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Determination of trace transition metals in environmental matrices by chelation ion chromatography

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Abstract Trace transition metals (Fe^{3+}, Mn, Cu, Cd, Co, Zn, Ni) in environmental samples were analyzed by chelation ion chromatography using a mixed bed ion-exchange column with pyridine-2,6-dicarboxylic acid (PDCA) and oxalic acid as eluent and large volume direct injection (1,000 μl). The two eluents, PDCA and oxalic acid, were tested, and repeatability and detection limits were compared. The total analysis time was ~15 min. The separation with PDCA was more successful than that obtained with acid oxalic. It was observed that utilizing PDCA resulted in lower detection limits, higher repeatability, and a quantitative detection of Cd and Mn, which coelute as a single peak when using the oxalic acid. At last, the PDCA calibration graphs resulted linear ($r^2 > 0.999$) in the range 0.4–1,000 μg/L. The procedure was applied to the analysis of metals in soils and in water samples. The results obtained from the analysis of natural waters have demonstrated that the method is simple and efficient, therefore, can be used for the determination of metals in natural waters using a continuous and automatic monitoring system.

Keywords Ionic chromatography · Heavy metal · PDCA · Validation · Natural sample monitoring · Automatic monitoring system

Introduction

The determination of trace heavy metals in environmental matrices has received particular attention in recent years. Several sensitive methods for the determination of heavy metals, including atomic absorption spectrometry, inductively coupled plasma optical emission spectroscopy, and ion chromatography have all been used. Furthermore, in the last decade, chelation ion chromatography (Shaw et al. 2003; Santoyo et al. 2000; Sarzanini and Bruzzoniti 2001; Cardellicchio et al. 1997, 1998, 1999; Basta and Tabatabai 1990; Sarzanini and Cavalli 1998; Rossi and Tubino 2003; Sarzanini and Mentasti 1997; Shaw and Haddar 2004; Divjak et al. 1998; Ding et al. 2000a, b; Motellier and Pitsch 1996; Nesterenko 2002; Jones and Nesterenko 1997; Siriraks et al. 1990; Lu et al. 1998; Bashir and Paull 2002; Nesterenko and Jones 1997; Bruno et al. 2006; Lasheen et al. 2006) has become one of the main powerful analytical methods for the analysis of some metals in complex matrices. Ion chromatography allows the determination of oxidation state speciation (i.e., Fe^{2+} and Fe^{3+}) and thus is a useful

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tool for bioavailability studies of toxic metals in the environment. Transition metals are separated as both cationic and anionic complexes using a mixed bed ion-exchange column (a bifunctional quaternary ammonium-sulfonate ion exchanger) and carboxylic acid chelating agent (oxalic acid and pyridine-2,6-dicarboxylic acid (PDCA)) as eluent (Cardellicchio et al. 1999). Hydrated and weakly complexed metals are separated as cations on cation exchange sites, while the metals that form strong anionic complexes are separated then by anionic exchange.

The aim of this work has been to optimize and validate heavy metals determination (Fe^{3+}, Mn, Cu, Cd, Co, Zn, and Ni) by chelation ion chromatography using oxalic acid or PDCA as eluents and to test the feasibility of this method for analysis of metals by a prototypical automatic monitoring system. This prototype, developed in our laboratory (Capocecera et al. 1999; Murgia et al. 2003), is a multiparametric analytical station that allows the simultaneous qualitative and quantitative determination of several chemical and chemical–physical parameters, which identify the quality of the water. The chemical and chemical–physical parameters detected are temperature, dissolved oxygen, conductivity, pH, ORP (redox), F^-, Cl^-, NO_2^-, Br^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, Li^+, Na^+, $NH4^+$, K^+, Mg^{+2}, and Ca^{+2}. Chemical parameters are detected by ion chromatography technique, while chemical–physical parameters are measured using a multiparameter probe with solid-state sensors.

Then, PDCA and oxalic acid eluents have both been tested and compared for repeatability and detection limits. For the two eluents, linearity and interference due to alkaline-earth metals (Mg and Ca) have also been discussed.

The method has been used to determine metals in water samples and in soil collected from a polluted area submitted to the reclamation plan of the Umbria region (Italy; regional reclamation plain of polluted sites October 2008, enclosure 1, 12–126) and is currently being tested by the automatic monitoring system developed in our laboratory.

Experimental

Reagents and standards

All reagents were of analytical grade. Solutions were prepared using ultrapure water (<18.2 mΩ at 25°C) from Simplicity system (Millipore, Bedford, MA, USA). Normal precautions for trace analysis were taken, e.g., all glassware was carefully cleaned in concentrated nitric acid and vigorously washed with deionized water.

PDCA, oxalic acid dihydrate, potassium hydroxide, potassium sulfate, ammonium hydroxide, sodium hydrogen carbonate, formic acid,

Table 1 Ion chromatographic conditions

	PDCA pH = 4.2 ± 0.1		Oxalic acid pH = 4.7 ± 0.1
		IonPac CG5A+ CS5A	
Eluent	5.95 mM PDCA		64 mM oxalic acid
	56.1 mM KOH		80 mM TMAOH
	4.76 mM K_2SO_4		40 mM KOH
	62.9 mM HCOOH		
Eluent flow rate ml/min		1	
V_{loop}		1,000 µl	
$\lambda_{detector}$		530 nm	
PCR		0.5 mM PAR	
		1 M DMAE	
		50 M NH_4OH.	
		3 M $NaHCO_3$	
PCR flow rate ml/min		0.8	

TMAOH tetramethylammonium hydroxide, *PCR* post-column reagent

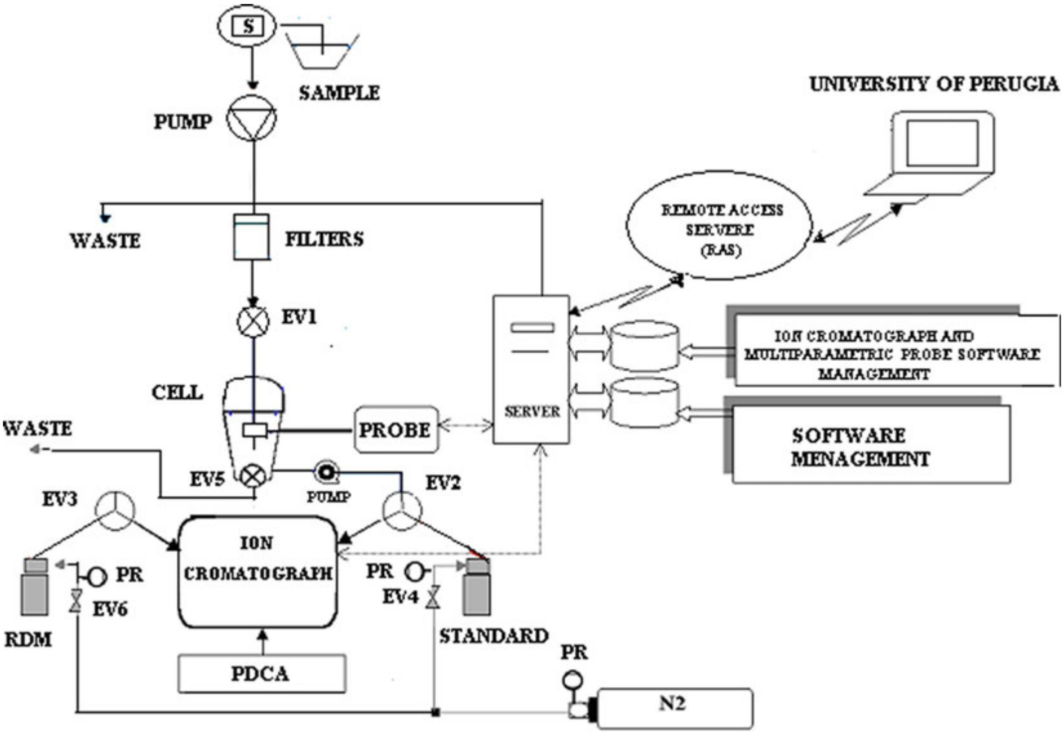

Fig. 1 Schematic diagram of the prototypal automatic monitoring system: *EV* electric valves; *PR* pressure reducer, *RDM* post-column reagent delivery module

2-dimethylaminoethanol (DMAE), tetramethylammonium hydroxide (TMAOH), standard solutions of each metal containing 1,000 mg/L were obtained from Fluka, Milwaukee, WI, USA; 4-(2-pyridylazo) resorcinol (PAR) was supplied by Dionex, Sunnyvale, CA, USA; Ultrapure

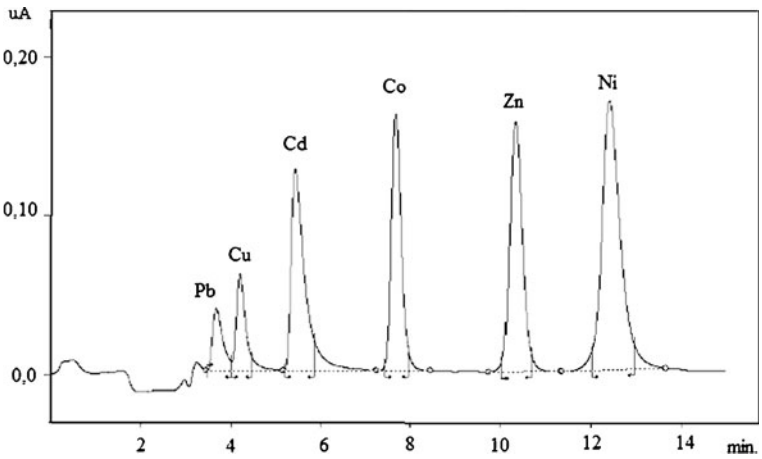

Fig. 2 Chromatogram of a metal standard solution. Chromatographic conditions: eluent: [Oxlic acid] = 64 mM, [TMAOH] = 80 mM, [KOH] = 40 mM; pH = 4.7 ± 0.1; concentrations of metals: Pb = 180 μg/l, Cu = 36 μg/l, Cd = 180 μg/l, Co = 90 μg/l, Zn = 90 μg/l, Ni = 180 μg/l; loop 1,000 μl; eluent flow rate 1 ml/min; flow rate post-column reagent 0.8 ml/min; detector λ = 530 nm

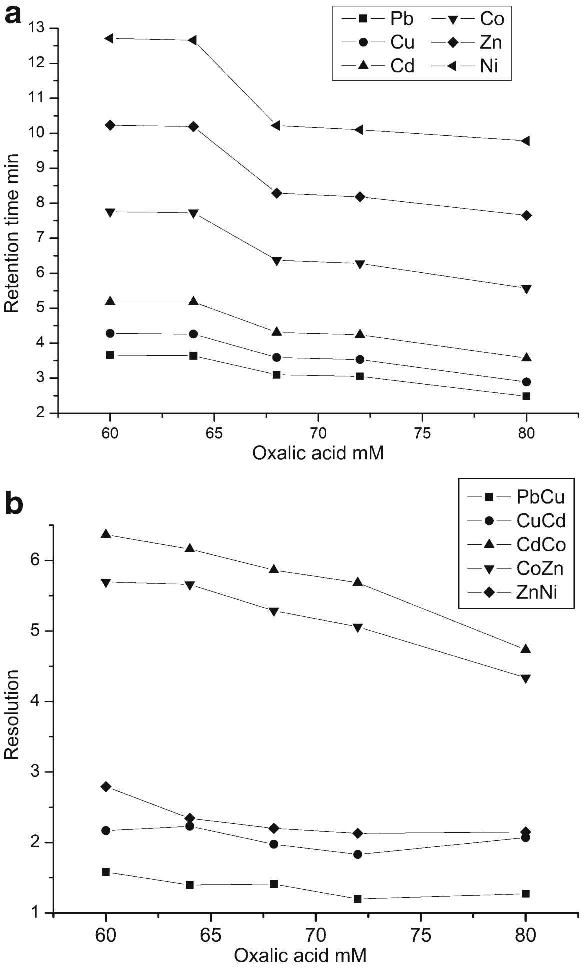

Fig. 3 **a** Influence of oxalic acid concentration on the retention times; **b** influence of oxalic acid concentration on the resolution of closest peaks

nitric (69%) and perchloric acid (70%) were obtained from Carlo Erba, Milano, Italy; certified reference material CRM 144R, Sewage Sludge from domestic origin, was purchased by BCR, European Commission, Brussels, Belgium.

Apparatus

Chromatographic analyses were performed on a metal-free high-pressure ion chromatograph model 4500i (Dionex, Sunnyvale, CA, USA) which included one gradient pump GPM-40, a Rheodyne 9125 injector valve fitted with 1,000 μl PEEK sample loop, a variable wavelength absorbance detector VDM-2 and a pneumatic controller for post-column reagent delivery. The analytical column was a 250 × 4 mm I.D. IonPac CS5A (a bifunctional quaternary ammonium-sulfonate mixed ion exchanger) by Dionex, preceded by a guard column (50 × 4 mm I.D. IonPac CG5A by Dionex; installation instructions for the IonPac® CS5A analytical column, Dionex Corporation 2001).

Data collection and processing were controlled by DX-RUN26 chromatography software (University of Perugia) and by CHROMuLAN© 0.79 (2004) software (Jindrich e Pikron Ltd).

Eluents and post-column reagents

The eluents (PDCA and oxalic acid) were prepared by dilution of concentrated solutions (×10).

The post-column reagent was 0.5 mM PAR, 1 M DMAE, 0.5 M ammonium hydroxide, and 0.3 M sodium hydrogen carbonate (Dionex Corporation 2001). The pH of the reagent was 10.4 ± 0.2. The eluents and PAR reagent were stored under nitrogen. The ion chromatographic conditions are shown in Table 1.

Prototypical automatic monitoring system

The prototypical automatic monitoring system (Fig. 1) was constituted by a shelter equipped

Table 2 Influence of oxalic acid concentration on the resolution of closest peaks (R)

Oxalic acid dilution %	Oxalic acid concentration mM	Pb/Cu R	Cu/Cd R	Cd/Co R	Co/Zn R	Zn/Ni R
–	80	1.273	2.070	4.735	4.337	2.149
5	72	1.198	1.831	5.685	5.060	2.130
10	68	1.412	1.975	5.864	5.288	2.201
20	64	1.397	2.231	6.162	5.659	2.342
25	60	1.582	2.169	6.366	5.697	2.793

The resolution of peaks was carried out by Origin 7.0 software (OriginLabs)

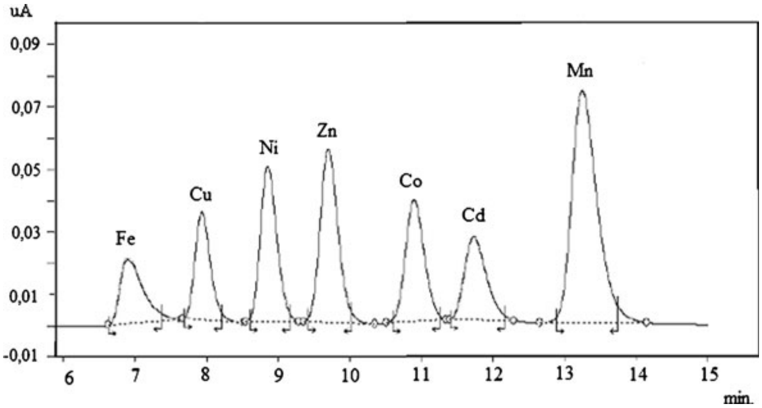

Fig. 4 Chromatogram of a metal standard solution. Chromatographic conditions: eluent: [PDCA] = 5.95 mM, [KOH] = 56.1 mM, [K_2SO_4] = 4.76 mM, [HCOOH] = 62.9 mM; pH = 4.2 ± 0.1, Standard Fe^{3+} = 30 µg/l, Cu = 30 µg/l, Ni = 90 µg/l, Zn = 30 µg/l, Co = 30 µg/l, Cd = 90 µg/l, Mn = 90 µg/l; loop 1,000 µl; eluent flow rate 1 ml/min; flow rate post-column reagent 0.8 ml/min; detector λ = 530 nm

with a multiparameter probe with solid-state sensors model Heron (Amic, Livorno, Italy) and a high-pressure ion chromatograph model Dx320 (Dionex, Sunnyvale, CA, USA), which include a IC25 ion chromatograph, a Rheodyne 9125 injector valve fitted with 1,000 µl PEEK sample loop, a variable wavelength absorbance detector AD20, and a pneumatic controller for post-column reagent delivery. The analytical column was a 250 × 4-mm I.D. IonPac CS5A by Dionex, preceded by a guard column (50 × 4 mm I.D. IonPac CG5A by Dionex). The water samples were collected by a centrifugal pump, filtered through four filters (10, 1.2, 0.6, and 0.22 µm, Millipore Corporation) and put in a glass measurement cell, where was installed the multiparameter probe. Few milliliters (~5 ml) of samples were taken from the cell by a peristaltic pump and injected in the chromatographic system. Likewise, before the sample injection, few milliliters (~5 ml) of a standard solution were injected in the chromatographic system by pressurization of the reservoir. Instrument control were effected by means of local software management, operating also in "remote mode" via network, while the analytical monitoring was carried out by a special Client–Server architecture, which interacts with the control process and the data output collection without affecting the accuracy of the analysis (Capocecera et al. 1999).

Sampling

The sampling was performed in December 2004. Ground waters were sampled from water wells at a depth of 50 cm below the phreatic surface; surface waters were sampled at a depth of 20 cm below the surface at the center of the channel, while soil samples were collected at a depth of 1 m in noncultivated areas.

Table 3 Influence of PDCA concentration on the resolution of closest peaks (R)

PDCA dilution %	PDCA concentration mM	Fe/Cu R	Cu/Ni R	Ni/Zn R	Zn/Co R	Co/Cd R	Cd/Mn R
–	7	1.014	1.719	1.599	2.096	1.165	2.060
5	6,5	1.160	2.001	1.704	2.183	1.237	2.146
10	6,3	1.215	2.005	1.710	2.186	1.359	2.191
15	5,95	1.321	1.979	1.762	2.347	1.436	2.388

The resolution of peaks was carried out by Origin 7.0 software (OriginLabs)

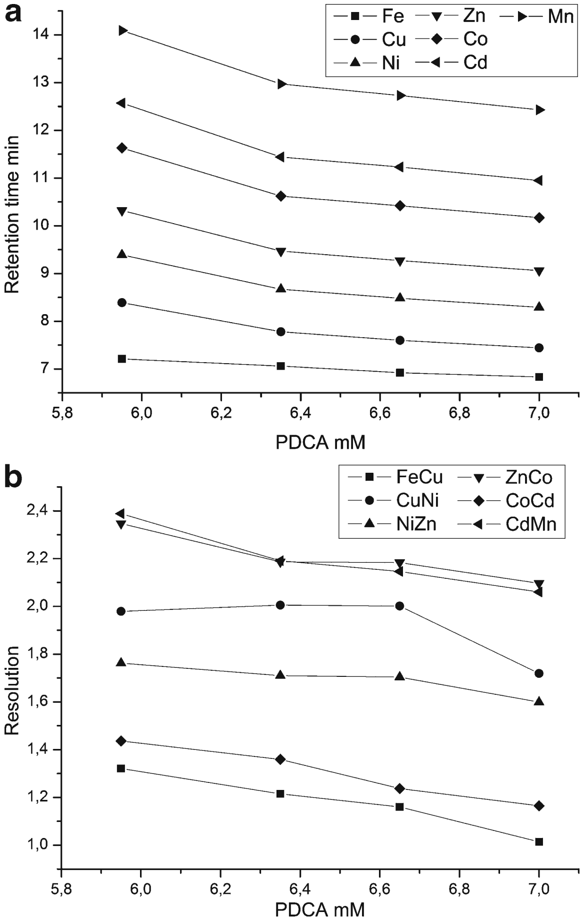

Fig. 5 **a** Influence of PDCA concentrations on the retention times; **b** influence of PDCA concentrations on the resolution of closest peaks (R)

The water and soil samples were collected in 500-ml polyethylene bottles and transported in coolers at 4°C. The water samples were kept in a refrigerator at 4°C until the analysis, while the soil samples were refrigerated at −20°C (APAT-IRSA-CNR 1985, 2003).

The water samples were acidified by addiction of ultrapure nitric acid (pH 2) immediately after collection and were filtered through a membrane with 0.2 µm pore size (Sartorius) before injection into the chromatograph. The soil samples and the certified reference material were digested as following (APAT-IRSA-CNR 1985): 10 ml concentrated ultrapure nitric acid was added to the sample (1.0 g, <100 mesh) and heated to 150°C. When the brown fumes disappeared completely, 2 ml of concentrated perchloric acid were added, and the flask was heated to 150°C for 4 h. Then, the vessel was cooled to room temperature and 1 ml concentrated nitric acid and 20 ml ultrapure water was added. The mixture was filtered (Whatman GF/C) and diluted with ultrapure water to 50 ml. All samples were diluted at pH 2 and filtered through a 0.2-µm (Sartorius) filter prior to injection.

Results and discussion

Optimization of the chromatographic method

The determination of heavy metals (Fe^{3+}, Mn, Cu, Cd, Co, Zn, and Ni) has been carried using a mixed bed ion-exchange column (CS5A, Dionex,), oxalic acid, and PDCA as eluents and a large sample loop (1,000 µl). The detection has been accomplished using PAR as post-column

Table 4 Detection limits and percentage relative standard deviations using PDCA and oxalic acid

Metal	Concentration µg/L	PDCA		Oxalic acid	
		RSD%	LOD_{ULA} µg/L	RSD%	LOD_{ULA} µg/L
Fe^{3+}	60	1.52	0.98	n.d.	n.d.
Cu	60	2.56	5.68	1.29	5.25
Ni	90	0.47	3.37	2.33	4.46
Zn	100	3.61	1.53	7.74	20.05
Co	60	1.68	0.88	3.14	0.71
Cd	180	2.77	3.66	4.07	4.21
Mn	180	2.79	3.92	n.d.	n.d.
Pb	180	n.d.	n.d.	6.95	7.19

Chromatographic conditions as in Table 1

LOD_{ULA} detection limits of the upper limit approach, Hubeaux–Vos method; *RSD%* percentage relative standard deviation

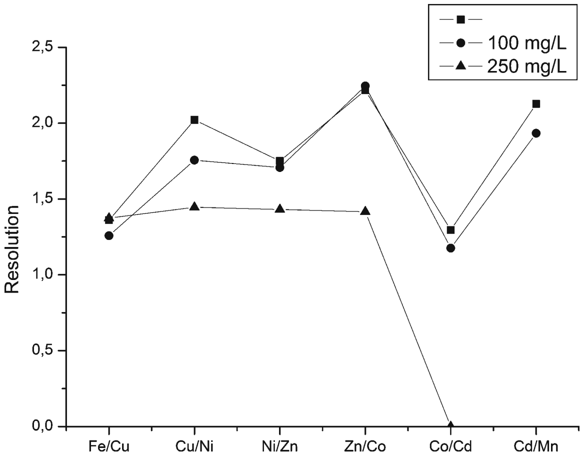

Fig. 6 Influence of Mg and Ca concentrations on the resolution of closest peaks using PDCA (the operating parameters are showed in Table 1)

reaction agent and absorbance monitoring at 530 nm. The ion chromatographic conditions are shown in Table 1.

Oxalic acid eluent

The separation with oxalic acid has an anion and cation exchange component. Pb and Cd form weak complexes with oxalate and are separated by cation exchange; instead, the other metals form stable complexes and are separated by anion exchange. Cd and Mn (Basta and Tabatabai 1990) coelute as a single peak, while Fe (III), which forms a trivalent complex with oxalate, cannot be determined, as it is strongly retained by the column. Figure 2 shows the chromatogram of a metal standard solution obtained using oxalic acid 64 mM as eluent.

In order to optimize the chromatographic separation, a series of experiments varying the eluent concentration have been carried out. In Fig. 3 and in Table 2, the influence of oxalic acid concentration on retention times and on closest peaks resolution is shown.

With oxalic acid (60 mM), the metals were efficiently separated and the time required for separation of Pb, Cu, Cd, Co, Zn and Ni was ~13 min. Eluent dilution was carried out to improve the separation of Pb and Cu; besides, the dilution necessary for the resolution of Pb and Cu peaks improved the resolution of the other metal couples ($R'1.5$) but produced longer retention times. Furthermore, oxalic acid also allowed the determination of Pb, but the detection limit was too high (7.2 μg/l).

PDCA eluent

PDCA forms strong anionic complexes with most metals (β2 > 108; Cardellicchio et al. 1998; Sarzanini and Cavalli 1998); thus, the separation of metals with PDCA and the IonPac CS5A column is an anionic-exchange separation.

In Fig. 4, the chromatogram of a metal standard solution obtained using PDCA 5.95 mM as eluent is shown. PDCA 5.95 mM allowed the separation of Fe^{+3}, Mn, Cu, Cd, Co, Zn, and Ni in ~15 min (Fig. 4). Also, in this case, eluent dilution carried out to improve the separation of Fe/Cu and Co/Cd produced excellent peak resolution of metal

Table 5 Influence of Mg and Ca concentrations on the resolution of closest peaks (R) and on the retention times using PDCA

Metal	Retention time min	R		Ca and Mg 100 mg/L			Ca and Mg 250 mg/L		
				Retention time min	R		Retention time min	R	
Fe^{3+}	7.08	Fe/Cu	1.360	7.11	Fe/Cu	1.258	7.11	Fe/Cu	1.374
Cu	7.97	Cu/Ni	2.021	7.98	Cu/Ni	1.756	8.01	Cu/Ni	1.446
Ni	8.90	Ni/Zn	1.751	8.89	Ni/Zn	1.707	8.90	Ni/Zn	1.431
Zn	9.74	Zn/co	2.216	9.74	Zn/co	2.245	9.76	Zn/co	1.416
Co	10.95	Co/Cd	1.295	10.94	Co/Cd	1.176	10.95	Co/Cd	
Cd	11.83	Cd/Mn	2.127	11.78	Cd/Mn	1.933		Cd/Mn	
Mn	13.37			13.28					

The operating parameter are shown in Table 1

Table 6 PDCA repeatability test based on five replica analyses of three metal standard solutions

Metal	Standard solution µg/L	Concentration µg/L					Concentration mean µg/L	σ[a]	RSD%[b]
Fe^{3+}	3	3.97	3.00	2.94	2.91	2.89	3.14	0.42	13.38
	60	61.21	60.97	59.63	61.45	59.15	60.48	0.92	1.52
	500	495.71	491.21	507.20	515.72	502.70	502.51	8.61	1.71
Cu	3	2.19	2.80	2.55	2.64	2.45	2.53	0.20	7.91
	60	60.48	60.82	57.83	62.30	59.00	60.09	1.54	2.56
	500	481.73	488.98	492.65	502.37	478.07	488.76	8.53	1.75
Ni	18	17.89	16.99	18.79	17.63	18.15	17.88	0.59	3.30
	90	90.10	90.12	89.47	90.75	89.84	90.06	0.42	0.47
	300	292.11	293.05	304.57	296.54	298.36	296.92	4.45	1.50
Zn	30	29.93	31.84	30.53	32.33	29.44	30.82	1.10	3.57
	100	97.66	104.93	101.20	99.76	94.16	99.54	3.59	3.61
	500	495.17	502.16	510.62	517.31	486.70	502.39	10.85	2.16
Co	1	0.89	0.83	0.86	0.80	0.90	0.86	0,036	4.19
	60	60.29	60.56	59.16	61.69	58.89	60.12	1.01	1.68
	750	756.09	744.09	732.38	767.79	768.02	753.67	13.83	1.84
Cd	3	3.27	3.15	3.01	2.95	3.07	3.09	0.11	3.56
	180	185.23	183.86	175.38	190.05	179.05	182.71	5.07	2.77
	300	304.73	300.61	313.62	290.89	283.86	298.74	10.43	3.49
Mn	3	2.53	2.87	2.76	2.85	2.64	2.73	0.13	4.76
	180	190.82	179.69	175.98	185.09	185.42	183.40	5.11	2.79
	300	292.02	299.12	301.38	312.39	282.62	297.51	9.9	3.33

Chromatographic conditions as in Table 1

[a] Standard deviation

[b] Percentage relative standard deviation

couples ($R > 1.3$) and longer retention times (Table 3 and Fig. 5).

With PDCA, it was possible to determinate both Cd and Mn that coeluted as a single peak with oxalic acid, although Pb could not be determined, as the Pb–PDCA complex was more stable than the corresponding chelate complex with the PAR reagent.

Detection limits and interferences

In Table 4 are shown the detection limits obtained using PDCA and oxalic acid. The determination with PDCA presents lower detection limits than oxalic acid.

It has also been possible to evaluate the interference of alkaline and alkaline-earth metals in water sample analysis. Alkaline metals do not interfere with heavy metals determination; instead, Mg and Ca that form insoluble complexes with oxalic acid elute with PDCA in the chromatogram, yet at low levels do not interfere in the determination of adjacent metals. It should be, however, mentioned that at high levels (≥250 mg/l), Ca and Mg interfere with peak integration of Co, Cd, and Mn.

In Fig. 6 and Table 5 is shown the influence of Mg and Ca concentrations on the resolution of closest peaks. At Mg and Ca high levels (250 mg/l), the Co, Cd, and Mn determination is not possible. No influence was observed on the retention times (Table 5).

Table 7 Results of the ordinary least-squares regression model obtained from PDCA chromatographic calibrations

Metal	Intercept ± SE	Slope ± SE	Linearity (r^2)
Fe	0.0726 ± 0.0993	0.1436 ± 0.0004	0.99999
Cu	0.0906 ± 0.6096	0.1575 ± 0.0023	0.9998
Ni	0.0643 ± 0.1926	0.0783 ± 0.016	0.9997
Zn	0.6482 ± 0.2375	0.2133 ± 0.0008	0.9999
Co	0.0233 ± 0.1263	0.2185 ± 0.006	0.99999
Cd	0.0702 ± 0.1591	0.0596 ± 0.0013	0.9996
Mn	0.0415 ± 0.4850	0.1804 ± 0.004)	0.9995

Chromatographic conditions as in Table 1

Repeatability

Experimental repeatability was calculated by performing five replicates analyses of three standards solutions (Analytical Methods Committee 1994). In Table 6, the PDCA RSDs obtained by the repeatability test are reported. The results indicate that the repeatability is good and in agreement with published literature values (Cardellicchio et al. 1998; Basta and Tabatabai 1990), and besides, PDCA presents higher repeatability than oxalic acid (lower RSD values) as shown in Table 4.

Linearity and accuracy

The separation with PDCA is preferable to that obtained with acid oxalic because lower detection limits and higher experimental repeatability were obtained (Table 4). For these reasons, we determined the linearity and accuracy only for the determination with PDCA.

Twelve concentration levels of each metal (Fe^{+3}, Mn, Cu, Cd, Co, Zn, and Ni) including a blank and six replicas of each concentration level were used for calibration purposes. Ordinary least-squares regression model (OLSR) was used for chromatographic calibrations (UNICHIM 2001).

Linearity between the peak area and concentration ($r^2 > 0{,}999$) was observed for all metals in the range 0.4–1,000 μg/L (Table 7; Analytical Methods Committee 1994; EURACHEM 1998).

In Table 8 are shown linear and dynamic ranges for all metals, while in Table 9 the detection limits (EURACHEM 1998; Long and Winefordner 1983; Jones et al. 1990; Vanatta and Coleman 1997; Thompson 1998) are summarized.

The accuracy test was carried out through the analysis of certified reference material, sewage sludge from domestic origin containing Cu, Ni, Zn, Co, Cd, and Mn. The sludge after digestion and dilution (1:100 and 1:200) was analyzed by ion chromatography using PDCA as eluent.

Table 9 PDCA detection limits (LOD and LOQ) estimated according to the 3σ method

Metal	Fe	Cu	Ni	Zn	Co	Cd	Mn
LOD μg/l	0.63	0.54	0.45	0.67	0.41	1.90	0.53
LOQ μg/l	1.90	1.64	1.36	6.61	1.26	5.78	1.61
N	10	10	10	10	10	10	10

Chromatographic conditions as in Table 1
LOD detection limit; *LOQ* quantification limit; *N* blank replica number

The concentrations obtained were compared with the certified values given in the certification report using *t* test. At a confidence level of 99%, no difference between the certified values and the detected values was observed.

In Table 10, the certified values and the values obtained by the analysis of certified reference material are reported.

Determination of metals in soils and in water samples

The applicability of the method was tested by analyzing soil and water samples collected from a polluted area submitted to the reclamation plan of Umbria region (Italy; regional reclamation plain of polluted sites October 2008). In this area (Casone, commune of Foligno, Umbria), there is a landfill characterized by large piles of waste completely open and lined underneath with a cement layer. The samples were analyzed using PDCA (chromatographic conditions as in Table 1). The data obtained are summarized in Tables 11, 12, and 13. The results indicate that the present method was useful for the determination of heavy metals in water and in soil samples. One of the most important advantages gained by using this method was that the samples could be directly injected (the soils were injected after sample digestion and dilution). The RSD% values obtained also show in this case a good repeatability.

Table 8 Linear and dynamic ranges obtained from PDCA chromatographic calibrations

Metal	Fe	Cu	Ni	Zn	Co	Cd	Mn
Dynamic range μg/L	0.6–1,500	0.5–1,500	0.5–4,500	0.7–1,500	0.4–1,000	1.9–2,250	0.5–2,250
Linear Range μg/L	0.6–1,000	0.5–1,000	0.5–1,000	0.7–1,000	0.4–750	1.9–1,000	0.5–1,000

Chromatographic conditions as in Table 1

Table 10 Certified values and the values obtained by the analysis of certified reference material

Metal	Concentration mean mg/kg	Confidence interval ± $t_{(95\%,\,n-1)}.s/\sqrt{n}$	Replica number	Certified values mean mg/kg	Confidence interval ± $t_{(95\%,\,n-1)}s/\sqrt{n}$	Replica number
Fe	7636	35.98	4	n.d.	n.d.	–
Cu	296.31	9.58	4	308	7	8
Ni	55.81	8.41	6	47.7	1.1	7
Zn	924.97	31.95	6	932	23	11
Co	13.95	3.38	6	15.0	0.6	7
Cd[a]	n.d.	n.d.	n.d.	1.82	0.10	11
Mn	202.02	7.04	4	208	3	10

n.d. not determined

[a] It was not possible to determine Cd, because of the dilution requirements to increase the pH (>2) was too large that the Cd concentration then dropper lower than the detection limit

Table 11 Summary of results obtained by IC metal analysis of well waters

Metal	Sample[a]	Concentration mean μg/L	Confidence interval ± $t_{(95\%,\,n-1)}s/\sqrt{n}$	RSD%	Guide values[b] μg/L
Fe^{3+}	A	10.37	2.61	5.78	100
	B	41.57	5.18	4.49	
	C	11.87	4.66	14.14	
	D	18.65	4.20	8.1	
	E	38.76	1.87	1.73	
Cu	A	5.48	1.39	9.16	20
	B	11.09	3.25	10.57	
	C	4.20	1.40	11.98	
	D	4.92	1.82	13.29	
	E	11.22	4.59	14.7	
Ni	A	<LOD	–	–	–
	B	<LOD	–	–	
	C	<LOD	–	–	
	D	26.03	1.13	4.33	
	E	<LOD	–	–	
Zn	A	47.28	5.09	3.54	500
	B	140.29	5.45	1.40	
	C	55.43	11.50	7.47	
	D	205.87	23.72	4.84	
	E	90.12	4.63	2.10	
Co	A	7.49	1.22	5.85	–
	B	<LOD	–	–	
	C	<LOD	–	–	
	D	1.78	0.10	1.54	
	E	<LOD	–	–	
Cd	A	<LOD	–	–	1
	B	<LOD	–	–	
	C	7.70	1.56	7.30	
	D	<LOD	–	–	
	E	<LOD	–	–	
Mn	A	2.61	0.43	5.91	50
	B	6.93	1.37	7.12	
	C	3.00	1.09	14.83	
	D	346.44	3.83	0.45	
	E	16.26	0.64	1.42	

[a] Replica number = 5

[b] Legislative Decree (2006; tap water)

Table 12 Summary of results obtained by IC metal analysis of surface water

Sample[a]	Metal											
	Conc. mean[a] µg/l	Confidence interval ± $t_{(95\%,\,n-1)}s/\sqrt{n}$[a]	RSD%	Conc. mean[a] µg/l	Confidence interval ± $t_{(95\%,\,n-1)}s/\sqrt{n}$[a]	RSD%	Conc. mean[a] µg/l	Confidence interval ± $t_{(95\%,\,n-1)}s/\sqrt{n}$[a]	RSD%	Conc. mean[a] µg/l	Confidence interval ± $t_{(95\%,\,n-1)}s/\sqrt{n}$[a]	RSD%
	Fe^{3+}			Cu			Ni			Zn		
1	1061.1	33.4	1.1	32.12	4.24	4.76	3.58	0.51	5.11	156.98	10.63	2.44
2	764.26	35.78	1.68	40.76	5.83	5.15	13.06	0.79	2.19	593.17	31.12	1.89
3	107.57	15.03	5.03	68.28	2.30	1.22	7.61	1.64	7.78	209.97	6.63	1.14
4	226.83	35.88	5.70	8.16	3.43	15.16	1.54	0.19	4.34	132.11	7.13	1.95
5	62.76	2.37	1.36	31.68	0.6	0.69	2.56	0.35	4.85	113.81	8.53	2.70
6	145.42	4.42	1.09	5.63	0.37	2.36	<LOD			42.73	4.38	3.69
7	61.51	3.71	2.17	11.03	1.28	4.17	<LOD			179.08	13.37	2.69
8	467.57	28.16	2.17	7.85	0.85	3.92	1,39	0,16	4,22	330.53	43.65	4.76
Quality[b] standard µg/l		–			–			20			–	
	Co			Cd			Mn					
1	<LOD	–	–	<LOD	–	–	257.27	21.27	2.97			
2	<LOD	–	–	20.07	1.65	2.97	300.34	22.84	2.74			
3	<LOD	–	–	<LOD	–	–	35.10	6.94	7.11			
4	<LOD	–	–	<LOD	–	–	84.25	2.13	1.0			
5	<LOD	–	–	99.80	6.43	2.32	32.03	1.2	1.34			
6	<LOD	–	–	53.6	2.87	1.93	–[c]	–	–			
7	<LOD	–	–	15.60	1.72	3.97	5.75	0.68	4.28			
8	<LOD	–	–	<LOD	–	–	69.2	5.37	2.80			
Quality[b] standard µg/l		–			1			–				

[a] Replica number = 5

[b] Legislative Decree (2006; surface water)

[c] It was not possible determine Mn, because of Mg interference

Table 13 Summary of results obtained by IC metal analysis of soils

Metal	Sample[a]	Concentration mean mg/kg	Confidence interval $\pm t_{(95\%,\,n-1)}s/\sqrt{n}$[a]	RSD%	TLVs[b] (residential areas) mg/kg s.s.	TLVs[b] (industrial areas) mg/kg s.s.
Fe^{3+}	1	25,002	5640	8.1	–	
	2	23,740	4480	6.8		–
Cu^{2+}	1	592.04	79.23	4.8	120	600
	2	768.91	111.01	5.2		
Ni^{2+}	1	31.95	3.02	3.4	120	500
	2	16.12	2.64	5.9		
Zn^{2+}	1	2,504.2	525.6	7.56	150	1500
	2	2,982.9	535.0	6.46		
Co^{2+}	1	–	–	–	20	250
	2	–	–	–		
Cd^{2+}	1	99.8	10.53	3.8	2	15
	2	41.74	5.31	4.6		
Mn^{2+}	1	977.9	26.53	9.8	–	
	2	553.0	12.56	8.2		–

[a] Replica number = 5

[b] Threshold limit values, Legislative Decree (2006)

Determination of metals in water samples by the prototypical automatic monitoring system

The good results obtained in the validation tests have encouraged to experiment the method by the automatic monitoring system developed in our laboratory. The automatic monitoring system at present, installed in our laboratory, was modified to effect the determination of Fe^{3+}, Mn, Cu, Cd, Co, Zn, and Ni in water samples. The system affected the standard and sample analysis at fixed time intervals, and metal concentrations were determined comparing standard with sample peak areas. The preliminary results confirmed a good repeatability and accuracy, the second tested using surface water samples previously analyzed

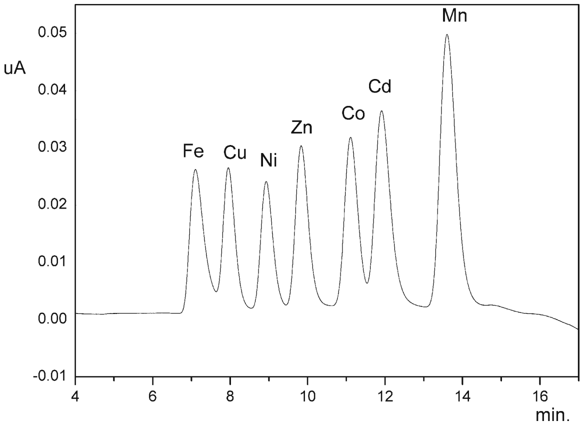

Fig. 7 Chromatogram of a metal standard solution obtained by the automatic monitoring system. Chromatographic conditions: eluent: [PDCA] = 5.95 mM, [KOH] = 56,1 mM, $[K_2SO_4]$ = 4.76 mM, [HCOOH] = 62,9 mM; pH = 4.2 ± 0.1, Standard Fe^{3+} = 30 μg/l, Cu = 30 μg/l, Ni = 45 μg/l, Zn = 15 μg/l, Co = 30 μg/l, Cd = 90 μg/l, Mn = 60 μg/l; loop 1,000 μl; eluent flow rate 1 ml/min; flow rate post-column reagent 0.8 ml/min; detector λ = 530 nm

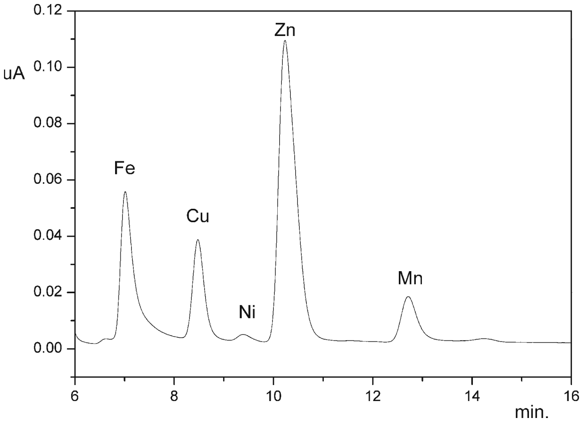

Fig. 8 Chromatogram of a surface water (sample 3, Table 12, dilution 50%) obtained by the automatic monitoring system. Chromatographic conditions: eluent: [PDCA] = 5.95 mM, [KOH] = 56.1 mM, $[K_2SO_4]$ = 4.76 mM, [HCOOH] = 62.9 mM; pH = 4.2 ± 0.1; loop 1,000 μl; eluent flow rate 1 ml/min; flow rate post-column reagent 0.8 ml/min; detector λ = 530 nm

in laboratory. In Figs. 7 and 8 are shown, respectively, the chromatograms of a metal standard solution and of a surface water (sample 3, Table 12) obtained using the automatic monitoring system. Shortly, the prototype will be installed near to a local hydric resource to test the method in field.

Conclusions

The procedure developed, i.e., PDCA and a 1,000-μl sample loop, allows the simultaneous determination of trace heavy metals (Fe^{3+}, Cu, Ni, Zn, Co, Cd, Mn). The separation is performed in few minutes with low detection limits and high repeatability and does not suffer interference from Ca and Mg, when present at low levels (<250 mg/L).

The results obtained from the analysis of environmental matrices have demonstrated that the method is simple, is efficient, shows a good repeatability, and can, therefore, be used for the determination of metals in natural waters using a continuous and automatic monitoring system. This method is currently being tested by the prototypal monitoring system developed in our laboratory with preliminary satisfactory results.

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