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Application of high-surface-area ZrO₂ in preconcentration and determination of 18 elements by on-line flow injection with inductively coupled plasma atomic emission spectrometry

Received: 4 October 2000 / Revised: 18 January 2001 / Accepted: 23 January 2001

Abstract A flow-injection analysis (FIA) system incorporating a micro-column of ZrO₂ has been used for the development of an on-line multi-element method for the simultaneous preconcentration and determination of Al, Bi, Cd, Co, Cr, Cu, Fe, Ga, In, Mn, Mo, Ni, Pb, Tl, V, Sb, Sn, and Zn by inductively coupled plasma atomic emission spectrometry (ICP–AES). The conditions for quantitative and reproducible preconcentration, elution, and subsequent on-line ICP–AES determination were established. A sample (pH 8) is pumped through the column at 3 mL min⁻¹ and sequentially eluted directly into the ICP–AES with 3 mol L⁻¹ HNO₃. With a sample volume of 100 mL and an elution volume of 1 mL signal enhancement 100 times better than for conventional continuous aspirating systems was obtained for the elements studied. The reproducibility (RSD %) of the method at the 10 ng mL⁻¹ level in the eluate is acceptable – less than 8% for five replicates. Recoveries between 95.4% and 99.9% were obtained for the elements analysed. ZrO₂, with a specific surface area of 57 m² g⁻¹ and a capacity of approximately 5 mg g⁻¹ for the elements studied, was synthesized by hydrolysis of ZrCl₄. The preconcentration system was evaluated for several simple synthetic matrices, standard water samples and synthetic seawater. The effect of foreign ions on the efficiency of preconcentration of the elements studied was investigated. The application of a micro-column filled with high-surface-area ZrO₂ and flow injection inductively coupled plasma atomic emission spectrometry enables preconcentration and simultaneous determination of 18 elements at low concentrations (ng L⁻¹) in different water samples.

Introduction

The accurate determination of trace elements in natural waters is an important and challenging task in analytical chemistry. Heavy metals are often routinely monitored in environmental water. Direct determination of trace elements at low concentrations by modern atomic spectroscopic techniques is often difficult, not only because of the insufficient sensitivity of the methods, but also because of matrix effects.

Nowadays, flow injection (FI) technology has significantly enhanced the performance of spectrophotometric methods [1–5]. In comparison with their off-line batch counterparts, these systems have a number of significant advantages for trace determination – greater efficiency, lower consumption of sample and reagent, improved precision, possibility of working in a closed system with a significant reduction of airborne contamination, and increased sampling frequency. Despite high detection power, ICP–AES often cannot be routinely used for the direct trace element analysis of many natural samples of environmental interest. The direct ICP–AES determination of trace metals in high-saline matrices such as seawater is difficult owing to problems with signal suppression and clogging of the sample introduction system, in particular when the sample also contains high concentrations of dissolved matter [6, 7]. Consequently, trace-matrix separation and preconcentration procedures are often required before the ICP–AES determination [8, 9]. More recently the use of different types of adsorbent for the preconcentration and separation of trace elements has gained popularity because of: 1. the high concentration factor achieved, 2. simple operation, 3. the possibility of using a closed circulation system, 4. combination with different modern analytical techniques, enabling, when inductively coupled plasma–mass spectrometry and ICP–AES are used, simultaneous multielement determinations. Inorganic ion exchangers, including metal oxides, have been used for a long time [10–12]. Studies are mainly restricted to the use of pure and modified silica, alumino-silicates [13–15],

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and activated alumina [16–19]. Investigations of the surface chemistry of highly dispersed oxides, e.g. TiO₂, ZrO₂, CeO₂, and ZnO indicate that these materials have a very high adsorptive capacity [20–24] and give promising results when used for trace-metal analyses of different types of water [25, 26] and solutions of high-purity alkali salts [27]. The adsorption properties of many oxides, including zirconia, strongly depend on the characteristics of the solid, e.g. crystal structure, morphology, defects, specific surface area, hydroxyl coverage, surface impurities, and modifiers [28]. Control of these factors can be achieved by using an appropriate synthetic method.

In this study on-line preconcentration and matrix separation was investigated for trace metals. The flow-injection (FI) manifold incorporates a micro-column filled with high-surface-area ZrO₂. The efficiency of this material for the preconcentration of trace elements was studied in detail, especially its dependence on pH, flow rate, precision, and interference of other ions. Attention was focused on optimization of the conditions for the multi-element preconcentration of trace elements from different types of water, their complete elution, and their subsequent simultaneous FI-ICP-AES determination.

Table 1 ICP-AES operating conditions and wavelengths of emission lines examined

Plasma gas flow	16.0 L min ⁻¹		
Intermediate gas flow	1.26 L min ⁻¹		
Aerosol carrier gas flow	1.10 L min ⁻¹		
Plasma generator frequency	27.12 MHz		
Incident power	1.30 kW		
Spectral species	Wavelength (nm)	Spectral species	Wavelength (nm)
Ag I	328.068	Ni II	231.604
Al II	167.079	Os I	326.229
As I	189.042	Pd II	340.458
Au I	267.595	Pb	220.351
Bi I	223.061	Rb I	780.023
Ca II	317.933	Re I	488.914
Cd II	226.502	Re II	346.047
Co II	228.616	Rh I	365.799
Cu I	654.738	Rh II	343.489
Ga I	417.206	Ru I	372.803
Ge I	265.118	Sb I	217.581
Fe II	259.94	Sc II	722.768
In I	325.609	Se I	196.090
Ir II	224.268	Sn II	189.989
Hg I	184.950	Ta II	268.511
Hf II	339.978	Te II	214.275
K I	766.491	Th II	401.913
Li I	670.784	Tl II	190.864
Mg II	279.079	V II	292.464
Mn II	257.610	W II	207.916
Mo II	202.030	Y II	321.669
Na I	589.592	Zn I	213.856
Nb I	405.893	–	–

Experimental

Reagents. Standard solutions (1000 mg mL⁻¹ for each element) were purchased from Kanto Chemical (Tokyo, Japan). Sample solutions were prepared daily, by serially diluting the stock solution, and stored in precleaned polypropylene containers. The HNO₃, and NH₃ used were of high purity grade (Tama Chemical, Japan). High-purity water was prepared by further purification of deionized water using a Milli-Q system (Milli-Q SP ICP-MS; Millipore, Tokyo, Japan). Suprapur grade salts (Merck) were used to prepare solutions and test samples. A synthetic seawater solution was prepared by dissolving 1.87 g CaCl₂·4H₂O, 0.4 g KCl, 13.8 g Mg(NO₃)₂·6H₂O, and 27.4 g NaCl in 1000 mL high-purity water. Laboratory-prepared samples of high-surface-area ZrO₂ were used. To synthesize this ZrCl₄ (p.a., Merck; 100 mL) was hydrolyzed carefully in water (1 L) for 3 days then the solution was adjusted to pH 9 by drop-wise addition of 12.5% ammonia solution. The precipitate produced was filtered, washed well with water, dried at 120 °C and calcined for 3 h at 450 °C. The powder obtained was ground in an agate mortar, washed again to remove residual chloride ions, and dried in air at 120 °C. The ZrO₂ so obtained had a specific surface area of 57 m² g⁻¹, as determined by low-temperature adsorption of N₂ in a laboratory built device.

River water standard solution (natural river water to which elements had been added) was obtained from Japan Analytical Chemical Society. Standard reference material 1643 c was obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA.

Apparatus. ICP-AES measurements were performed with an Spectroflame Compact S/E ICP spectrometer with two polychromators setting gratings of 3600 grooves mm⁻¹ and 1800 grooves mm⁻¹, and one monochromator setting a grating of 2400 grooves mm⁻¹. The polychromators have 43 simultaneous analytical channels. The operating conditions and the wavelengths of the emission lines used are summarized in Table 1. The analytical lines for the monochromator were selected on the basis of their net and background intensities and their freedom from spectral interference overlap. All measurements were performed in transient scan mode with integration time for each element of 50 ms, interval time 50 ms, and 1000 point per peak. Peak areas were used for quantification.

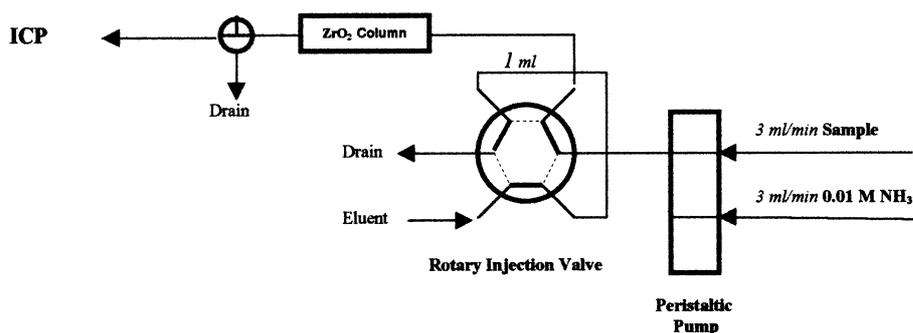
pH adjustment was performed by means of a Basis pH meter (Denver Instrument Company, Colorado, USA).

Infrared spectra were recorded on a Specord M-80 IR apparatus (Carl Zeiss, Jena, Germany) at a spectral resolution of 2 cm⁻¹. Self-supporting discs were prepared from the samples investigated and treated directly in an IR cell connected to a vacuum-adsorption apparatus (residual pressure 10⁻⁵ Torr).

Column preparation. The ZrO₂ micro-column was prepared by mixing 0.1 g high-surface-area ZrO₂ and 0.1 g glass beads (Hewlett-Packard, 40–60 mesh) and packing the mixture as a dry powder in a Teflon tube (0.4 mm i.d., length 40 mm). The aim in the construction of the micro-column was to prepare a column with high capacity, capable of handling high flow rates and enabling elution of the analytes in a small volume. To reduce blank values, before use the column was washed with HNO₃ (3 mol L⁻¹) and high-purity water (3 × 20 mL).

General procedure for FI-ICP-AES measurement. A schematic diagram of the FIA system is shown in Fig. 1. The micro-column was conditioned by pumping ammonia solution (0.01 mol L⁻¹, 6 mL) at a rate of 3 mL min⁻¹. To prevent the precipitation of some elements the pH was adjusted to 8, on-line, by adding ammonia solution (0.01 mol L⁻¹) at a flow rate of 3 mL min⁻¹. During the preconcentration procedure (100 mL sample volume) the flow rate of sample was 3 mL min⁻¹. The adsorbed trace elements were eluted with HNO₃ (3 mol L⁻¹, 1 mL) at a flow rate of 0.5 mL min⁻¹. The eluted sample was introduced into the ICP-AES. Total time for conditioning of the column, preconcentration, elution, and determination was approximately 30 min.

Fig. 1 Schematic diagram of the preconcentration flow-injection system



Test solutions. Pure water test samples (100 mL) or artificial seawater test samples (100 mL) were prepared by spiking high-purity water or artificial seawater with trace elements. The concentration of the trace element in the test samples was 10 ng mL^{-1} .

The influence of sample flow rate was studied with use of a constant flow rate of eluent (1 mL min^{-1}). Changes in the flow rate of the sample between 1 and 6 mL min^{-1} resulted in small variations in the measured peak areas of the elements studied. The peak areas of all the elements decreased at higher flow rates. Only for Cr(VI) was a lower rate of adsorption detected, probably because aqua-Cr(VI) complexes are chemically inert. In accordance with the results obtained a flow rate of 3 mL min^{-1} was chosen for all further investigations. Preliminary tests showed that the sample volume was not an important factor when the mass of analyte adsorbed at the column was kept constant.

Determination of exchange capacity. Standard solution of each investigated element ($500 \text{ } \mu\text{g mL}^{-1}$, 25 mL) was added to ZrO_2 (0.1 g). The pH was adjusted to 8 by appropriate addition of HNO_3 or NH_4OH (0.1 mol L^{-1}). The mixture was equilibrated by stirring overnight. The solution was filtered and the filter washed several times with high-purity water. The concentration of elements, concentrated on high-surface-area ZrO_2 was determined after elution with HNO_3 (3 mol L^{-1}) and appropriate dilution. The concentration of ions in the liquid phase was determined directly by ICP-AES. Exchange capacity was determined under dynamic conditions also; it was not significantly different from that obtained under batch conditions.

Results and discussion

Influence of pH

pH is a critical condition affecting quantitative recovery of trace elements. Under batch conditions the effect of the pH of a pure water sample on solid-phase extraction by high-surface-area ZrO_2 was investigated. The dependence on solution pH of the amounts adsorbed, calculated as a percentage of the amount introduced, (R %), for a series of elements shows that pH in the range 7.5–8 was most appropriate for quantitative preconcentration of many elements – Al, Bi, Co, Cd, Cu, Cr, Ga, Ge, Fe, Hf, In, Ir, Mo, Mn, Nb, Ni, Os, Pb, Ru, Rh, Sb(III), Sb(V), Sc, Sn, Ta, Te, Tl, V, W, Y, and Zn. For some elements – As(III), As(V), Cr(VI), Se(IV), and Se(VI) – quantitative recovery (> 95%) is possible only at low pH (1–2). Au, Hg, Re, and Pd are not quantitatively adsorbed, irrespective of pH. For Ag adsorption is low from very acidic and very basic solutions (R is between 0 and 10%). High recovery (> 98%) over a wide pH range (from 1 to 10) was observed for Ge, Hf, Mo, Sb(III), Sb(V), Sn, Te, V, and W.

On the basis of these results all subsequent investigations of the simultaneous preconcentration of mixtures of elements were conducted at pH 8. The elements of group IA are not adsorbed in this range whereas group IIA cations – the major constituents of seawater – are partially adsorbed at pH 8 (ca 60% Mg and 70% Ca at a concentration level of $1 \text{ } \mu\text{g mL}^{-1}$). Indeed, compared with the selectivity for cations such as Ca, Mg, Na, and K, that for transition elements is higher and their preconcentration from natural water on ZrO_2 is based on fixation under conditions when the matrix elements are only ionogenically bound, or not bound at all. In seawater their concentrations are 5–7 orders of magnitude lower than those of the matrix elements. As a result, one might expect some trace elements to be partly adsorbed on ZrO_2 .

These results show the possibility of simultaneous preconcentration and matrix separation for several heavy metals on high-surface-area ZrO_2 . For example, at pH 8, of the elements studied only Ag, Au, Hg, Pd, and Re were not quantitatively adsorbed. ZrO_2 has advantages in comparison with the commonly used silica – adsorption of cations on amphoteric oxides such as zirconia is usually accomplished when pH of the solution is higher than the isoelectric point (IEP) of the oxide, whereas for anion adsorption pH values lower than the IEP are required [29]. It is, in general, postulated that the adsorption of ions on oxide surfaces proceeds by participation of the surface hydroxyl groups [23, 29, 30]. At a pH higher than the IEP, the oxide surface is covered by OH^- groups and is negatively charged. As a result, it becomes an active absorber of cations. Testing of the zirconia surface with CO adsorption and IR spectroscopy revealed the presence of two kinds (λ and β) of Lewis acid site (coordinatively unsaturated Zr^{4+} ions), which differ in their coordination. At pH 8 (ammonia solution) some of elements studied (Cd, Co, Cu, Cr, Ni, and Zn) form positively charged amino complexes and are strongly adsorbed on zirconia. Under these conditions no λ sites were detected by CO adsorption, i.e. they were blocked. At pH 8 Mo and V occur as positively charged ions and neither λ or β sites were observable on zirconia samples with pre-adsorbed Mo and V ions at this pH. IR investigations with CO adsorption for the rest of elements studied show the presence of the both types of site. These results indicate that they are retained on the oxide surface, probably after their precipitation at pH 8, as poorly soluble hydroxides. The detailed mechanism, and

Table 2 Adsorption capacity of ZrO_2 (surface area $57 \text{ m}^2 \text{ g}^{-1}$) determined by means of a batch procedure

Element	Capacity, mg g^{-1}
Cd	5200
Co	4965
Cu	7890
Mn	6240
Ni	5621
Pb	4897
Zn	5920

the nature of the active sites and of cation adsorption on zirconia, are the main purposes of our further investigations.

In addition to cation adsorption, zirconia adsorbs many anions; such behavior is not characteristic of acid silica, but is typical of high-surface-area TiO_2 (anatase) [31, 32].

Evaluation of the capacity

The capacity of ZrO_2 was evaluated for several elements. The values for batch capacity are presented in Table 2. For most of the elements the values obtained are closed to 5 mg g^{-1} . The data presented also show that the capacity of zirconia is significantly higher than that of silica [25]. The capacity for the other elements has not been studied but on the basis of recovery results the capacity of ZrO_2 is sufficient for a wide range of elements. The adsorption capacity should, however, be strongly affected by the specific surface area and the morphology of the zirconia. In our investigation the capacity was determined after adsorption of the ions from their solutions at pH 8, then washing of the column. Thus this value applies to irreversible adsorption only.

It was of interest to check whether or not the adsorption capacity changes after several adsorption/elution steps. The high stability of zirconia resulted long column lifetime, enabling hundreds of load and elution cycles to be performed without loss of analytical performance. Our results indicate that zirconia is a suitable substance for multi-element-extraction procedures and effective matrix separation.

The high capacity of the mini-column meant that 0.5 mg could be used for preconcentration from sample volumes up to 300 mL without degradation of performance. Quantitative recovery of Mn was achieved from seawater sample volumes up to 150 mL . 100 mL was the upper limit selected for the evaluation because larger volumes required unrealistically long loading times.

The column capacity should be large compared with the amounts of trace elements yet at the same time be sufficiently small to ensure that only a small part of the matrix components can be bound to the adsorbent. The column capacity must be optimized at the sample-loading/elution and determination stages to balance the tolerance capacity for the interferences present.

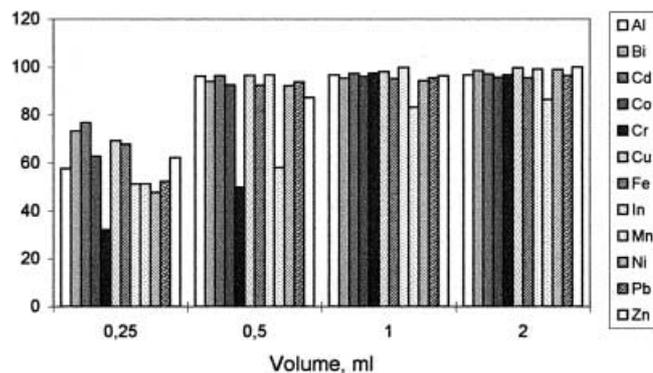


Fig. 2 Dependence on the volume of eluent ($3 \text{ mol L}^{-1} \text{ HNO}_3$) used of the elution (%) of $1 \mu\text{g}$ of the investigated elements from 0.1 g ZrO_2

Elution

Figure 2 is an elution histogram for the elements studied after preconcentration of each by the column from 100 mL solution of concentration $10 \mu\text{g L}^{-1}$. It is apparent that $1 \text{ mL } 3 \text{ mol L}^{-1} \text{ HNO}_3$ is appropriate for elution of the elements for subsequent FI-ICP-AES determination. One possible disadvantage of using metal oxides as solid-phase extractants is possible partial dissolution of the oxide during elution. The concentration of Zr in the elution solution did not exceed $20 \mu\text{g mL}^{-1}$, a concentration which does not cause a problem in the analysis step. The influence of the elution flow rate on recovery and precision for triplicate determination of an element at a concentration of $10 \mu\text{g L}^{-1}$ was investigated in the range $0.2\text{--}2 \text{ mL min}^{-1}$. Maximum recovery and high precision were obtained in the range $0.2\text{--}1 \text{ mL min}^{-1}$ for all the elements studied, except Mn. For this element recovery was maximum in the flow range $0.2\text{--}0.5 \text{ mL min}^{-1}$. Thus, a flow rate of 0.5 mL min^{-1} was used for elution for all further investigations.

Preconcentration efficiency

The efficiency of the preconcentration system was determined by passing 100 mL solution, concentration 10 ng mL^{-1} and pH 8, through the column. An elution loop for flow-injection sample introduction directly into the nebulizer was used. The integrated signals after preconcentration were compared with the corresponding integrated signals for $1 \text{ mL } 1 \mu\text{g mL}^{-1}$ standard solution passed through the ZrO_2 minicolumn not loaded with sample. Both analyses were performed in triplicate. Integrated intensities were corrected for the background. Table 3 summarizes the data characterizing the recovery of metals from pure water and seawater by use of preconcentration on a ZrO_2 micro-column and FI-ICP-AES determination. For both types of sample the preconcentration system enhances the absolute sensitivity compared with the direct aspiration of the analytes in $1\% \text{ HNO}_3$.

Table 3 Recovery (%) of metal ions in the preconcentration procedure from a micro-column filled with 100 mg ZrO₂. The values presented are averages from three determinations (X ± SD)

Element	Pure water (%RSD)	Sea water (%RSD)
Al	97.3 ± 8.0 (8.2)	95.0 ± 2.2 (2.3)
Bi	97.3 ± 6.0 (6.2)	90.9 ± 2.6 (2.9)
Cd	98.2 ± 2.6 (2.8)	95.2 ± 6.2 (6.5)
Cr	97.6 ± 2.0 (2.0)	93.6 ± 5.8 (6.2)
Co	95.0 ± 5.2 (5.5)	88.2 ± 3.6 (4.1)
Cu	98.1 ± 3.4 (3.5)	97.2 ± 2.1 (2.2)
Fe	96.3 ± 5.0 (5.2)	92.1 ± 2.1 (2.3)
In	95.6 ± 5.3 (5.5)	95.0 ± 5.3 (5.6)
Mn	93.1 ± 2.3 (2.5)	74.9 ± 5.8 (7.7)
Mo	95.8 ± 4.0 (4.2)	96.6 ± 4.3 (4.5)
Ni	96.0 ± 4.3 (4.5)	92.2 ± 6.3 (6.8)
Pb	97.8 ± 2.7 (2.8)	95.2 ± 6.0 (6.3)
Sb	96.6 ± 1.3 (1.3)	91.8 ± 2.8 (3.0)
Tl	96.6 ± 4.0 (4.1)	95.3 ± 5.3 (5.6)
V	98.8 ± 1.4 (1.4)	95.1 ± 5.2 (5.5)
Zn	97.1 ± 3.3 (3.4)	95.5 ± 6.7 (7.1)

For pure water, quantitative (> 95%) recovery was obtained for all the elements investigated except Mn (93.1%). The relative precision, measured as % RSD, was between 1.3 and 5% except for Al (8.2%) and Bi (6.2%).

For artificial seawater the procedure described enables quantitative recovery of almost all the elements studied – exceptions were Bi, Co, Fe, Mn, and Sb (see Table 3). The relative precision for preconcentration of a 100-mL sample of seawater (concentration 10 µg L⁻¹ of each element) was between 2.2% and 7.7%. For seawater the recovery could be increased by reducing the sample volume used. This, however, competes with the enrichment factor attained.

Effect of foreign ions on the preconcentration of trace elements

One might expect that for the analysis of natural water the exchange sites not occupied by trace metals remain as magnesium or calcium complexes. The higher exchange capacity of the separation column results in larger remaining amounts of alkaline earth metals. The low affinity of zirconia for alkali and alkaline earth elements results in excellent exclusion of these elements from the column and easy operation with saline water. Despite this, the column becomes loaded with Ca and Mg on sites not occupied by heavy metals.

We investigated the effect of Ca²⁺, Mg²⁺, Na⁺, and K⁺ (the major constituent of natural water) and of Fe³⁺ and Mn²⁺ on the preconcentration of some of the elements studied (Tables 4 and 5). The matrix concentrations were varied and the concentration of the analytes was kept at 10 µg L⁻¹. It can be seen that the Group IA metal ions have the weakest effect, whereas even low concentrations of Fe³⁺ and Mn²⁺ noticeably suppress the adsorption of the trace elements investigated.

Preconcentration efficiency for Cr, Mn, Ni, Pb, Tl, and Zn was reduced only in the presence of relatively high concentrations of Ca and Mg, because these elements can be adsorbed by zirconia (obviously the other elements also, but with less stability) and compete with other trace elements for the active sites. On the other hand, in a separate study a slight increase of the ICP emission signals of Al, Tl, and Zn was observed in the presence of a high concentration of K.

The final amounts of Ca and Mg on the column after passage of 100 mL seawater were 600 µg mL⁻¹ Ca and 500 µg mL⁻¹ Mg, and the total matrix concentration in the acidic eluate was approximately 0.1%. Such concentration is sufficiently low to exclude the possibility of interference in subsequent FI-ICP-AES. The observation that only ions of the d-elements are strongly adsorbed on zirconia provided the possibility of preconcentrating the lat-

Table 4 Effect of foreign cations on the recovery (%) of the studied elements after preconcentration on a micro-column filled with 100 mg ZrO₂ and subsequent ICP-AES determination. The values presented are averages from three determinations

Foreign cation	Concentration µg mL ⁻¹	Al	Bi	Cd	Cr	Co	Cu	Ga	In
Na	1000	101	99.4	99.8	97.1	99.8	99.8	102	100
	3000	104	99.8	99.3	93	97.5	99.8	100	98.5
K	50	100.2	100	99	100	99.8	99.6	100	99.1
	100	103.6	99.8	99	100	98.3	95.4	100	98.2
	200	104	99.6	98.2	99	98.1	98	100	97.0
	500	106	98.4	98	93	97	97	98	96.4
Ca	500	99.2	100	99.2	95.7	99.4	99	98.2	99.4
	1000	98	99.6	98.2	93.6	99.2	98.7	97.4	99.0
	3000	93	99.6	95.4	82.4	96.5	93.5	95	97.6
Mg	50	98.2	97.6	99	99.3	98.8	93	96.5	98.4
	1000	98	97.3	98.7.3	97.7	96.4	99.1	94.1	97.3
	3000	97.7	96.4	97.6	92.6	93.7	100	91	98.4
Fe	5	96	95.4	92.8	95.3	93.9	98	98.8	97.3
Mn	5	97.6	98	94.3	96.7	97.3	95.4	98.2	98.0

Table 5 Effect of foreign cations on the recovery (%) of the studied elements after pre-concentration on a micro-column filled with 100 mg ZrO₂ and subsequent ICP–AES determination. The values presented are averages from three determinations

Foreign cation	Concentration $\mu\text{g mL}^{-1}$	Mn	Mo	Ni	Pb	Sb	Sn	Tl	V	Zn
Na	1000	93.5	99.4	99.4	99.7	97.8	98.8	101.2	100	100.8
	3000	87.7	95.8	95.3	99.3	96.5	97.6	106.1	98.3	103.6
K	50	92.1	99	100	99	99.8	97.3	101.3	98.1	100
	100	91.6	95	100	98	97.3	95.6	104.6	97.2	102.3
	200	85.9	93.6	98.0	95.4	96.1	94.9	103.8	96.9	103
	500	87.4	92.4	95.0	99.6	95	93.2	106.9	95.4	103
Ca	500	89.4	97.8	95.8	99.6	96.4	97.6	94.3	97.4	99.6
	1000	82.1	97.6	95.0	92.4	95.2	96.7	88.2	96.9	99.3
	3000	76.2	92.9	86.1	93.6	93.8	96.8	87.8	95.6	94.6
Mg	50	93.2	97.6	97.6	97.2	98.8	96.3	95.6	98.6	96.7
	1000	90.1	93.3	91.6	93.7	97.4	95.1	91.4	97.1	92.5
	3000	82.1	92.4	79.6	90.2	95.7	94.1	90.7	93.4	90.3
Fe	5	96.4	96.4	93.8	97.5	94.6	97.1	96.2	95.3	95.2
Mn	5	–	97.2	95.2	97	97.5	97.6	96.9	94.2	96.8

Table 6 Blanks and limits of detection (LOD)

Element	Blank, ng ^a	LOD, ng mL ⁻¹	Element	Blank, ng ^a	LOD, ng mL ⁻¹
Al	3.2	0.04	Mn	0.4	0.006
Bi	< LOD	0.09	Mo	1.1	0.036
Cd	0.4	0.003	Ni	5.2	0.09
Cr	0.57	0.006	Pb	1.9	0.02
Co	0.38	0.004	Sb	1.8	0.027
Cu	2.1	0.033	Sn	< LOD	0.07
Fe	1.06	0.007	Tl	< LOD	0.09
Ga	< LOD	0.01	V	2.2	0.033
In	< LOD	0.009	Zn	0.5	0.009

^aBlanks are based on the analysis of 100 mL buffered water and standards. Limits of detection ($\mu\text{g L}^{-1}$) are based on three times the standard deviation of the signal for buffered water ($n = 10$)

Table 7 Results obtained from ICP–AES analysis of certified RM SRM 1643c (river water) after preconcentration and trace element-matrix separation by use of a micro-column filled with 100 mg ZrO₂. The values presented are averages from three determinations ($X \pm \text{SD}$). The sample volume was 30 mL

Element	Results obtained, ng mL ⁻¹	Certified values, ng mL ⁻¹
Al	124.30 \pm 8.82	127.6 \pm 3.5
Sb	59.30 \pm 6.94	54.1 \pm 1.1
Cd	5.90 \pm 0.96	6.47 \pm 0.37
Cr	15.80 \pm 3.72	18.53 \pm 0.2
Co	19.86 \pm 3.32	25.00 \pm 0.59
Cu	19.82 \pm 2.12	20.5 \pm 3.8
Fe	196.2 \pm 8.3	191.2 \pm 3.9
Pb	16.98 \pm 2.22	18.15 \pm 0.64
Mo	114.6 \pm 3.1	112.9 \pm 1.7
Ni	57.93 \pm 4.11	58.1 \pm 2.7
V	34.90 \pm 3.23	35.1 \pm 1.4
Zn	76.12 \pm 4.50	72.48 \pm 0.65

Table 8 Results obtained from ICP–AES analysis of certified river water standard solution (JACS) after preconcentration and trace elements-matrix separation by use of a micro-column filled with 100 mg ZrO₂. The values presented are averages from three determinations ($X \pm \text{SD}$). The sample volume was 30 mL

Element	Results obtained, ng mL ⁻¹	Certified values, ng mL ⁻¹
Pb	9.81 \pm 0.38	9.90 \pm 0.2
Cr	9.98 \pm 0.30	10.1 \pm 0.2
Cd	1.06 \pm 0.10	1.00 \pm 0.02
Cu	10.31 \pm 0.30	10.5 \pm 0.2
Fe	56.1 \pm 0.32	57.0 \pm 2.0
Mn	4.12 \pm 0.12	5.4 \pm 0.1
Zn	11.21 \pm 0.30	11.3 \pm 0.4
Al	60.8 \pm 2.80	61.0 \pm 2.0
Ni	9.63 \pm 0.50	10.2 \pm 0.3

Blank values and detection limits

ter from solutions containing relatively high concentration of alkali and alkaline earth metal ions.

The results obtained enable the development of an efficient flow-injection method for simultaneous ICP–AES determination of trace elements in different waters on the basis of solid-phase extraction by zirconia, as described below.

The accurate determination of ng mL⁻¹ levels of transition metals in natural waters, especially by use of a method that preconcentrates the analytes, requires low and reproducible blanks. The absolute blank was obtained by following the preconcentration and determination with 100 mL high-purity water adjusted to pH 8. The results shown in Table 6 were determined by performing ten replicate determinations of high-purity water. The blanks

observed for Ga, In, Tl, and Bi are very close to, or below, their detection limits. The low values obtained (except those for Al and Ni) support the conclusion that with on-line FI systems it is possible to process the sample and transfer it to the ICP–AES with minimum exposure to the environment.

The major contributor to the blank values was always found to be ZrO₂ itself; this contribution could be substantially reduced by cleaning with 3 mol L⁻¹ HNO₃.

Limits of detection (LOD) for the elements determined are also summarized in Table 6. The limits of detection for the elements studied by direct aspiration are compared with those obtained by on-line FI–ICP–AES. Detection limits obtained in our investigations were two orders of magnitude lower than those obtained by continuous nebulization.

The limit of detection of this method could be improved still further by reducing the blank value. This could be achieved by further purification or by reducing the volume of the solutions used to process the sample.

Application to natural water

To test the accuracy of the method and its applicability to the analysis of real samples, several reference materials were analysed. The analytes were quantified by external calibration against multi-element pure water standard processed through the manifold. Three analyses were conducted at each concentration. Results for the certified reference material are given in Tables 7 and 8. They show that the system furnishes analytical data within the range of the certified value. Good agreement between found and

certified values was obtained for all elements measured except Mn. This agreement indicated that the concentrations of Ca, Na, Mg, and K in the standard river water solutions (30 mg L⁻¹ or 20 mg L⁻¹) were reduced to amounts which did not interfere with the analytes. The consistently low result for Mn is probably because of elution problems.

To apply the method to the determination of the elements investigated in different types of water, 1 mL of 1.5 µg mL⁻¹ standard solutions were added to pure water and synthetic seawater. The results indicate excellent recovery in all instances from pure water; the reproducibility of the method was, however, slightly poorer when seawater was analyzed. Table 9 shows the results obtained for some of the elements investigated. For pure water there was good agreement between added and found values for all the elements investigated. For seawater recovery of Mn, Co, Fe, and Ni was < 95% and standard addition is required for their determination. One possible explanation is that seawater is a complex matrix. Speciation changes in this complex matrix are involved – the formation of stable chloride-complex ions in seawater could be one reason for low recovery of Fe, Sb, and Bi (see also Tables 4 and 5). Good agreement between added and found values was achieved for all the other elements investigated.

Conclusions

Combination of a high-surface-area ZrO₂ micro-column and flow injection analysis is a very simple, but powerful technique which can be used when the trace element concentrations is at the ng L⁻¹ level. For the different elements analyzed preconcentration factors of 100 were obtained and detection limits were approximately 0.003–0.09 ng mL⁻¹. The major drawback of the proposed analytical scheme is the time-consuming enrichment procedure (33 min for a 100-mL sample). The analytical scheme for the proposed procedure is much simpler than that for off-line procedures.

It has been shown that 18 elements were preconcentrated quantitatively and that the method investigated can be applied successfully for the analysis of different types of natural water (river water, tap water and rainwater). With seawater the complex matrix caused problems in the preconcentration step. Standard addition is required for FI–ICP–AES determination of Bi, Co, Cr, Fe, Mn, Ni, and Tl in seawater samples. For all other elements investigated the proposed analytical procedure can be used with external calibration and without standard addition.

References

1. Fang Z (1991) *Spectrochim Acta Rev* 14: 235
2. Fang Z, Sperling M, Welz B (1990) *J Anal At Spectrom* 5:639
3. Tyson J (1991) *Spectrochim Acta Rev* 14:169
4. Fang Z, Xu Sh, Tao G (1996) *J Anal Atom Spectrom* 11:1
5. McLaren JW, Mykytiuk AP, Willie SN, Berman SS (1985) *Anal Chem* 57:2907

Table 9 Accuracy and precision of ICP–AES analysis of spiked pure water and seawater after preconcentration and trace elements-matrix separation by use of a micro-column filled with 100 mg ZrO₂. The values presented are averages from three determinations ($X \pm SD$). The sample volume was 100 mL and the pH = 8

Element	Amount added, µg Pure water	Amount found, µg Pure water	Amount found, µg Seawater
Al	1.5	1.46 ± 0.12	1.43 ± 0.16
Bi	1.5	1.45 ± 0.05	1.42 ± 0.04
Cd	1.5	1.47 ± 0.10	1.43 ± 0.13
Cr	1.5	1.47 ± 0.05	1.42 ± 0.09
Co	1.5	1.43 ± 0.08	1.31 ± 0.05
Cu	1.5	1.49 ± 0.10	1.47 ± 0.12
Fe	1.5	1.45 ± 0.10	1.37 ± 0.06
Ga	1.5	1.41 ± 0.13	1.42 ± 0.10
In	1.5	1.49 ± 0.09	1.42 ± 0.12
Mn	1.5	1.38 ± 0.06	1.12 ± 0.13
Mo	1.5	1.45 ± 0.06	1.45 ± 0.09
Ni	1.5	1.44 ± 0.10	1.38 ± 0.13
Pb	1.5	1.47 ± 0.04	1.44 ± 0.13
Tl	1.5	1.45 ± 0.08	1.43 ± 0.09
V	1.5	1.52 ± 0.07	1.48 ± 0.12
Zn	1.5	1.58 ± 0.09	1.43 ± 0.10

6. McLaren JW, Lam JV, Berman SS, Akatsuka K, Azeredo MA, (1993) *J Anal Atom Spectrom* 8:279
7. Kantipuly CJ, Westland AD (1988) *Talanta* 8:279
8. Hartenstein SD, Ruzicka J, Christian CD (1985) *Anal Chem* 57:21
9. Hirata S, Umezaki Y, Ikeda M (1986) *Anal. Chem* 58:2602
10. Brajter K, Dabek-Zlotrozyńska E (1990) *Talanta* 37: 613
11. Yeh SJ, Lo JM, Tseng CL (1988) *J Radioanal Nucl Chem* 124:157
12. Tong A, Akama Y, Tanaka S (1990) *Analyst* 115:947
13. Tikhomirova T, Fadeeva V, Kudryavstev G, Nesterenko P, Ivanov V, Savitchev A, Smirnova N (1991) *Talanta* 38:267
14. Pu Q, Su Z, Hu Z, Chang X, Yang M (1998) *J Anal Atom Spectrom* 13:249
15. Ji H, Liao Z, Sun J, Jiang Z (1998) *Fresenius J Anal Chem* 360:721
16. Sperling M, Xu S, Welz B (1992) *Anal Chem* 64:3101
17. Furuta N, Brushwyler KR, Hieftje GM (1989) *Spectrochim Acta* 44B:349
18. Ebdon L, Fisher AS, Worsfold PJ (1994) *J Anal Atom Spectrom* 9:611
19. Smichowski P, Beatriz De La Calle M, Madrid Y, Gloria Cobo M, Camara C (1994) *Spectrochim Acta* 49B:1049
20. Hadjiivanov K, Klissurski K, Kantcheva M, Davydov A (1991) *J Chem Soc Faraday Trans* 87:907
21. Fuerstenau DM, Osseo-Asare K (1987) *J Colloid Interface Sci* 118:524
22. Vassileva E, Hadjiivanov K, Mandjukov P (1994) *Colloids Surf A* 90:9
23. Ragai J, Selim STJ (1987) *Colloid Interface Sci* 115:139
24. Bolis V, Fubini B, Giamello E (1991) *Mater Chem Phys* 29: 153
25. Vassileva E, Proinova I, Hadjiivanov K (1996) *Analyst* 121: 607
26. Vassileva E, Varimezova B, Hadjiivanov K (1996) *Anal Chim Acta* 336:141
27. Vassileva E, Hadjiivanov K (1997) *Fresenius J Anal Chem* 357:881
28. Davydov AA (1984) *IR Spectroscopy Applied to Oxide Surfaces*, Nauka, Novosibirsk
29. Brunelle JP (1978) in *Proc Second Int Symp on the Preparation of Catalysts*, Louvain-La-Neuve, Belgium
30. Kantcheva M, Hadjiivanov K, Klissurski D (1992) *J. Catal* 134:229
31. Dugger DL, Stanton JH, Irby BN, McConnell BL, Cummings WW, Maatman RW (1964) *J Phys Chem* 68:757