex, Sunnyvale, CA, USA) 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 at 530 nm. A Rheodyne Model 9126 injector was used with different volume sample loops. The injection volume was selected in relation to metal concentration.

Trace of metals in the chromatographic system were removed by flushing all flow paths, pump and columns with 5 \times concentrated eluent at 1 ml/min prior to use.

The 250 \times 4 mm I.D. IonPac CS5A (Dionex) analytical column was used for the separation of transition metals. The 50 \times 4 mm I.D. IonPac CG5A guard column is placed prior to the IonPac CS5A to prevent potential fouling of the analytical column. In order to remove oxygen from columns, a solution of 0.1 M sodium sulfite was pumped through the columns for 1 h.

All measurements were made isocratically and at room temperature. In all cases, injection of the sample was done at least in triplicate. All the samples were filtered through 0.45 μm filter. The sample loop ranged from 50 to 1000 μl and 750 μl

Table 1
Ion chromatographic conditions

	Fe(III), Cu, Ni, Zn, Co, Cd, Mn, Fe(II)
Column	IonPac CG5A+CS5A
Eluent	7 mM PDCA 66 mM KOH 5.6 mM K ₂ SO ₄ 74 mM HCOOH (pH 4.2)
Eluent flow-rate	1.0 ml/min
Injection volume	750 μl
Detection	Visible absorbance (530 nm)
Post-column reagent	0.3 mM PAR 1 M 2-dimethylaminoethanol 0.5 M NH ₄ OH 0.3 M NaHCO ₃ (pH 10.4)
PCR flow-rate	0.6 ml/min

was chosen for all the determinations. Chromatographic conditions are summarized in Table 1.

Data manipulation and the operation of all components in the system were controlled by Dionex AI-450 chromatography software and interfaced via an ACI-2 Advanced Computer Interface to a 80486 based computer (Olivetti, Ivrea, Italy).

2.2. Reagents and standards

All reagents were analytical grade and must contain very low concentrations of trace metals. Nitric acid and hydrochloric acid were Suprapur (Merck, Darmstadt, Germany). Pyridine-2,6-dicarboxylic acid (PDCA) and 4-(2-pyridylazo)resorcinol (PAR) were obtained from Aldrich (Milwaukee WI, USA). Potassium hydroxide, potassium sulfate, formic acid, 2-dimethylaminoethanol, ammonium hydroxide and sodium bicarbonate were analytical reagent grade (Novachimica, Milan, Italy). Ultrapure water with conductivity <0.1 μS (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. Mixed-bed ion-exchange column

The IonPac CS5A has been designed to separate a broad range of chelated metal complexes by anion- and cation-exchange chromatography. The column has a 55% cross-linked, microporous, hydrophobic poly(ethylvinylbenzene–divinylbenzene) based resin core that has been agglomerated with 2 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. Hydrated and weakly complexed metals can be separated as cations on cation-exchange sites. By adding a chelating carboxylic acid to the eluent the net charge on the metal is reduced, and if the chelating agent concentration is high and the β constant is $>10^3$ then the net charge of metal complexes is negative and the metal ion complexed can be separated by anion-exchange.

2.4. Eluent

The eluent is 7.0 mM PDCA, 66 mM potassium hydroxide, 5.6 mM potassium sulfate and 74 mM formic acid. The pH of the eluent was 4.2. The PDCA eluent was purged with nitrogen for 20 min before use, since ferrous ion is easily oxidized to ferric ion.

Eluent flow-rate was 1 ml/min.

2.5. Post-column reagent

The post-column reagent was 0.3 mM PAR, 1 M 2-dimethylaminoethanol, 0.5 M ammonium hydroxide and 0.3 M sodium bicarbonate. The pH of the reagent was 10.4. Prior to use, the reagent must be filtered on 0.2 μm filter. Since PAR is readily oxidized by oxygen, the reagent was degassed and store under nitrogen. The reagent flow-rate was set at 0.6 ml/min.

2.6. Samples

Water samples were collected using a poly(ethylene) bottle washed with nitric acid and DI water before use. Samples were acidified immediately after collection by the addition of 6 M hydro-

chloric acid (pH 2). The acidification of the sample eliminates the adsorption of metals on organic colloids and lowers oxidation rate of Fe(II) [26].

Waste water contains organic ligands that complex with trace metals. Therefore, when using IC without sample treatment, only the free metal and moderately complexed metal ions will be determined. Organic interferences cannot always be removed by acidification: however, it is very important to have knowledge of this fraction as it is most toxic to organisms. Filtration is an essential step in the collection of this type of sample. Before filtration, the filter was leached with 500 ml of ultrapure water. After acidification, samples were filtered through a Millipore membrane with 0.2 μm nominal pore size and stored at 4°C. The samples were analysed within one week after filtration.

3. Results and discussion

3.1. Chromatographic separation

Since the IonPac CS5A has both anion- and cation-exchange capacity, metals can be separated by cation- and anion-exchange. Thus, major selectivity changes can be made by simply changing the eluent. For example, a separation of transition and heavy metals such as Pb(II), Cu(II), Cd(II)+Mn(II), Co(II), Zn(II), and Ni(II) is achieved using an oxalic acid eluent. This separation has both an anion- and cation-exchange component since metals such as Pb(II) and Cd(II) form relatively weak complexes with oxalate. With the oxalate eluents, Mg(II) and Ca(II), which are typically present at relatively high levels in many water samples may precipitate on the column as insoluble oxalate complexes. There is also a need for injecting large volumes of samples (up to 1 ml) in order to detect metal concentrations at the $\mu\text{g/l}$ level.

PDCA forms strong anionic complexes, cumulative stability constant $\beta_2 > 10^8$, with most metal ions. Thus, the separation of metals with PDCA and the IonPac CS5A column is an anion-exchange separation chosen despite longer retention times (about 20 min) as in Fig. 1. For waste water samples, the PDCA separation is superior to the oxalic separation since Mg(II) elutes without interfering with Mn(II)

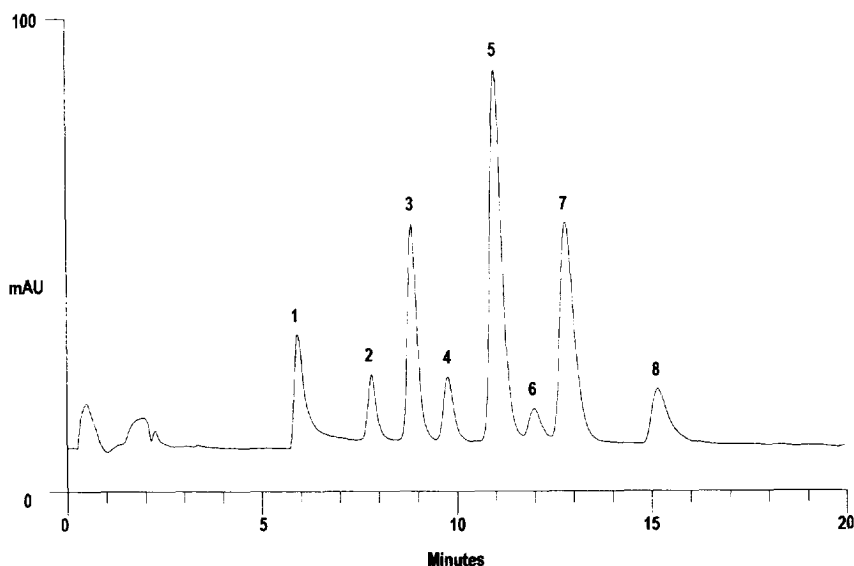


Fig. 1. Chromatogram of a standard solution of eight transition and heavy metals (chromatographic conditions as in Table 1). Peaks: 1=Fe³⁺, 2=Cu²⁺, 3=Ni²⁺, 4=Zn²⁺, 5=Co²⁺, 6=Cd²⁺, 7=Mn²⁺ and 8=Fe²⁺. Concentration 30 µg/l each.

and Fe(II) and Ca(II) only slightly affects retention time of the other metals. In addition, the PDCA eluent allows for the Cd(II) and is possible to make Fe(II,III) speciation. Analysis time can be reduced by increasing the temperature to 40°C, increasing the flow-rate to 1.2 ml/min and using gradient elution, but in these cases faster elution increases Mg interference with Mn(II) and Fe(II). The elution is influenced also by pH and concentration of the eluent [27].

Because of the necessity of sample acidification, the influence of sample pH was also investigated. No relevant influence of sample pH was observed on the separation to pH 1. Fig. 2 shows chromatograms of deionized water acidified at pH 2 with hydrochloric acid.

3.2. Interferences

The selectivity of IonPac CS5A was evaluated in order to avoid the potential interference of main cationic components in water samples, i.e., alkali and alkaline-earth metals. Alkali metals do not interfere with the determination, while Mg and Ca reacts with PAR, but the sensitivity in these IonPac CS5A operating conditions is 100–500 times lower than that of transition metals [28]. Mg elute in the

chromatogram, can thus interfere at high levels. High levels of Mg and Ca can overload the PDCA eluent and anion-exchange portion of the column due to the formation of Mg[PDCA]₂²⁻ and Ca[PDCA]₂²⁻. Thus efficiency and retention times of transition metals will be adversely affected. An evaluation of limiting concentration of Mg and Ca was made and Fig. 3 shows the chromatogram of eight metals spiked with 0.1 g/l of Mg(II) and 0.3 g/l of Ca(II).

3.3. Linearity and detection limits

This method shows a good linearity for all considered metals ($r^2 > 0.986$) for concentrations ranging from 5 to 5000 µg/l. The use of a large loop (750 µl) lowers the detection limits and does not have any detrimental effect on peak efficiency or asymmetry. Under these large volume injections, the relatively large quantity of water injected into the eluent stream does not elute the metals present in the sample. Instead, the metals concentrate at the head of the column. The detection limits, calculated according IUPAC suggestions [29], are summarised in Table 2.

3.4. Samples

Samples relative to River Lenne water, inlet and

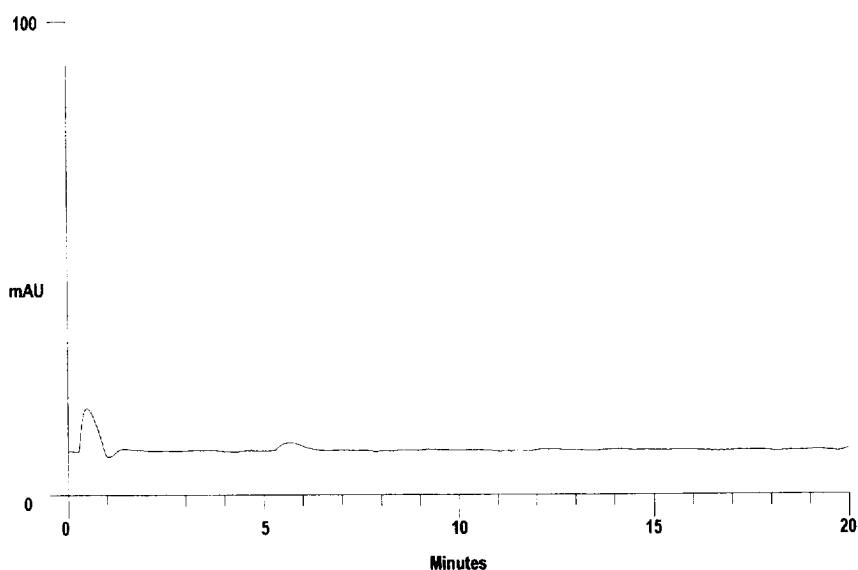


Fig. 2. Chromatogram of a blank. Sample solution was HCl (pH 2) then diluted 1:10 (v/v) prior to injection (chromatographic conditions as in Table 1).

outlet stream of a sewage treatment plant, and well water were analysed. Samples were acidified with 6 M hydrochloric acid to pH 2 then filtered and diluted 1:10 (v/v) with DI water. Chromatograms relative to River Lenne, inlet stream and outlet stream and well

water are shown in Figs. 4–7, respectively. IC data for these samples are summarised in Table 3.

The knowledge of chemical speciation of trace metals in natural waters is essential for the interpretation of biological cycling of metals. The non-labile

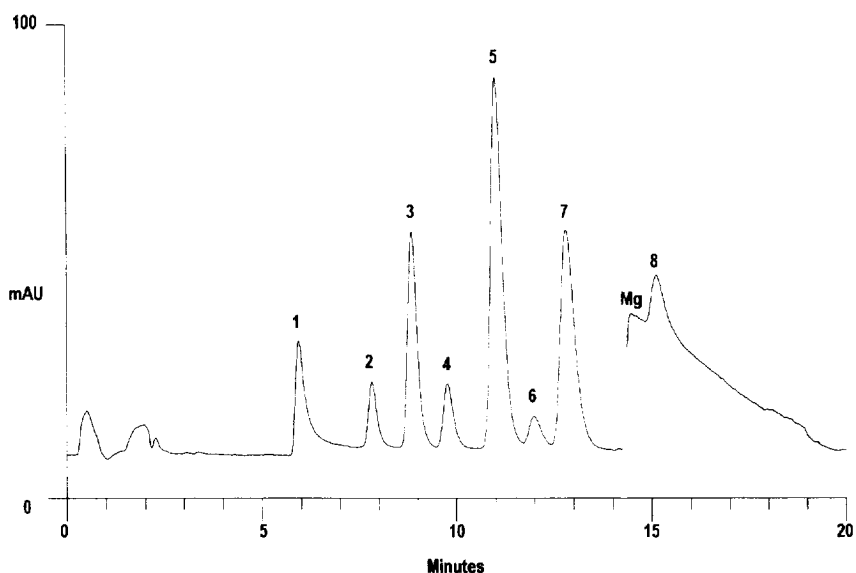


Fig. 3. Chromatogram of an eight-metals standard solution (300 $\mu\text{g/l}$ each) and spiked with 0.1 g/l of Mg^{2+} and 0.3 g/l of Ca^{2+} . Sample solution was HCl (pH 2) then diluted 1:10 (v/v) prior to injection (chromatographic conditions as in Table 1).

Table 2

Limit of detection (LOD) and limit of quantitation (LOQ) for different metals calculated on IonPac CS5A column according IUPAC guidelines [29]

Element	LOD**	LOQ ^a
Fe(III)	0.15	0.28
Cu(II)	0.32	0.59
Ni(II)	0.12	0.19
Zn(II)	0.33	0.60
Co(II)	0.06	0.10
Cd(II)	0.61	1.1
Mn(II)	0.09	0.17
Fe(II)	0.38	0.70

^a Values in $\mu\text{g/l}$. Injected volume 750 μl .

fraction is the one not determined by IC and likely includes stable metal complexes with fulvic and/or humic acids and metals strongly associated with colloidal particles. This fraction could be determined by difference if total metal concentration is determined, for example after sample acidic digestion.

In natural waters, complexation of trace metals by humic acids is dependent on the pH value [30]. At $\text{pH} > 5$ a large fraction of transition metals is complexed. Under these conditions, there is a lower concentration of H^+ ions to compete for binding sites on the humic and fulvic acids. Thus, the metals

will be bound more strongly to the humic and fulvic acids.

The capability of forming more or less stable complexes depends on both metal and ligand type. In river water, for example, Cd(II) and Zn(II) exist primarily as labile metal species [31–33], while a significant fraction of Cu(II) is strongly associated with organic matter. About 30% of Cu(II) in humic acid solution and river water samples were bound to species with size greater than 5.1 nm [34], thus acidification and filtration of the sample are fundamental together with standard addition method for quantitation.

4. Conclusions

The novel IonPac CS5A allows the simple and efficient determination of trace levels of transition metals in natural and waste waters. Low detection limits can be achieved using larger (750 μl) sample volumes.

The possibility of labile or weak complexed metals determination by direct injection of the sample without any further manipulation is very important for reduction of analysis time and for

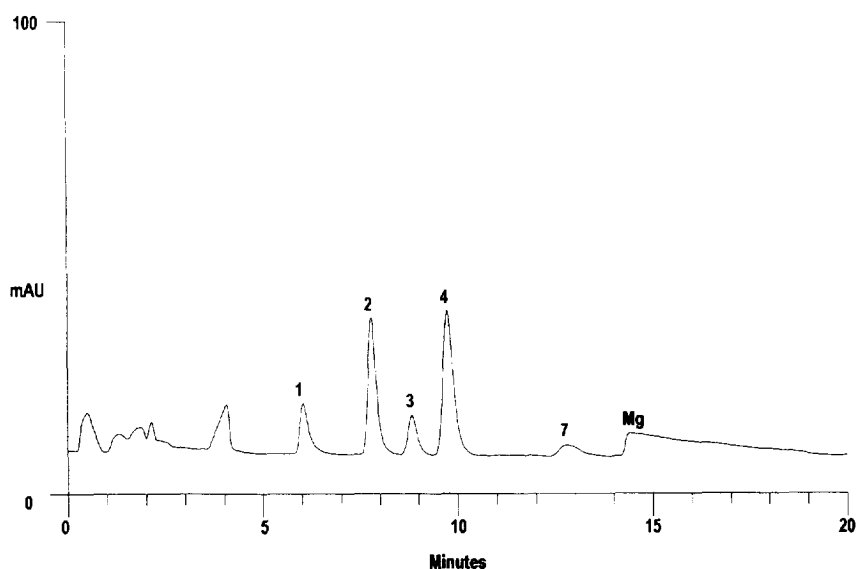


Fig. 4. Chromatogram of River Lenne water. Sample solution was HCl ($\text{pH} 2$) then diluted 1:10 (v/v) prior to injection (chromatographic conditions as in Table 1). Peaks: 1= Fe^{3+} (0.11 mg/l), 2= Cu^{2+} (0.64 mg/l), 3= Ni^{2+} (56.8 $\mu\text{g/l}$), 4= Zn^{2+} (0.78 mg/l), 7= Mn^{2+} (22.9 $\mu\text{g/l}$).

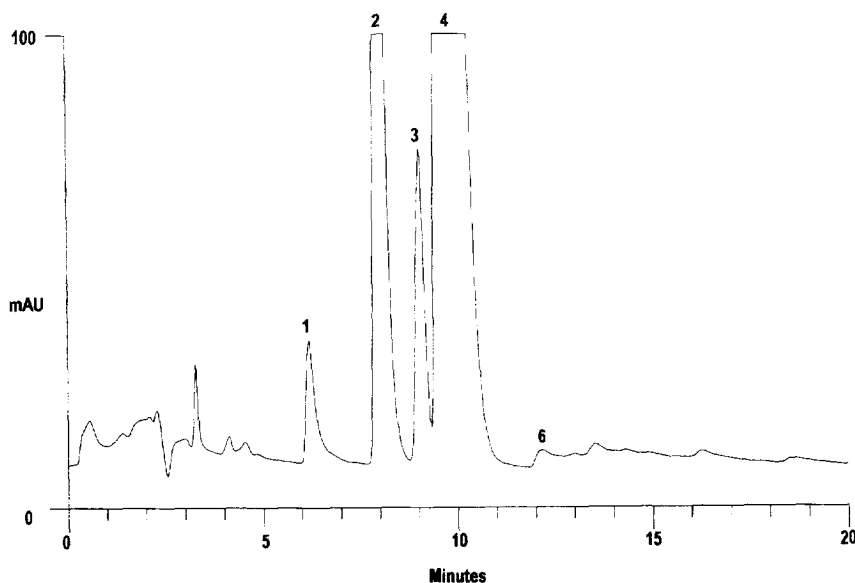


Fig. 5. Chromatogram of the inlet stream of sewage treatment plant. Sample solution was HCl (pH 2) then diluted 1:10 (v/v) prior to injection (chromatographic conditions as in Table 1). Peaks: 1= Fe^{3+} (0.29 mg/l), 2= Cu^{2+} (5.87 mg/l), 3= Ni^{2+} (0.42 mg/l), 4= Zn^{2+} (23.8 mg/l), 6= Cd^{2+} (0.12 mg/l).

lowering the risk of chemical contamination of the sample. Examples shown demonstrate the applicability to the analysis of real samples, such as

natural waters and waste waters. In this last case, particularly for the ease of automation, the method represents a valuable alternative for metals controlled

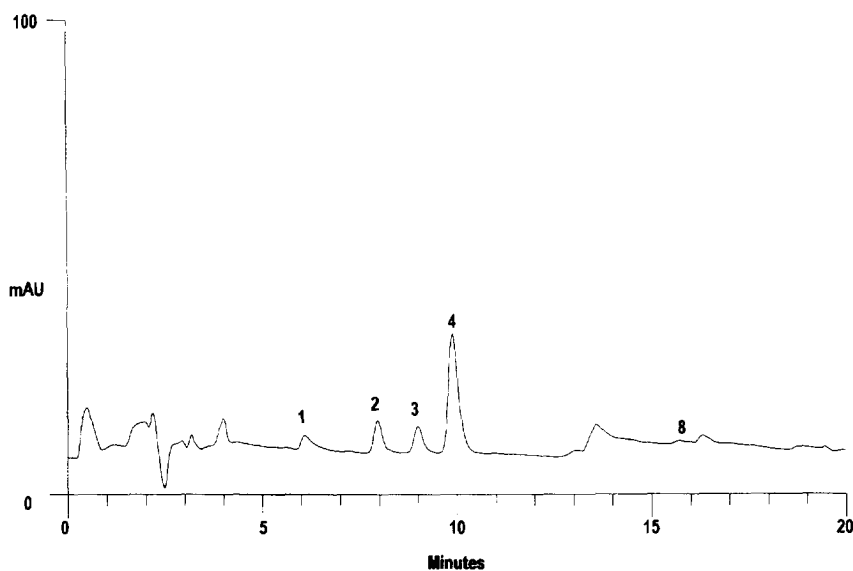


Fig. 6. Chromatogram of the outlet stream of sewage treatment plant. Sample solution was HCl (pH 2) then diluted 1:10 (v/v) prior to injection (chromatographic conditions as in Table 1). Peaks: 1= Fe^{3+} (35.4 $\mu\text{g/l}$), 2= Cu^{2+} (0.14 mg/l), 3= Ni^{2+} (35.6 $\mu\text{g/l}$), 4= Zn^{2+} (0.57 mg/l), 8= Fe^{2+} (tr.).

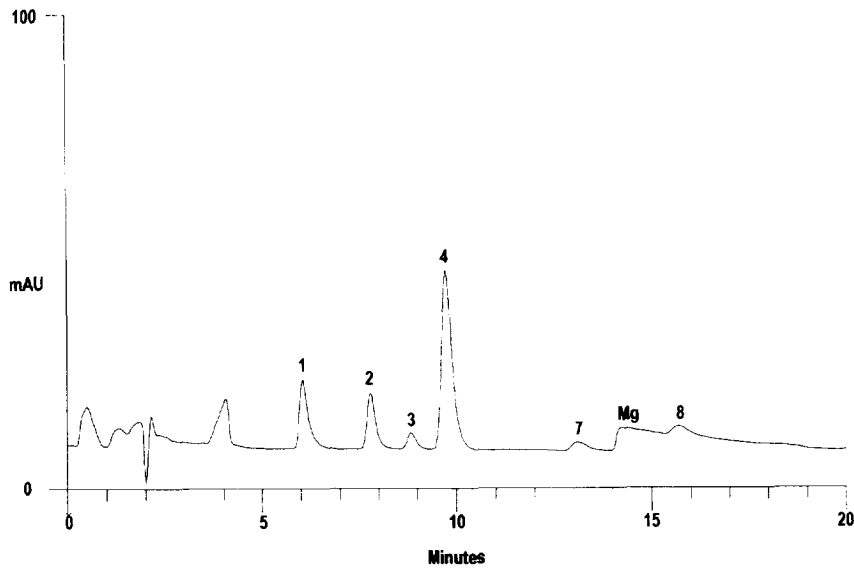


Fig. 7. Chromatogram of a sample of well water. Sample solution was HCl (pH 2) then diluted 1:5 (v/v) prior to injection (chromatographic conditions as in Table 1). Peaks: 1= Fe^{3+} (75.8 $\mu\text{g/l}$), 2= Cu^{2+} (0.13 mg/l), 3= Ni^{2+} (15.6 $\mu\text{g/l}$), 4= Zn^{2+} (0.61 mg/l), 7= Mn^{2+} (18.2 $\mu\text{g/l}$), 8= Fe^{2+} (25.7 $\mu\text{g/l}$).

in different processes of water treatment and the control of final effluent.

It should be remembered that only free and moderately labile metal fractions are determined by the IC method. If the total concentration is required, the sample must be digested.

Table 3
Summary of results in IC metal analysis of different water samples related to sewage treatment plant streams

Elements	Samples			
	River Lenne	Inlet stream	Outlet stream	Well water
Fe(III)	0.11	0.29	0.035	0.076
Cu	0.64	5.87	0.14	0.13
Ni	0.057	0.42	0.036	0.016
Zn	0.78	23.8	0.57	0.61
Co	–	–	–	–
Cd	–	0.12	–	–
Mn	0.023	–	–	0.018
Fe(II)	–	–	tr.	0.026

Values in mg/l. R.S.D. $\pm 10\%$ (range 0.005–0.100 mg/l); $\pm 4\%$ (range 0.010–5.00 mg/l).

Acknowledgments

Thanks to Dr. Strisciullo for the generous supply of River Lenne sample and a well water of the province of Lecce.

References

- [1] A. Siriraks, H.M. Kingston and J.M. Riviello, *Anal. Chem.*, 62 (1990) 1185.
- [2] J.M. Riviello, A. Siriraks, R.M. Manabe, R. Roehl and M. Alforque, *LC·GC*, 9 (1991) 704.
- [3] O.J. Challenger, S.J. Hill and P. Jones, *J. Chromatogr.*, 639 (1993) 197.
- [4] L. Ebdon, A. Fisher, H. Handley and P. Jones, *J. Anal. At. Spectrom.*, 8 (1993) 979.
- [5] R. Caprioli and S. Torcini, *J. Chromatogr.*, 640 (1993) 365.
- [6] S. Mou, A. Siriraks and J.M. Riviello, *Sepu*, 12 (1994) 166.
- [7] B. Paull, M. Foulkes and P. Jones, *Analyst (London)*, 119 (1994) 937.
- [8] N. Cardellicchio, S. Cavalli and J.M. Riviello, *J. Chromatogr.*, 640 (1992) 207.

- [9] S. Reiffenstuhl and G. Bonn, *J. Chromatogr.*, 482 (1989) 289.
- [10] X. Cui and F. Dong, *Sepu*, 7 (1989) 293.
- [11] J. Hradil, F. Svec, A.A. Aratskova, L.D. Belyakova and V.I. Orlov, *J. Chromatogr.*, 509 (1990) 369.
- [12] K.A. Ruth and R.W. Shaw, *J. Chromatogr.*, 546 (1991) 243.
- [13] V.I. Orlov, A.A. Aratskova, A.R. Timerbaev and O.M. Petrukhin, *Zh. Anal. Khim.*, 47 (1992) 686.
- [14] M.D.H. Amey and D.A. Bridle, *J. Chromatogr.*, 640 (1993) 323.
- [15] P. Alumaa and J. Pentsuk, *Chromatographia*, 38 (1994) 566.
- [16] X.S. Zhang and X.P. Jiang, *J. Chromatogr. A*, 671 (1994) 23.
- [17] J. Carnevale and P.E. Jackson, *J. Chromatogr. A*, 671 (1994) 115.
- [18] S. Zappoli and C. Bottura, *Anal. Chem.*, 66 (1994) 3492.
- [19] R.D. Rocklin, *Anal. Chem.*, 56 (1984) 1959.
- [20] T. Tanaka, *Fresenius Z. Anal. Chem.*, 320 (1985) 125.
- [21] F.I. Brouček, R.A. Demetrashvili and O.V. Orlova, *Izv. Akad. Nauk. Gruz. SSR. Ser. Khim.*, 14 (1988) 232.
- [22] O.N. Obrezkov, V.I. Slyamin and O.A. Shpigun, *Anal. Sci.*, 6 (1990) 617.
- [23] Z. Lei, S. Tian and J. Chen, *Gaodeng Xuexiao Huaxue Xuebao.*, 10 (1989) 156.
- [24] H. Siren and M.L. Riekkola, *Mikrochim. Acta*, 2 (1989) 77.
- [25] E.M. Basova, T.A. Bol'shova, E.N. Shapolova and V.M. Ivanov, *Zh. Anal. Khim.*, 45 (1990) 1947.
- [26] C.O. Moses, A.T. Herlihy, J.S. Herman and A.L. Mills, *Talanta*, 35 (1980) 15.
- [27] J. Riviello, A. Woodruff and C. Pohl, *PittCon 96*, paper No. 1193.
- [28] J. Riviello, personal communication.
- [29] G.L. Long and J.D. Winefordner, *Anal. Chem.*, 55 (1983) 712A.
- [30] Y. Liu and J.D. Ingle Jr., *Anal. Chem.*, 61 (1981) 525.
- [31] G.E. Batley and T.M. Florence, *Mar. Chem.*, 4 (1976) 347.
- [32] T.M. Florence, *Water Res.*, 11 (1977) 681.
- [33] P. Figura and B. McDuffie, *Anal. Chem.*, 52 (1980) 1433.
- [34] R.D. Guy and C.L. Chakrabarti, *Can. J. Chem.*, 54 (1976) 2600.