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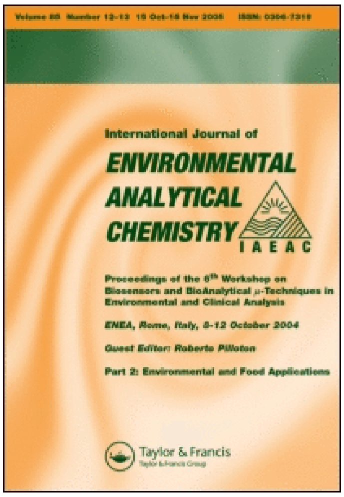

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Sensitivity Enhancement in ICP Emission Spectrometry with Microcolumn Preconcentration and Ultrasonic Nebulisation

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SENSITIVITY ENHANCEMENT IN ICP EMISSION SPECTROMETRY WITH MICROCOLUMN PRECONCENTRATION AND ULTRASONIC NEBULISATION

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To improve the measurement capability of ICP emission spectrometry, microcolumn preconcentration using an iminodiacetate chelating resin (Muromac A-1) has been combined with ultrasonic nebulisation for determination of ultratrace elements (V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and U) in natural waters including seawaters. Trace element deposition was achieved at pH 5 and elution was effected by injection of nitric acid (250 µl, 2.0 M). Sensitivity enhancement factors between 26 and 44 were achieved with on-line preconcentration (sample volume of 10 ml) and detection limits were improved by up to two orders of magnitude relative to conventional pneumatic nebulisation of original water samples. The method was successfully applied to mineral, rain and sea water samples.

Keywords: ICP emission spectrometry; Axial viewing; Flow injection; Microcolumn preconcentration; Ultrasonic nebulisation; Natural waters

INTRODUCTION

Inductively coupled plasma–atomic emission spectrometry (ICP-AES) is widely used for determination of trace metals in environmental samples. Difficulties remain in determining trace metals in natural waters including seawater due to the concentrations being at or below quantification limits and also because of susceptibility to matrix effects. Axially viewed ICP-AES provides improved sensitivity relative to radial measurement, but this is offset by an increased susceptibility to matrix effects [1,2]. Ultrasonic nebulisation (USN) has been widely used in ICP-AES for high efficiency sample introduction to improve sensitivity, however matrix interferences may result [2–8]. Sample preconcentration techniques effectively improve method sensitivity and can also separate analytes from matrix elements [9,10], thus effectively improving

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measurement capability of ICP-AES. Among many preconcentration approaches applied for ICP-AES, microcolumn extraction performed in a miniature flow system is considered simple, rapid and reproducible and also desirable from the standpoint of minimised sample/reagent consumption and contamination [10,11].

Over the past 15 years, a wide range of microcolumn systems, including activated alumina, activated carbon, ion-exchange resins, chelating reagent-immobilised resins/ silica/ cellulose/ porous glass, and hydrophobic resins/ C_{18} sorbent/ knotted reactor, have been coupled to ICP-AES [11]. Chelating ion exchangers with iminodiacetate (IDA) functional group are commonly used for selective retention of transition and heavy metals in the presence of alkali and alkaline-earth metals. Chelex-100 resin has been extensively used for multi-element preconcentration in natural waters [12–14]. Other commercially available IDA materials , such as IDAEC [15], Novarose [16], Metpac CC-1 [17], Toyopearl AF-Chelate 650M [18] and Muromac A-1 [19], have been investigated lately. Compared with readily available Chelex-100, Muromac A-1 chelating resin, a styrene-divinyl benzene copolymer, is of high purity and does not swell and shrink with change in pH [19–28]. It has been applied for determination of Ti, Fe(III), [19] Al, V, [19,28] Cr(III) [19,21,23], Mn [28], Co, Ni [25,27,28], Cu [27,28], Zn [28], Ga [22], Mo [23,24,27], Cd [20,25,28], Pb and U [28] in fresh and sea waters.

The combination of on-line microcolumn preconcentration with USN has been recently employed to achieve ultimate sensitivity enhancement of over two orders of magnitude in ICP-AES [29–33]. Land and Yang [29] achieved detection limits of 0.07, 0.054 and 0.016 $\mu g\, l^{-1}$ (sample volume of 25 ml), respectively, for the determination of Co, Ni and Cd in seawater. Arsenic speciation was formed in the $ng\, l^{-1}$ range in extracts of sediment, sludge and soil [30]. Moyano *et al.* [31] reported on the determination of Bi in urine with a detection limit of 0.03 $\mu g\, l^{-1}$ (sample volume of 100 ml). Determination of Pb [32] and V [33] in drinking water was implemented with total sensitivity enhancement factors of 140 and 180 (detection limits of 0.2 and 0.019 $\mu g\, l^{-1}$, sample volume of 10 ml), respectively.

The aim of the present study was to establish a reliable flow injection (FI) microcolumn preconcentration approach using Muromac A-1 resin in conjunction with USN for sample introduction to improve the sensitivity of axially viewed ICP-AES to a level competitive with that of ICP-mass spectrometry (ICP-MS). This approach would enable ultratrace level determination by ICP-AES to be made in difficult matrices. Matrix removal by the microcolumn is an added advantage. In addition to the on-line elution strategy utilising transient signal measurement, off-line elution was also investigated since for this approach the steady-state signals recorded are compatible with the standard data acquisition software of the ICP instrumentation.

EXPERIMENTAL

Reagents and Materials

High purity water (Milli-Q grade, Millipore, Molsheim, France), ammonium hydroxide (UpA grade, Romil, Cambridge, UK), ammonium acetate, acetic acid and nitric acid (Aristar grade, BDH, Poole, UK) were used throughout. Chelating resin Muromac A-1 (Muromachi, Tokyo, Japan) served as the enrichment medium. Working standard solutions of V(V), Mn, Fe(III), Co, Ni, Cu, Zn, Cd, Pb and U were prepared from 1000 $mg\, l^{-1}$ stock standard solutions (Romil). Certified reference materials, CASS-3 (nearshore seawater for trace metals, NRCC, Ottawa, Canada) and SRM 1643d (fresh water for trace elements, NIST Gaithersburg, MD, USA), were used for method validation. Rainwater was collected around Sheffield and seawater was collected from the Irish sea. Mineral water was purchased locally. All water samples were acidified with 0.1% nitiric acid immediately after collection/filtration and stored in a cold room at 4°C till analysis. Calibrated polypropylene tubes (15 and 50 ml, Sarstedt, Germany) were used for standard and sample solutions.

Flow Injection Manifold and Instrumentation

The flow systems, shown in Fig. 1, were used for effecting deposition/elution of analytes in on-line and off-line modes, respectively. Main components of the on-line manifold included a peristaltic pump (Miniplus 3, Gilson, Villiers-le-Bel, France) and two rotary injection valves (Omnifit, Cambridge, UK) fitted with a 250-μl loop and a Muromac A-1 microcolumn (5.0 cm long and 1.5 mm i.d., 150 μm particle size), respectively. The eluent was loaded with a syringe. The on-line system was connected directly to the USN inlet tubing. A flow rate of 2 ml min^{-1} was maintained for both deposition and elution stages, which was compatible with the USN aspiration requirement.

An axially viewed ICP emission spectrometer (Ciros CCD, Spectro Analytical Instruments, Kleve, Germany), utilising an ultrasonic nebuliser (U-5000AT$^+$, CETAC Technologies, Omaha, NE, USA), was used for all measurements. Instrumental parameters listed in Table I were optimised with continuous sample aspiration. The ICP

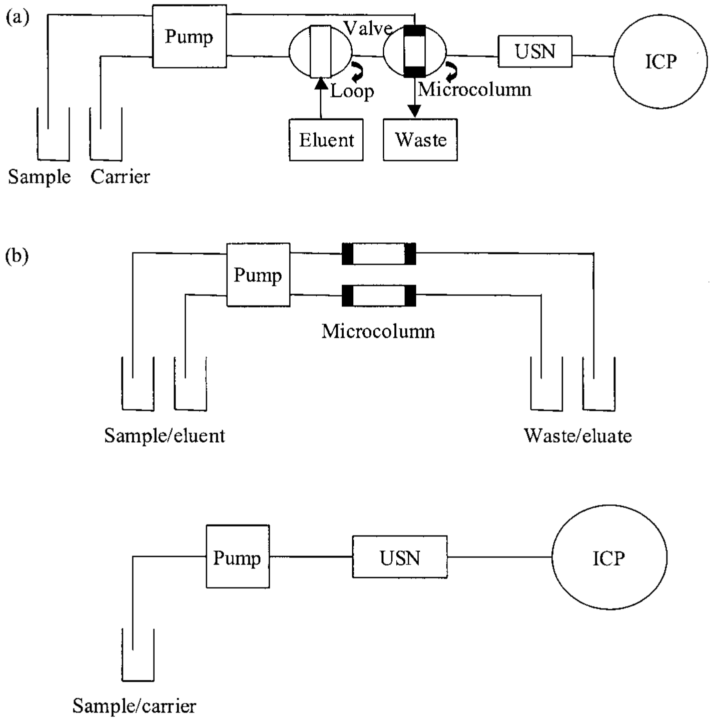

FIGURE 1 Schematic diagrams of on-line (a) and off-line (b) microcolumn preconcentration for USN-ICP-AES.

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TABLE I Operating parameters of ICP-AES, USN and FI system

ICP-AES (Spectro CIROS^{CCD})	
RF Power	1400 W
Coolant Argon	12.0 l min^{-1}
Auxiliary Argon	1.0 l min^{-1}
Nebuliser Argon	0.65 l min^{-1}
USN (Cetac U-5000AT^{+})	
Heater temperature	140°C
Condenser temperature	2°C
FI Manifold	
Flow rate	2 ml min^{-1}

emission lines utilised were 292.464 (V), 257.61 (Mn), 259.94 (Fe), 228.615 (Co), 231.604 (Ni), 324.754 (Cu), 213.856 (Zn), 226.502 (Cd), 220.351 (Pb) and 409.86 (U) nm. For on-line preconcentration, the transient signals were recorded in the "fast mode" as replicate measurements and evaluation of transient signals were achieved using Microsoft Excel software. For off-line preconcentration, triplicate measurements were made with each eluate in the "sensitive mode".

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Procedure

All samples were buffered to pH 5 using ammonium acetate buffer (from 2.0 to 0.1 M). The buffer (0.1 M) was also used as the carrier stream. Microcolumns were pre-washed with 2 ml of 2 M nitric acid and conditioned with 2 ml of 0.1 M acetate buffer before use. For on-line processing, sample solutions (10 ml) were directly passed through the microcolumn (see Fig. 1a). This resulted in analyte deposition while allowing the matrix cations to flow to waste. For seawater, the column was then washed with 0.1 M ammonium acetate buffer (3 ml) to remove residual matrix before analyte elution with injections of 2 M nitric acide (250 µl). Transient signals produced were monitored for 60 s. Two extra injections of the eluent were made to clean the column. For off-line processing, sample solutions (20 ml) were passed through the microcolumn and, after elution with 2 M nitric acid (250 µl), the eluate volume was made up to 2 ml with water for conventional analysis. Nitric acid (2 M) was used for column cleaning (30 s period) followed by ammonium acetate buffer (0.1 M, 60 s) for re-conditioning before the processing of the next sample.

RESULTS AND DISCUSSION

Parameter Optimisation

While Muromac A-1 resin has high affinity for cationic species, sample pH has been shown to be a critical experimental factor for specifically tested analytes [19–28]. Thus the effect of sample pH on analyte deposition was studied with a view to performing simultaneous multi-element analysis. As can be seen in Fig. 2, as a compromise value, Muromac A-1 exhibited good performance for all tested analytes at pH 5, which was thus used for the following studies.

Nitric acid has served as the eluent for Muromac A-1 with concentrations of between 0.7 and 4.0 M depending on the analyte under study [19,21,23–28]. Hence the effects of nitric acid concentration and volume as eluent were studied. It was found that optimum

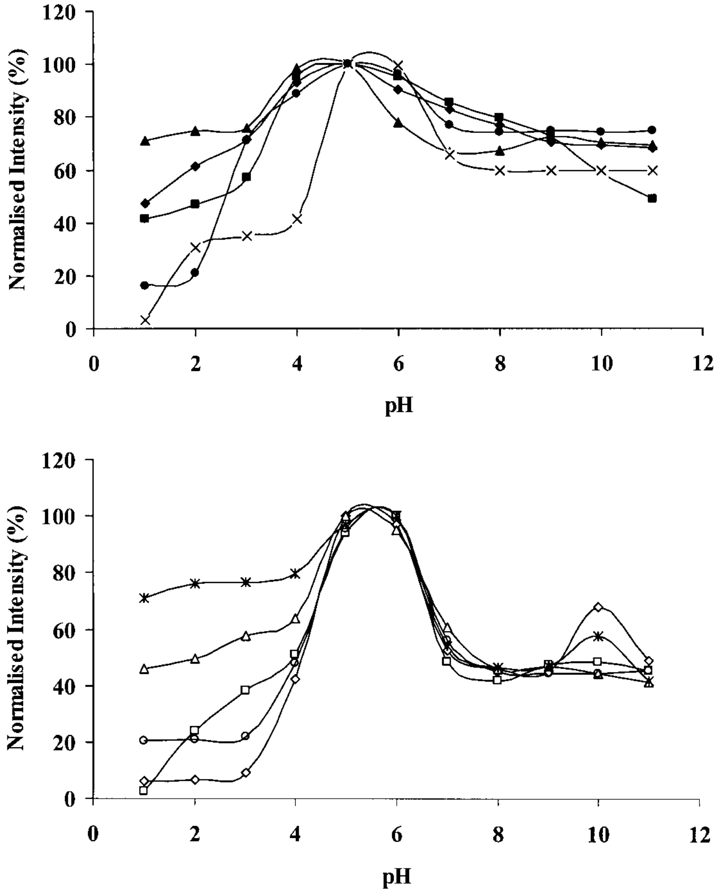

FIGURE 2 Effect of sample pH on analyte deposition on Muromac A-1 microcolumn (■, V; ◆, Mn; ▲, Fe; ×, Co; ●, Ni; □, Cu; ◇, Zn; △, Cd; ✱, Pb; ○, U).

peak height response for on-line elution (multi-element analysis) was obtained using 250 μl of 2 M nitric acid.

Deposition/Elution Performance

Figure 3 illustrates typical FI transient signals obtained for the analytes under study. On injection of sample (point A) via the carrier channel with the column on-line, the analytes underwent deposition and after a period of 300 s, an injection of nitric acid (2 M, 250 μl) was made to effect elution (point B). A further two injections of eluent were made (points C and D) to check on elution efficiency. During sample loading (between points A and B), breakthrough was not observed for any elements (except for a small Fe contribution, ~3%; possibly due to oxidation-state impurity). After the first elution, however, residual Fe, Co and Cu remained on the column as revealed by subsequent elution cycles. An improvement in this aspect would require the use of more concentrated acid and/or larger acid volume, which would result in a more rapid deterioration of microcolumn performance and/or reduce the enrichment

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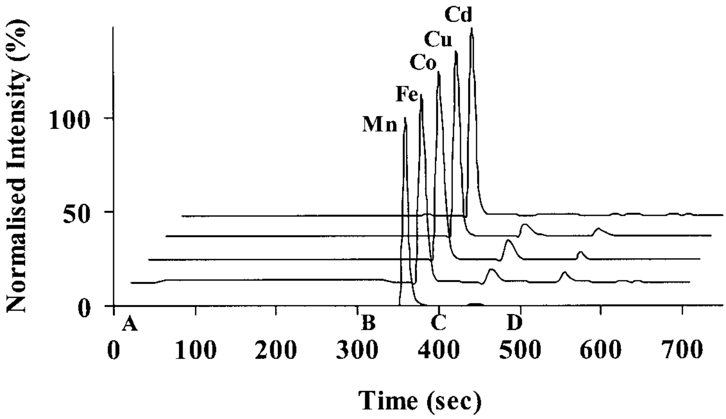

FIGURE 3 Real time response for on-line processing of multi-element standard (10 ml). Transient signals derived from consecutive injections of eluent (250 μl, 2 M HNO_3).

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factor. Two extra injections of nitric acid effectively eliminated the potential carryover to the following sample.

On-line/Off-line Preconcentration

A multi-element standard solution ($10\,\mu g\,l^{-1}$) was processed to study the effect of sample volume on sensitivity using both on-line and off-line preconcentration. Signal intensities increased linearly with the loaded sample volume from 1 to 20 ml (the maximum tested). Enrichment factors between 26 and 44 folds were achieved based on the peak height signals from on-line preconcentration of 10 ml sample as listed in Table II. The low enrichment factor for Fe would be due to its poor elution characteristics. In contrast, for off-line preconcentration (20 ml sample), the enrichment factors were between 7 and 10 fold (Table II). In general, the on-line approach generated enhanced enrichment by a factor of about 4, as expected based on calculation of respective processed/elution volumes.

TABLE II Sensitivity enhancement factors by microcolumn preconcentration and USN

Element	*USN*	*Microcolumn*		*USN/Microcolumn*[a]	
		On-line[b]	*Off-line*[c]	*On-line*	*Off-line*
V	10	43	10	430	100
Mn	11	40	10	440	110
Fe	11	26	7	286	77
Co	10	32	9	320	90
Ni	9	37	10	333	90
Cu	10	36	10	360	100
Zn	10	44	9	440	90
Cd	9	44	10	396	90
Pb	7	44	10	308	70
U	8	40	10	320	80

[a] The product of the two measures; [b] sample volume of 10 ml; [c] sample volume of 20 ml.

Ultrasonic Nebulisation Enhancement

The sensitivity enhancement effect by using USN was estimated by comparison of respective signal responses with that using conventional pneumatic nebulisation. Enhancement factors of between 7 and 11 were achieved (Table II). Thus the USN/on-line microcolumn preconcentration combination could yield a sensitivity enhancement of about 400 fold (Table II) based on the processing of a sample volume of 10 ml.

Analytical Performance

Both on-line and off-line procedures were evaluated for trace analysis. The respective method blank, precision and limits of detection (LOD) are summarized in Table III, together with the detection limits of conventional ICP-AES obtained under standard conditions for comparison. All detection limits were calculated as three times the standard deviation of the blank. In the on-line approach, real-time signal intensities recorded via the instrument software were further manually integrated in Excel software for quantification purpose. The standard deviation of the blank for detection limit calculation was based on 10 single integrated values. In the off-line procedure, triplicate steady-state data acquisition was made for each eluate and the standard deviation of blank was based on 10 mean values. Consequently, the on-line approach produced just slightly lower limits of detection than the off-line procedure. Relative to conventional ICP-AES, the practical limits of detection were improved up to two orders of magnitude and this permitted the determination of trace metals in seawater at the ng l^{-1} level. The precision for seven replicate measurements of 10 μg l^{-1} standard was between 2.1 and 5.0%.

Concerning the on- and off-line preconcentration route, the two routes provided essentially similar detection performance. The on-line mode, however, required a much longer instrument time particularly when column washing was necessary before elution for seawater analysis and during which instrument drift was sometimes observed. Sample throughput was 8 h^{-1} for fresh water and 6 h^{-1} for seawater while it was around 30 h^{-1} for off-line processing. Another potential advantage of the off-line method is that several samples could be processed simultaneously with a multi-channel pump to reduce the overall sample processing time.

TABLE III Analytical performance of the developed method

Element	*On-line*			*Off-line*			*Conventional*^{a}
	Blank (μg l^{-1})	*LOD* (μg l^{-1})	*RSD* (%)^{b}	*Blank* (μg l^{-1})	*LOD* (μg l^{-1})	*RSD* (%)^{b}	*LOD* (μg l^{-1})
V	0.06	0.01	2.1	0.03	0.02	3.5	1.10
Mn	0.009	0.006	3.0	0.04	0.01	2.7	0.25
Fe	0.05	0.05	5.0	0.06	0.06	4.1	0.80
Co	0.008	0.01	2.9	0.01	0.03	3.1	0.86
Ni	0.005	0.01	5.0	0.008	0.04	5.0	1.00
Cu	0.03	0.02	4.0	0.04	0.07	4.5	1.73
Zn	0.08	0.03	4.5	0.05	0.05	4.8	0.26
Cd	0.02	0.005	2.8	0.009	0.02	2.5	0.36
Pb	0.08	0.05	3.6	0.09	0.06	3.8	4.01
U	0.12	0.40	4.9	0.05	0.59	4.2	75.5

[a] Direct pneumatic nebulisation; [b] at 10 μg l^{-1}, $n = 7$.

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Interference and suppression problems caused by the high concentration of matrix elements (Na, K, Ca, Mg, etc.) in waters were insignificant as those elements were separated from the analytes by microcolumn processing. Those analytes, which are badly affected by special interference in ICP-MS (e.g., Fe by ArO and ArOH) can be easily determined by ICP-AES using this methodology.

Analysis of Fresh and Sea Waters

Both on-line and off-line preconcentration procedures were applied to a range of natural water samples. Fresh waters were analysed in the on-line mode (Table IV), while seawaters were processed in the off-line mode (Table V). All samples were run in duplicate. The accuracy was checked with certified reference materials, CASS-3 (nearshore seawater) and SRM 1643d (fresh water). Results listed in Tables IV and V were in good agreement with the certified values. Spiking tests produced recoveries ranged between 90 and 110% for both fresh and sea waters.

TABLE IV Results for seawater samples by off-line preconcentration

Element (μg l^{-1})	*CASS-3*		*Irish seawater*		
	Certified value	*This work*	*Sample 1*	*Sample 2*	*Recovery (%)*[a]
V	NA[b]	0.50 ± 0.01	1.75 ± 0.02	1.60 ± 0.03	105
Mn	2.51 ± 0.36	2.22 ± 0.01	0.79 ± 0.02	1.56 ± 0.01	96
Fe	1.26 ± 0.17	1.41 ± 0.13	13.42 ± 0.07	39.14 ± 0.08	110
Co	0.041 ± 0.009	0.031 ± 0.009	0.25 ± 0.01	0.31 ± 0.01	98
Ni	0.386 ± 0.062	0.33 ± 0.09	0.86 ± 0.03	1.85 ± 0.03	97
Cu	0.517 ± 0.062	0.59 ± 0.06	3.02 ± 0.03	13.55 ± 0.04	93
Zn	1.24 ± 0.25	1.14 ± 0.10	18.20 ± 0.13	15.27 ± 0.14	110
Cd	0.030 ± 0.005	0.025 ± 0.005	0.110 ± 0.005	0.092 ± 0.007	105
Pb	0.012 ± 0.004	ND[c]	0.93 ± 0.04	1.35 ± 0.03	104
U	2.84[d]	3.03 ± 0.13	2.43 ± 0.19	3.57 ± 0.19	105

[a] At 10 μg l^{-1}; [b] not available; [c] not detected; [d] informative value only.

TABLE V Results for fresh water samples by on-line preconcentration

Element (μg l^{-1})	*SRM 1643d*		*Rainwater*		*Mineral water*		
	Certified value	*This work*	*Sheffield*	*Hope*	*Badoit (France)*	*Buxton (UK)*	*Recovery (%)*[a]
V	35.1 ± 1.4	35.47 ± 0.04	0.48 ± 0.02	0.83 ± 0.04	0.18 ± 0.05	0.26 ± 0.03	101
Mn	37.66 ± 0.83	35.87 ± 0.02	8.80 ± 0.03	3.15 ± 0.05	0.10 ± 0.02	0.06 ± 0.03	91
Fe	91.2 ± 3.9	93.12 ± 0.15	33.02 ± 0.11	43.56 ± 0.13	181.00 ± 0.16	54.20 ± 0.17	107
Co	25.00 ± 0.59	24.35 ± 0.15	0.30 ± 0.02	0.18 ± 0.05	0.25 ± 0.07	0.20 ± 0.04	90
Ni	58.1 ± 2.7	57.36 ± 0.08	5.61 ± 0.05	1.48 ± 0.07	0.79 ± 0.06	0.47 ± 0.03	92
Cu	20.5 ± 3.8	19.28 ± 0.11	10.19 ± 0.10	6.86 ± 0.11	9.20 ± 0.12	2.50 ± 0.13	103
Zn	72.48 ± 0.65	71.95 ± 0.11	10.71 ± 0.09	32.39 ± 0.10	1.64 ± 0.11	0.58 ± 0.12	108
Cd	6.47 ± 0.37	6.05 ± 0.06	0.19 ± 0.05	0.15 ± 0.04	0.09 ± 0.07	0.16 ± 0.04	106
Pb	18.15 ± 0.64	17.78 ± 0.08	1.36 ± 0.08	0.94 ± 0.06	0.11 ± 0.05	0.14 ± 0.02	95
U	NA[b]	ND[c]	ND[c]	ND[c]	2.05 ± 0.06	5.56 ± 0.09	104

[a] At 10 μg l^{-1}; [b] not available; [c] not detected.

CONCLUSIONS

The methods developed in this study demonstrate a good capability for trace multi-element analysis of environmental water samples by ICP-AES. The sensitivity was enhanced by up to 400 fold and the matrix interference problems associated with difficult samples such as seawater was overcome to provide a procedure competitive with ICP-MS. In the future, it will be possible to extend the work to include field sampling, whereby water samples would be processed at the sampling site and trace elements preserved on microcolumns until laboratory measurement is performed [17,34,35].

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References

[1] J.C. Ivaldi and J.F. Tyson, *Spectrochim. Acta*, **50B**, 1207–1226 (1995).
[2] I.B. Brenner and A.T. Zander, *Spectrochim. Acta*. **55B**, 1195–1240 (2000).
[3] C.E. Taylor and T.L. Floyd, *Appl. Spectros.*, **35**, 408–413 (1981).
[4] P. Galli and N. Odo, *Microchem. J.*, **46**, 327–334 (1992).
[5] T. Uchida, H. Isoyama, H. Oda, H. Wada and H. Uenoyama, *Anal. Chim. Acta*, **283**, 881–886 (1993).
[6] A. Clement, C. Brechet and M. Geoffroy, *Analusis*, **22**, 311–325 (1994).
[7] M. Hoenig, H. Docekalova and H. Baeten, *J. Anal. At. Spectrom.*, **13**, 195–199 (1998).
[8] W. Hoenig, H. Docekalova and H. Baeten, *Analusis*, **28**, 419–425 (2000).
[9] Z.B. Alfassi and C.M. Wai, *Preconcentration Techniques for Trace Elemets*. CRC Press, Boca Raton (1992).
[10] Z. Fang, *Flow Injection Separation and Preconcentration*. VCH, Weinheim (1993).
[11] A. Sanz-Medel, (Ed.), *Flow Analysis Atomic Spectrometric Detection*. Elsevier, Amsterdam (1999).
[12] W.W. Vanberkel, A.W. Overbosch, G. Feenstra and F.J.M.J. Maessen, *J. Anal. At. Spectrom.*, **3**, 249–257 (1988).
[13] Z. Samczynski and R. Dybczynski, *J. Chromatog.*, **789A**, 157–167 (1997).
[14] T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba and H. Haraguchi, *Bull. Chem. Soc. Japan*, **72**, 2253–2260 (1999).
[15] S. Carolis, A. Alimonti, F. Petrucci and Z. Horvath, *Anal. Chim. Acta*, **248**, 241–249 (1991).
[16] P. Hashemi and A. Olin, *Talanta*, **44**, 1037–1053 (1997).
[17] R.A. Nickson, S.J. Hill and P.J. Worsfold, *Intern. J. Environ. Anal Chem.*, **75**, 57–69 (1999).
[18] K.W. Warnken, D. Tang, G.A. Gill and P.H. Santschi, *Anal. Chim. Acta*, **423**, 265–276 (2000).
[19] S. Hirata, Y. Umezaki and M. Ikeda, *Anal. Chem.*, **58**, 2602–2606 (1986).
[20] T. Kumamaru, H. Matsuo, Y. Okamoto and M. Ikeda, *Anal. Chim. Acta*, **181**, 271–275 (1986).
[21] B. Pasullean, C.M. Davidson and D. Littlejohn, *J. Anal. At. Spectrom.*, **10**, 241–246 (1995).
[22] C.R.M. Rao, *Anal. Chim. Acta*, **318**, 113–116 (1995).
[23] Y. Sung, Z. Liu and S. Huang, *Spectrochim. Acta*, **52B**, 755–764 (1997).
[24] Y. Sung, Z. Liu and S. Huang, *J. Anal. At. Spectrom.*, **12**, 841–847 (1997).
[25] H. Chang, Y. Sung and S. Huang, *Analyst*, **124**, 1695–1699 (1999).
[26] S. Hirata, K. Honda, O. Shikino, N. Maekawa and M. Aihara, *Spectrochim. Acta*, **55B**, 1089–1099 (2000).
[27] P. Lin, K.S.K. Danadurai and S. Huang, *J. Anal. At. Spectrom.*, **16**, 409–412 (2001).
[28] S. Hirata, Y. Ishida, M. Aihara, K. Honda and O. Shikino, *Anal. Chim. Acta*, **438**, 205–214 (2001).
[29] C. Lan and M. Yang, *Anal. Chim. Acta*, **287**, 111–117 (1994).
[30] M. Ochsenkuhn-Petropulu and P. Schramel, *Anal. Chim. Acta*, **313**, 243–252 (1995).
[31] S. Moyano, J.A. Gasquez, R. Olsina, E. Marchevsky and L.D. Martinez, *J. Anal. At. Spectrom.*, **14**, 259–262 (1999).

[32] J.A. Salonia, R.G. Wuilloud, J.A. Gasquez, R.A. Olsina and L.D. Martinez, *J. Anal. At. Spectrom.*, **14**, 1239–1243 (1999).

[33] R.G. Wuilloud, J.A. Salonia, R.A. Olsina and L.D. Martinez, *Spectrochim. Acta*, **55B**, 671–680 (2000).

[34] J. Wei, M.L. Mena, C.W. McLeod and J. Rollins, *Intern. J. Environ. Anal. Chem.*, **57**, 99–106 (1994).

[35] R. Ma, G.D. Woods and C.W. McLeod, In: A. Sanz-Medel (Ed.), *Flow Analysis Atomic Spectrometric Detection*, Elsevier, Amsterdam, pp. 439–458 (1999).

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