



Application of iminodiacetate chelating resin muromac A-1 in on-line preconcentration and inductively coupled plasma optical emission spectroscopy determination of trace elements in natural waters[☆]

E. Vassileva^{*,1}, N. Furuta

Faculty of Science and Engineering, Department of Applied Chemistry, Chuo University, 1-13-27, Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Received 4 October 2002; accepted 7 May 2003

Abstract

On-line system incorporating a microcolumn of Muromac A-1 resin was used for the developing of method for preconcentration of trace elements followed by inductively coupled plasma (ICP) atomic emission spectrometry determination. A chelating type ion exchange resin has been characterized regarding the sorption and subsequent elution of 24 elements, aiming to their preconcentration from water samples of different origins. The effect of column conditioning, pH and flow rate during the preconcentration step, and the nature of the acid medium employed for desorption of the retained elements were investigated. A sample (pH 5) is pumped through the column at 3 ml min⁻¹ and sequentially eluted directly to the ICP with 3 M HNO₃/HCl mixtures. In order to remove residual matrix elements from the column after sample loading a short buffer wash was found to be necessary. The effectiveness of the matrix separation process was illustrated. The procedure was validated by analyzing several simple matrices, Standard River water sample as well as artificial seawater. Proposed method can be applied for simultaneous determination of In, Tl, Ti, Y, Cd, Co, Cu and Ni in seawater and for multielement trace analysis of river water. Recovery at 1 μg l⁻¹ level for the determination of investigated 24 elements in pure water ranged from 93.1 to 96% except for Pd (82.2%) and Pb (88.1%). For the same concentration level for seawater analysis recovery was between 81.9 and 95.6% except for Hg (38.2%).

© 2003 Elsevier B.V. All rights reserved.

Keywords: Inductively coupled plasma optical emission spectrometry; On-line preconcentration; Iminodiacetic acid resin; Trace elements; Natural waters

[☆] This paper was presented at the 5th European Furnace Symposium and 10th International Solid Sampling Colloquium with Atomic Spectroscopy, held in Blagoevgrad, Bulgaria, September 2002 and is published in the Special Section of *Spectrochimica Acta Part B*, dedicated to that conference.

*Corresponding author.

E-mail address: emvassileva@hotmail.com (E. Vassileva).

¹ On leave from: University of Sofia, Faculty of Chemistry, 1, James Bourchier av., 1126 Sofia, Bulgaria.

1. Introduction

Direct determination of trace elements in extremely low concentrations by modern atomic spectroscopy techniques is in many cases difficult. This is not only due to the insufficient sensitivity of the methods, but also to the matrix effect. Many papers published recommend the use of off-line and on-line preconcentration and separation systems as a means of reducing or eliminating spectroscopic and non-spectroscopic interferences in sample with high saline content. Nowadays there is considerable interest in the development of new methods or in adaptations of existing methods, for use 'on-line' with the measurement instrument [1–4]. The major advantage of the on-line procedure is in general the possibility of working in a closed system with a significant reduction of airborne contamination and a fairly high sample throughput, which justifies current trends towards an increasing use of on-line preconcentration techniques. More recently, the use of various types of adsorbent for the preconcentration and separation of trace elements has gained popularity because of: (i) The high concentration factor achieved; (ii) The simple operation; (iii) The possibility of using a closed circulation system; and (iv) The combination with different modern analytical techniques permitting in the case of inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-OES) simultaneous multi-element determination. Although systems for separation and preconcentration of analytes from the matrix by extraction [5] and co-precipitation methods [6] have also been investigated, the on-line column preconcentration systems using chelating ion-exchange resins have aroused most interest. Two chelating functional groups namely iminodiacetate (IDA) and 8-hydroxyquinoline (8-HQ) have mainly been used for the analysis of seawater. Different successful flow-injection methods using a column of silica-immobilized 8-HQ for the determination of trace elements in natural waters have been reported [7,8]. The disadvantage of the 8-HQ procedures are that there is no commercial source of 8-HQ at present and the material must be synthesized. Several groups have automated the preconcentration of

analytes using chelating resins incorporated into the flow manifold with subsequent atomic absorption spectrometry (AAS) or ICP-OES [2,9–11] detection. This method gives simultaneously multi-element detection limits, which are over 20 times better than for conventional continuously aspirated systems for Ba, Be, Cd, Co, Cu, Mn, Ni and Pb. These studies show that CHELEX 100 has the disadvantage of swelling and shrinking at different pH value. Kingston et al. [12] demonstrated the applicability of a CHELEX 100 column procedure to the isolation and 100-fold concentration of Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn from seawater. It was claimed that prior to the elution of the trace elements, alkali and alkaline earth metals are eluted almost completely from the resin with 1 M ammonium acetate solution. The simplicity of the procedure as proposed by Kingston et al. [12] together with its attractive analytical performance and wider field of application, induced many analysts to apply the IDA resins to the trace analysis of different types of water and biological samples [13].

Muromac A-1 is more highly cross-linked IDA resin based on a macroporous substrate with no tendency for volume change. This is an important advantage over CHELEX 100. Unfortunately, the selectivity of all IDA resins is less favorable for seawater than the selectivity of 8-HQ and the removal of matrix component is essential for the success of the method [13–15]. From the experiences with IDA resin to date, it becomes apparent that the optimum experimental condition for enrichment and elution procedure is still elusive. Additional work is required to establish the best condition for the extraction and determination of a large number of elements simultaneously from a variety of aqueous samples.

In the present study, on-line preconcentration and matrix separation method was investigated. The manifold incorporates a microcolumn of Muromac A-1 resin. Attention was focused on optimization of the conditions for the multi-element preconcentration of trace elements in different type waters, their complete elution and subsequent simultaneous ICP-OES determination.

2. Experimental

2.1. Reagent

Standard solutions (1000 mg l^{-1}) for investigated elements were purchased from Kanto Chemical Co. (Tokyo, Japan). Working standard solutions were prepared daily with distilled and deionized water and stored in precleaned polypropylene containers. The HNO_3 , NH_4OH and CH_3COOH (HOAc) used in this work were high purity grade (Tama Chemical Co., Tokyo, Japan). The water used was Milli-Q water, prepared by further purification of de-ionized water by a Milli-Q system (Milli-Q SP ICP-MS, Millipore, Tokyo, Japan). Suprapur grade salts (Suprapur, Merck, Darmstadt, Germany) were used for the preparation of test solutions. Artificial seawater solution, which was 10 times more concentrated than normal seawater was prepared by dissolving 22.8 g of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ (Suprapur, Merck, Darmstadt, Germany), 7.4 g of KCl (Suprapur, Merck, Darmstadt, Germany), 106.8 g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Pro Analysis, Merck, Darmstadt, Germany) and 274 g of NaCl (Suprapur, Merck, Darmstadt, Germany) in 1000 ml Milli-Q water (the concentration of Ca, Mg, Na and K in this solution were 5 g l^{-1} , 10 g l^{-1} , 107.8 g l^{-1} and 3.9 g l^{-1} respectively)

A solution of 1 M $\text{CH}_3\text{COONH}_4$ was prepared by diluting 14.7 ml of 96% w/v HOAc and 17 ml 25% w/v NH_4OH solution in 250 ml Milli-Q water. The pH was adjusted with 2 M HNO_3 or NH_4OH solutions. Muromac A-1 50-100 mesh, Na form resin was obtained from Muromachi Kagaku Kogyo Kaisha, Ltd (Tokyo, Japan). River water standard solution (natural river water in which some elements were added purposely) was obtained from Analytical Chemical Society of Japan.

2.2. Instrumentation

The ICP-OES measurements were performed with an ICP spectrometer (Spectroflame Compact S/E with two polychromators setting grating of $3600 \text{ grooves mm}^{-1}$ and $1800 \text{ grooves mm}^{-1}$, respectively, and one monochromator setting a grating of $2400 \text{ grooves mm}^{-1}$). The polychro-

Table 1
ICP-OES operating conditions

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

mators has 43 simultaneous analytical channels. The operating conditions are summarized in Table 1. The analytical lines for the monochromator were selected on the basis of their net and background intensities as well as their freedom from spectral interference overlaps. All measurements were made using the transient scan mode with integration time for each element 50 ms, interval time 50 ms and 1200 point per peak. Peak area was used for all quantification work.

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

2.3. General procedure for on-line preconcentration and ICP-OES measurement

A schematic diagram of the instrumental set-up is shown in Fig. 1. The microcolumn was conditioned by flowing 10 ml of 1 M and 0.05 M acetate buffer solutions through it at a rate of 4 ml min^{-1} . During the preconcentration step (the volume of sample preconcentrated was varied in order to optimize the analyte signal) the flow rate of sample was 3 ml min^{-1} . After washing procedure with 20 ml 0.1 M $\text{CH}_3\text{COONH}_4$ at a flow rate 5 ml min^{-1} , the adsorbed trace elements were eluted by the injection of 1 ml of 3 M HNO_3 /3 M HCl in ratio 3:1 and flow rate 0.5 ml min^{-1} . The eluted sample was introduced into the ICP, where investigated elements were measured simultaneously. Total time for conditioning of the column, preconcentration, washing procedure, elution and determination was 25–40 min (according to the sample volume).

When seawater was analyzed to overcome the problem with salts deposition on the tip of the central tube of the ICP torch, the sample passed through the column during the preconcentration step was discarded into a drain.

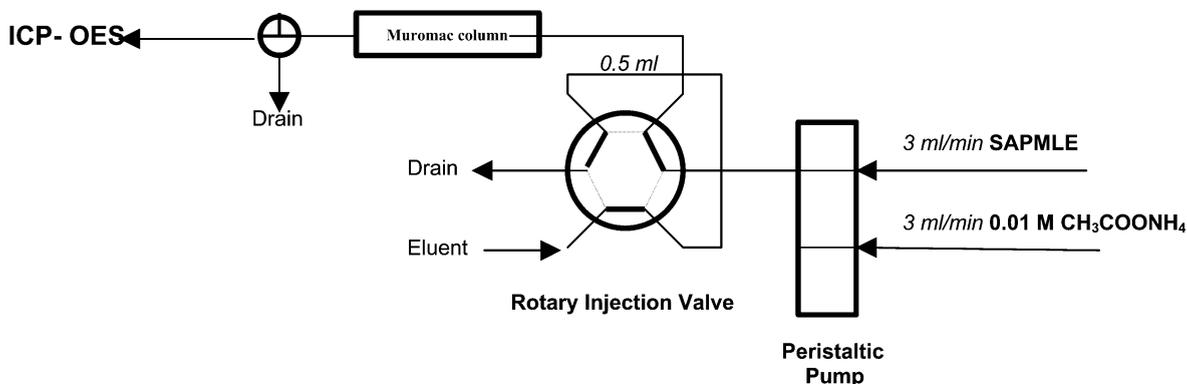


Fig. 1. Schematic diagram of the on-line pre-concentration set-up.

2.4. Column preparation

The Muromac A-1 microcolumn was made by packing 0.1 g of the resin into a Teflon tube (i.d.: 0.4 mm, length: 40 mm). The aim in the construction of the microcolumn was to prepare a column with high capacity, capable of handling large flow rate and allowing elution of the sample in a small volume. In order to decrease blank values the column was washed two times with 20 ml of 3 M HNO_3 /3 M HCl (3:1) and water. Washing procedure allows elution of potentially trace element contamination.

In order to prevent the precipitation of trace elements from the start of the pre-concentration procedure and to avoid any change in the pH of the column content during the passage of the sample, the resin was treated with 1 M $\text{CH}_3\text{COONH}_4$ solution and the column was rinsed with 0.05 M $\text{CH}_3\text{COONH}_4$ solution. The pH of the $\text{CH}_3\text{COONH}_4$ solution was adjusted with nitric acid to the 'working' pH 5. Whether the initially precipitated hydroxide comes in contact with the conditioned resin they dissolve partly or completely during the pre-concentration step. This is the reason for the poor agreement of recovery results reported in the literature for Mn, Fe and Al [16,17].

2.5. Test solutions

Pure water test sample (100 ml) was prepared by dissolving trace elements in 95 ml Milli-Q

water. After addition of 5 ml of 1 M $\text{CH}_3\text{COONH}_4$, the pH was controlled and adjusted to pH 5. Artificial seawater test sample (100 ml) was prepared by mixing 85 ml water (pH adjusted previously to 5), 10 ml of a solution of seawater salts (pH 5) with 10 times concentrated seawater and finally 5 ml of 1 M $\text{CH}_3\text{COONH}_4$ was added. Two types of test solutions have been prepared with concentrations of trace element in the test samples $0.001 \mu\text{g l}^{-1}$ and $0.01 \mu\text{g l}^{-1}$, respectively. During the pre-concentration step in the case of seawater analysis, the pH of the initial effluent showed a sharp decreasing. Considering the acidity constant of iminodiacetic acid, it follows that at pH 5 considerable part of the available acid groups are protonated when seawater sample is passed through the column and as a consequence, the H_3O^+ concentration in the liquid phase of the column increases. The changes in pH during the pre-concentration step of seawater could be prevented if 5 ml of 1 M $\text{CH}_3\text{COONH}_4$ is added during dilution of 10 times concentrated seawater and the pH of obtained artificial seawater solution is adjusted to 5. The influence of the sample flow rate was studied using a constant flow rate of the eluent acid. Changes in flow rate of the sample between 1 and 6 ml min^{-1} resulted in small variations in the signal, if the total volume is constant. 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 the analyte arriving at the column was kept constant.

2.6. Determination of exchange capacity

2.6.1. Batch determination

A separate solution for each of investigated element (500 mg ml⁻¹ was prepared in ammonium acetate buffer (0.1 M at pH 5; pH 2 was used in the case of Bi) and added to 0.05 g Muromac A-1 resin. The mixture was equilibrated with stirring overnight. The solution was decanted and the concentration of element in the supernatant liquid was measured vs. the original concentration. The decrease in the concentration of elements was used to evaluate the capacity using the following equation:

$$C = \frac{(c_i - c_f) \times V}{m \times 1000 \times M_r}$$

where C is the capacity (mmol g⁻¹), c_i and c_f are the concentration of the elements before and after equilibrium, respectively (mg l⁻¹), M_r is the atomic mass of the element and V is the volume of a solution (ml) equilibrated with a mass m (g) of the resin.

2.6.2. Dynamic determination

Dry resin Muromac 1 was packed into the column. Two moles/litre buffer solution was used because of high acidity of the standard solution (100 mg l⁻¹ concentration). The capacity was evaluated in terms of the concentration of elements in the solution after column. The concentration beyond with no further decrease after passing the column was accepted to represent the dynamic capacity limit. The dynamic capacity was evaluated using the equation:

$$C_d = \frac{(c_i - c_f) \times V}{m \times 1000 \times M_r}$$

where C_d is the dynamic capacity mmol g⁻¹, c_i and c_f are the concentration of standard solutions before and after column, V is the volume of standard solution (ml), m is the mass of sorbent

in the column and M_r , the atomic mass of the element.

3. Results and discussions

3.1. Influence of pH

pH is a critical parameter for achieving quantitative preconcentration of trace elements. A pH in the range 4.8–5.0 appeared to be the most appropriate for preconcentration with Muromac A resin of the following investigated elements: Al, Bi, Co, Cd, Cu, Cr, Fe, Hg, Ga, In, Mo, Mn, Ni, Pb, Sc, Tl, Ti, Sn, U, V, W, Y, Zn and Zr. For some elements quantitative recovery is already attained at pH 2: Ti, Zr, U, In, Ga, Th. These observations are in compliance with the stability constant of these elements with similar chelating agent such as ethylenediaminetetraacetic acid and nitrilotriacetic acid [18,19]. pH 5 was selected for the future investigation. Below this range, elution losses from the resin occurred, whereas at pH > 5.5 precipitation of Al, Fe and Mn hydrous oxides may become significant. In the case of seawater at pH 6–7 not only trace elements can be chelated, but also Ca and Mg as well. Indeed, compared with cations such as Ca, Mg, Na and K, the selectivity for transition elements is higher, but their concentrations are 5–7 orders of magnitude lower than those of the matrix elements in seawater. As a result, trace elements are not or are only partly sequestered on the resin. The above results show the possibility of concentrating simultaneously a number of trace elements working at a constant pH, which make Muromac A-1 resin promising resin as a solid-phase extractant in multielement trace analysis.

3.2. Dynamic and batch column capacity evaluation

Evaluation of the capacity of Muromac A-1 was performed in bath and dynamic conditions. Good agreement between the dynamic and batch capacity for all investigated elements was obtained (Table 2). This illustrates that under the condition of dynamic operation, the column retains analytes rapidly. Capacity values are in many cases consis-

Table 2
Capacity, mmol g⁻¹ of Muromac A-1 resin in static and dynamic conditions

Element	Static conditions	Dynamic conditions
Al	0.87	0.98
Bi	0.42	0.94
Co	1.09	1.11
Cr	0.89	0.95
Cu	1.32	1.27
Hg	0.87	0.99
In	0.87	0.83
Mo	0.51	0.63
Mn	0.98	1.02
Ni	1.01	1.08
Pb	0.87	0.98
Pd	0.71	0.98
V	1.20	1.11
Y	1.01	0.96
Zn	1.12	1.14
Zr	0.38	0.34

tent with values reported from the manufacture of the resin. The capacity observed for Bi and Zr was lower than 1 mmol g⁻¹. The possible explanation is the phenomena described as 'polymer effect' [19]. The dynamic capacity of column was between 40 and 60% lower when the investigation was performed from artificial seawater. Preconcentration of trace elements using ion-exchange-chelating resin is based on its chelation under conditions where the matrix elements are only ionogenically bound or not bound at all. Such conditions can be obtained by changing the amount of resin. Its total capacity should be large in respect of the amounts of trace elements retained on the column and in the same time sufficiently small to ensure that only small part of matrix components is bound to the resin. In our investigation the total amount of test elements is under resin's capacity, whereas the amount of the matrix elements exceeds the column capacity more than 40 times.

3.3. Elution

Since almost all of investigated elements form stable complexes (formation constants are in the range from 1×10^{14} for Mn to 1×10^{25} for Fe), one can expect that the acid concentration required

for elution increases with increasing the formation constant of the element-IDA complex. When 3 M HNO₃ was used quantitative recovery was obtained for the majority of investigated elements. However, complementary addition of HCl improves the recovery of Hg, Sn, W and Pd. To minimize the time needed for quantitative elution and eluate dispersion during elution step the volume of eluent should be reduced. It is possible only if a highly efficient eluent is used. The injection of smaller volume eluent contributes to obtain higher preconcentration factor, to reduce blank value and is more convenient for work in flow conditions. As can be noticed from Fig. 2, 1 ml 3 M HNO₃/HCl (3:1) is appropriate eluent volume for elution and the subsequent ICP-OES determination. The influence of the flow rate on the recovery of studied elements was checked in the range of 0.2–2 ml min⁻¹. Maximum recovery was obtained in range from 0.2 to 1 ml min⁻¹. Thus, a flow rate of 0.5 ml min⁻¹ was used for elution.

3.4. Effect of the matrix

The problematic nature of seawater (0.47 mol l⁻¹ sodium chloride and 0.01 mol l⁻¹ potassium chloride) [16,20,21] made it incompatible with direct ICP-OES analysis. The cationic part of this matrix is easily removed by chelating ion exchange because of the low complex formation constant of alkali ions with IDA. In the other side the exchange sites not occupied by trace metals remain as magnesium or calcium complexes and their amount is dominated by the exchange capacity of the separation column. The higher exchange capacity of the separation column causes a higher remaining amount of alkaline earth metals. This problem is quite important in on-line application. As one can expect the concentration of the analyte and the remaining matrix elements increases during the elution step. This may lead to serious interference problems by molecular ions or to changes in the plasma conditions [16,22].

Using the fact that alkaline earth metals are partially removed by buffer solution [14,20] one investigation of residual matrix concentration after seawater preconcentration and optimization of suitable washing procedure was undertaken. Fig. 3

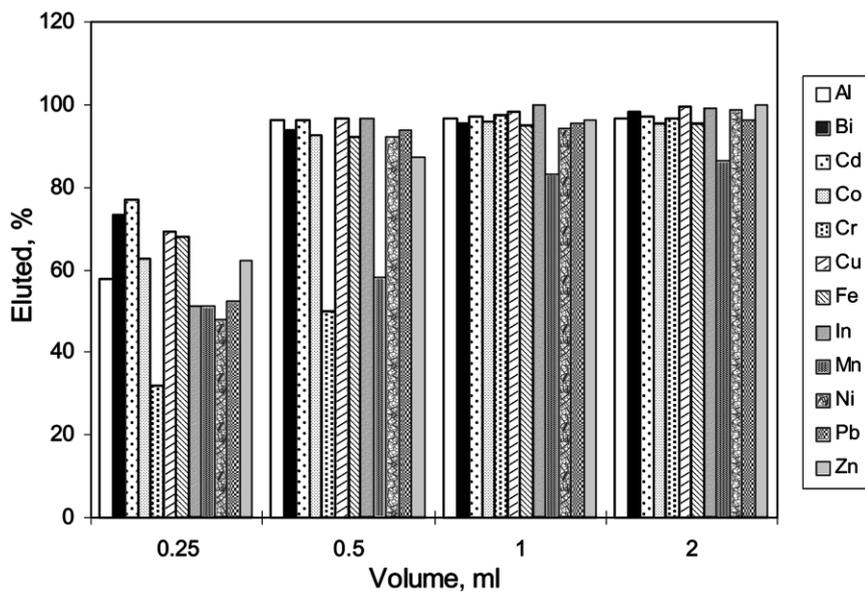


Fig. 2. Elution histogram for 0.1 μg of investigated elements, bound to 0.1 g of Muromac A-1 resin. Eluent-3 M HNO_3/HCl acid mixture in ratio 3:1.

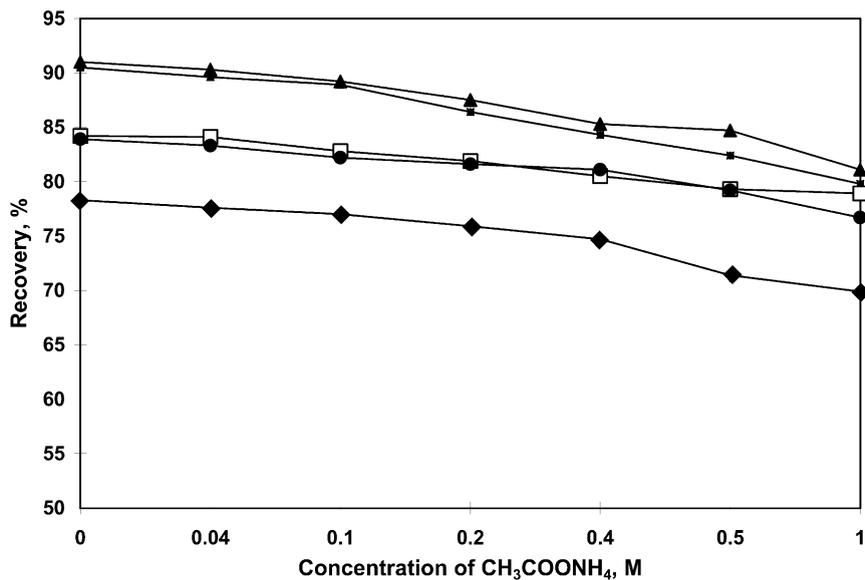


Fig. 3. Recovery of trace elements as a function of the $\text{CH}_3\text{COONH}_4$ concentration, used for column washing (pH 5.2). (●) – Bi, (□) – Mo, (◆) – Pb, (■) – Tl, (▲) – V.

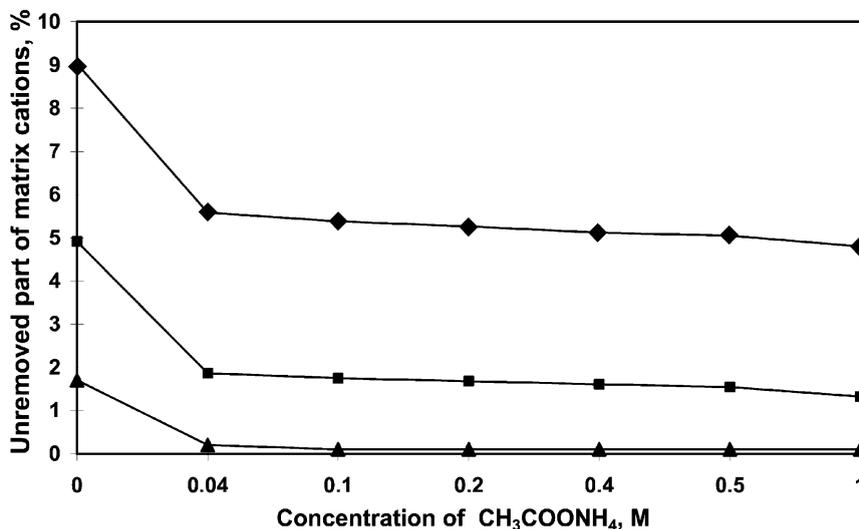


Fig. 4. Matrix removal as a function of the $\text{CH}_3\text{COONH}_4$ concentration, used for column washing after pre-concentration on the microcolumn of 100 ml artificial seawater. (◆) – Ca, (■) – Mg, (▲) – Na.

indicates that the recovery of trace elements in our investigation tends to decrease, when molarity of washing $\text{CH}_3\text{COONH}_4$ solution increases more than 0.1 M. The recovery of Pb, Tl and Bi appears to be more susceptible to concentration of $\text{CH}_3\text{COONH}_4$ solution than the recovery of V and Mo. Washing solution with concentration above 0.1 M does not contribute significantly for further matrix removal—Fig. 4. In this study 0.1 M $\text{CH}_3\text{COONH}_4$ was selected as the appropriate concentration of the washing solution.

It is of interest to establish the final proportion of Na, Ca and Mg on the column after 100 ml seawater has been passed through the column. It might be assumed that Ca is dominant in the final solution as the affinity for Ca ions is the highest among these three metal ions. Pai et al. [23] found for CHELEX 100 resin that after a large amount of seawater had passed through, the resin were equilibrated with all ions and the ratio of major ions on the exchange sites gradually reached constant values no matter what the original concentration was.

In the present investigation Ca, Mg and Na was removed by 95, 98, 99.9%, respectively, and the total matrix concentration in the acidic eluate is approximately 0.6%. Such a concentration is suf-

ficiently low to exclude the occurrence of interferences in on-line ICP-OES analysis of the studied element during the measurement step. Ca and Mg ions are completely retained on the resin, when their total concentration in the sample is under capacity of the column. Following the washing procedure in this case does not contribute for the matrix removal at all.

Fig. 5 shows matrix removal as a function of volume of washing solution (0.1 M $\text{CH}_3\text{COONH}_4$, pH 5.2) used for 4-mm diameter column, containing 0.1 g resin. It can be concluded that 20 ml $\text{CH}_3\text{COONH}_4$ assures considerable reduction of residual matrix concentration, whereas a larger volume does not contribute significantly to further matrix removal.

As regards the amount of resin we should stress again that in the enrichment step the amount of resin in the column must be kept to a minimum for several reasons: (i) amount of acidic and washing solutions required for the elution of trace elements and washing of the column, respectively, increases with increasing the amount of resin; (ii) the amount of matrix elements not removable from the resin also increases; (iii) total time of pre-concentration and ICP determination of trace elements become longer; and (iv) the loss of retained trace

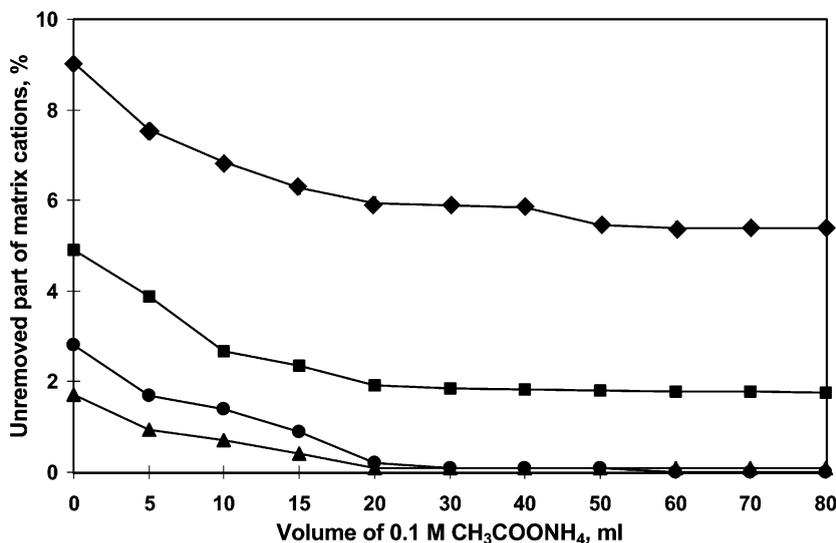


Fig. 5. Matrix removal as a function of the volume of 0.1 M CH₃COONH₄, used for column washing after preconcentration on the microcolumn of 100 ml artificial seawater. (◆) – Ca, (●) – K, (■) – Mg, (▲) – Na.

elements is connected with increasing the volume of a washing solution.

3.5. Preconcentration efficiency

The efficiency of preconcentration system was determined by passing through the column two samples with volume 50 ml and concentration of 1 $\mu\text{g l}^{-1}$ and 10 $\mu\text{g l}^{-1}$, respectively, at pH 5. The integrated signals for 0.05 $\mu\text{g ml}^{-1}$ and 0.5 $\mu\text{g ml}^{-1}$ for each of the analytes in 1% HNO₃ were compared with integrated signals after preconcentration. All analyses were performed in duplicate and the integrated intensities were corrected for the background. Since the integrated intensities were compared, two values should be the same, irrespective of the preconcentration factor, if the preconcentration is quantitative and sensitivity remains constant. Table 3 gives the result of the comparison for pure water solution and artificial seawater. In the case of pure water, the quantitative recovery (above 95%) was obtained for all investigated elements, except for Pd, Pb and Mn for both concentration levels. The precision, measured as %R.S.D., was between 1.5 and 5% (except for Pd 7.1% and for W 5.9% at

concentration level 1 $\mu\text{g l}^{-1}$). In the case of artificial seawater, the investigated analytical procedure allows quantitative recovery for some elements – Co, Cu, Ga, In, Sc, Ti and Zr. The precision for preconcentration of 50 ml seawater sample with a concentration of 10 $\mu\text{g l}^{-1}$ was between 2.9 and 14.9%, where as the precision for the preconcentration of the same sample volume at concentration level 1 $\mu\text{g l}^{-1}$ was in the range of 4.9–18.9%.

3.6. Blank values and detection limits

The accurate determination of ng ml^{-1} levels of transition metals in natural waters required low and reproducible procedural blanks. In Table 4, the blank associated with on-line preconcentration and ICP-OES determination of 100-ml buffered water sample are presented. Blank values observed for Pd, Sn, W and Zr are very close or below their detection limits.

The limits of detection for investigated elements are also shown in Table 4. The limits of detection for studied elements by direct aspiration are compared to those obtained with described analytical

Table 3

Recovery (%) \pm R.S.D. (%) of metal ions in the preconcentration procedure, using Muromac A-1 microcolumn, Sample volume 50 ml, $n=3$

Element	Wavelength (nm)	Pure water (1 $\mu\text{g l}^{-1}$)	Pure water (10 $\mu\text{g l}^{-1}$)	Seawater (1 $\mu\text{g l}^{-1}$)	Seawater (10 $\mu\text{g l}^{-1}$)
Al	167.079	96.0 \pm 4.0	97.0 \pm 2.8	90.3 \pm 7.3	90.1 \pm 3.6
Bi	223.061	95.1 \pm 3.6	97.3 \pm 2.6	89.4 \pm 4.6	83.9 \pm 5.1
Cd	226.502	95.9 \pm 4.8	98.0 \pm 4.6	89.9 \pm 6.1	92.1 \pm 4.2
Co	228.616	95.6 \pm 4.2	97.0 \pm 3.9	95.1 \pm 6.7	96.9 \pm 5.8
Cu	654.738	96.1 \pm 4.7	96.8 \pm 2.4	95.6 \pm 7.2	96.2 \pm 2.9
Fe	259.94	93.8 \pm 4.6	95.6 \pm 4.4	86.0 \pm 8.9	89.6 \pm 6.5
Ga	417.206	95.0 \pm 4.2	96.2 \pm 2.1	95.5 \pm 4.9	95.8 \pm 3.3
Hg	184.950	95.2 \pm 4.9	96.0 \pm 4.4	38.2 \pm 18.9	48.2 \pm 14.9
In	325.609	96.6 \pm 5.0	97.6 \pm 3.3	95.6 \pm 5.9	95.6 \pm 4.0
Mn	257.610	90.0 \pm 2.4	91.3 \pm 5.5	89.1 \pm 14.2	69.3 \pm 12.6
Mo	202.030	93.1 \pm 5.0	95.2 \pm 5.0	82.1 \pm 7.5	84.9 \pm 6.0
Ni	231.604	95.0 \pm 4.3	96.0 \pm 4.0	95.3 \pm 7.9	92.3 \pm 7.9
Pb	220.351	88.1 \pm 3.6	90.1 \pm 3.6	83.1 \pm 5.6	90.0 \pm 4.1
Pd	340.458	82.2 \pm 7.1	83.9 \pm 5.1	81.9 \pm 6.6	83.9 \pm 5.1
Sn	189.989	95.6 \pm 4.0	97.0 \pm 3.9	89.1 \pm 6.7	91.9 \pm 5.8
Sc	722.768	96.1 \pm 3.6	96.1 \pm 3.2	95.1 \pm 4.9	95.4 \pm 3.7
Ti	334.941	95.0 \pm 5.7	96.1 \pm 4.7	95.4 \pm 7.2	95.6 \pm 6.2
V	292.464	94.8 \pm 5.9	96.8 \pm 3.6	83.0 \pm 11.9	86.0 \pm 5.9
Tl	190.864	92.0 \pm 4.8	95.0 \pm 4.2	90.5 \pm 5.5	91.5 \pm 4.5
Y	321.669	95.2 \pm 4.9	96.0 \pm 4.4	94.2 \pm 11.9	95.2 \pm 14.9
W	207.916	93.5 \pm 5.9	95.6 \pm 4.0	94.0 \pm 7.2	95.6 \pm 4.0
Zn	213.856	96.0 \pm 4.4	97.0 \pm 2.4	88.1 \pm 5.2	90.1 \pm 4.2
Zr	213.856	95.0 \pm 6.2	95.1 \pm 5.4	93.1 \pm 6.5	87.1 \pm 4.5

procedures. For all investigated elements, the column blank seems to be a limited factor. Peak area detection limits were approximately 20–200 times lower to those obtained by continuous nebulization of the same elements.

The limit of detection could be still improved by reducing the blank value. Procedural blank could be minimized by further purification of the resin or by reducing the volume of the sample solutions.

Table 4

Absolute amount of procedural blank and limits of detection (LOD)

Element	Blank (ng)	LOD (ng ml $^{-1}$)	Element	Blank (ng)	LOD (ng ml $^{-1}$)
Al	3.54	0.005	Pb	1.4	0.01
Bi	<LOD	–	Pd	<LOD	–
Cd	0.51	0.001	Ni	0.34	0.006
Co	0.40	0.003	Sn	<LOD	–
Cr	0.31	0.003	Ti	0.22	0.002
Cu	0.62	0.007	Tl	<LOD	–
Fe	0.66	0.008	V	1.21	0.006
Hg	2.0	0.02	W	<LOD	–
In	0.50	0.001	Y	0.36	0.006
Mn	0.27	0.001	Zn	0.28	0.006
Mo	0.81	0.009	Zr	<LOD	–

*Blanks are based on the on-line preconcentration of 100 ml buffered water. Limits of detection (ng ml $^{-1}$) are calculated as three times standard deviation of the concentrations of investigated elements in buffered water ($n=3$), after direct nebulization.

Table 5

Results obtained for the analysis of certified reference material after preconcentration with Muromac A-1 microcolumn, $n=3$

Element	Results obtained ($\mu\text{g l}^{-1}$)	Certificate values ($\mu\text{g l}^{-1}$)
Al	62.8 ± 2.8	61.0 ± 2.0
Cd	0.67 ± 0.10	1.0 ± 0.02
Cr	10.27 ± 0.30	10.1 ± 0.2
Cu	10.39 ± 0.30	10.5 ± 0.2
Fe	58.60 ± 0.32	57.0 ± 2.0
Mn	3.89 ± 0.12	5.4 ± 0.1
Ni	9.76 ± 0.50	10.2 ± 0.3
Pb	9.74 ± 0.38	9.9 ± 0.2
Zn	11.59 ± 0.30	11.3 ± 0.4

The preconcentration procedure was validated by analysis of one certified reference material—river water from Analytical Chemical Society of Japan. The analytes were quantified by external calibration against acidified multi-element pure water standard processed through the same mani-

Table 6

Accuracy and precision of the on-line flow injection preconcentration and ICP-OES determination of trace elements in pure and seawater, using Muromac A-1 microcolumn, $n=3$, Sample volume 100 ml, Amount added 2.00 μg

Element	Amount found ($\mu\text{g} \pm \text{S.D.}$) pure water	Amount found ($\mu\text{g} \pm \text{S.D.}$) seawater
Al	1.92 ± 0.13	1.71 ± 0.18
Bi	1.93 ± 0.10	1.68 ± 0.12
Cd	1.96 ± 0.12	1.89 ± 0.16
Co	1.91 ± 0.10	1.83 ± 0.20
Cu	1.94 ± 0.12	1.88 ± 0.16
Fe	1.94 ± 0.18	1.66 ± 0.10
Hg	1.92 ± 0.20	0.98 ± 0.25
In	1.93 ± 0.12	1.96 ± 0.12
Mn	1.84 ± 0.09	1.32 ± 0.21
Mo	1.82 ± 0.26	1.69 ± 0.14
Ni	1.91 ± 0.14	1.78 ± 0.23
Pb	1.87 ± 0.22	1.56 ± 0.12
Pd	1.52 ± 0.21	1.11 ± 0.20
Sn	1.92 ± 0.16	1.38 ± 0.12
Ti	1.93 ± 0.11	1.86 ± 0.16
Tl	2.07 ± 0.13	1.83 ± 0.19
V	1.94 ± 0.07	1.72 ± 0.10
W	1.79 ± 0.17	1.22 ± 0.22
Y	1.86 ± 0.15	1.87 ± 0.14
Zn	1.95 ± 0.17	1.79 ± 0.18
Zr	1.95 ± 0.14	1.84 ± 0.12

fold. Three repeated measurements were made for each element. The calibration curve showed good linearity in the concentration range 0–20 ng ml^{-1} . Results for the certified reference material analysis are given in Table 5. Good agreement between the found and certified values was obtained for all elements measured, except for Mn and Cd. A consistently low result for Mn is probably due to partial hydrolysis of Mn at pH 5.

Table 6 shows the results of the added–found method applied on pure and artificial seawater samples for investigated elements. A good agreement with the added–found value was achieved for all the investigated elements (except for Pd) in the case of pure water. For seawater, the results became somewhat erratic for certain elements. Speciation changes in this complex matrix are involved – the formation of stable chloride complex ions in seawater could be one of the reasons for low recovery of Hg, Sn, Pb and Bi (see also Table 3). Good agreement with the added–found value was achieved for Co, Cu, In, Ni, Y and Zr elements with high value of the formation of the Me–IDA complex constant.

For other investigated elements in the case of seawater analysis the method of standard addition is required.

4. Conclusions

The use of a chelating ion exchange with appropriate exchange capacity is in many aspects favorable for the analysis of natural waters. Rapid surface reactivity and wide elemental application of Muromac A-1 made this resin a highly effective reagent for preconcentration procedure undertaken in this study. It has been shown that the number of elements were preconcentrated quantitatively and the proposed method can be applied successively for trace analysis of different types of natural waters (river water, tap water, rainwater). In the case of seawater, the complex matrix caused problems in the preconcentration step and for on-line ICP-OES determination of some elements the standard addition method is required. For determination of In, Tl, Ti, Y, Cd, Co, Cu and Ni in seawater, the described method can be applied directly. The preconcentration factor was between

20 and 200 times, and the detection limits are in order of 0.001–0.02 ng ml⁻¹.

References

- [1] M.S. Jimenez, R. Velarte, J.R. Castillo, Performance of different preconcentration columns used in sequential injection analysis and inductively coupled plasma-mass spectrometry for multielemental determination in seawater, *Spectrochimica Acta Part B* 57 (2002) 391–402.
- [2] L.C. Azeredo, R.E. Sturgeon, A.J. Curtius, Determination of trace metals in seawater by graphite furnace atomic absorption following on-line separation and preconcentration, *Spectrochim. Acta Part B* 48 (1) (1993) 91–98.
- [3] D.B. Taylor, H.M. Kingston, D.J. Nogay, D. Koller, R. Hutton, On line solid-phase chelation for the determination of 8 metals in environmental waters by inductively coupled plasma-mass spectrometry, *J. Anal. At. Spectrom.* 11 (1996) 187–191.
- [4] S.N. Willie, H. Tekgul, R.E. Sturgeon, Immobilization of 8-hydroxyquinoline onto silicone tubing for the determination of trace elements in seawater using flow-injection inductively coupled plasma-mass spectrometry, *Talanta* 47 (1998) 439–445.
- [5] M.N.A. Dasilva, V.L.A. Frescura, A.J. Curtius, Determination of trace elements in water samples by ultrasonic nebulization inductively coupled plasma-mass spectrometry after cloud point extraction, *Spectrochim. Acta Part B* 55 (7) (2000) 800–813.
- [6] H. Sawatari, E. Fujimori, H. Haraguchi, Multielement determination of trace elements in seawater by gallium coprecipitation and inductively coupled plasma-mass spectrometry, *Anal. Sci.* 11 (1995) 369–374.
- [7] B.W. Wen, X. Shan, S. Xu, Preconcentration of ultratrace rare earth elements in seawater with 8-hydroxyquinoline immobilized on polyacrylonitrile hollow-fiber membrane for determination by inductively coupled plasma-mass spectrometry, *Analyst* 124 (1999) 621–626.
- [8] S.D. Lofthouse, G.M. Greenway, S.C. Stephen, Miniaturization of a matrix separation/preconcentration procedure for inductively coupled plasma-mass spectrometry using 8-hydroxyquinoline immobilized on a microporous silica frit, *J. Anal. At. Spectrom.* 14 (1999) 1839–1842.
- [9] S. Caroli, A. Alimonti, F. Petrucci, On-line preconcentration and determination of trace elements by flow injection—inductively coupled plasma-atomic emission spectrometry, *Anal. Chim. Acta* 248 (1991) 241–249.
- [10] X. Wang, R. Barnes, Chelating resins for on-line flow injection preconcentration with inductively coupled plasma-atomic emission spectrometry, *J. Anal. At. Spectrom.* 4 (1989) 509–518.
- [11] D. Beauchemin, S.S. Berman, Determination of trace elements in reference water standards by inductively coupled plasma-mass spectrometry with on-line preconcentration, *Anal. Chem.* 61 (1989) 1857–1862.
- [12] H.M. Kingston, I.L. Barnes, T.Y. Brady, T.C. Rains, M.A. Champ, *Anal. Chem.* 50 (1978) 2064.
- [13] S.M. Nelms, G.M. Greenway, D. Koller, Evaluation of controlled-pore glass-immobilized iminodiacetate as a reagent for automated on-line matrix separation for inductively coupled plasma-mass spectrometry, *J. Anal. At. Spectrom.* 11 (1996) 907–912.
- [14] R.A. Nickson, S.J. Hill, P.J. Workfold, Behavior of matrix cations (Ca²⁺, K⁺, Mg²⁺ and Na⁺) during on-line preconcentration and atomic spectrometric detection of trace metals in natural waters, *Anal. Chim. Acta* 351 (1997) 311–317.
- [15] P. Hashemi, A. Olin, Equilibrium and kinetic properties of a fast iminodiacetate based chelating ion exchanger and its incorporation in a FI-ICP-OES system, *Talanta* 44 (1997) 1037–1053.
- [16] J.W. McLaren, J.W.H. Lam, S.S. Berman, K. Akatsuka, M.A. Azeredo, On-line method for the analysis of seawater for trace elements by inductively coupled plasma-mass spectrometry, *J. Anal. At. Spectrom.* 8 (1993) 279–285.
- [17] J.W. Jones, S.G. Capar, T.C. O'Haver, Critical evaluation of a multi-element scheme using plasma emission and hydride evolution atomic-absorption spectrometry for the analysis of plant and animal tissues, *Analyst* 107 (1982) 353–377.
- [18] M. Pesavento, R. Biesuz, M. Gallori, A. Profumo, Sorption mechanism of trace amounts of divalent metal ions on a chelating resin containing iminodiacetate groups, *Anal. Chem.* 62 (1993) 2522–2527.
- [19] A. Yuchi, T. Sato, Y. Morimoto, H. Mizuno, H. Wada, Adsorption mechanism of trivalent metal ions on chelating resins containing iminodiacetic acid groups with reference to selectivity, *Anal. Chem.* 69 (1997) 2941–2944.
- [20] A. Seubert, G. Petzold, J.W. McLaren, Synthesis and application of an inert type of 8-hydroxyquinoline-based chelating ion exchanger for sea-water analysis using on-line inductively coupled plasma mass spectrometry detection, *J. Anal. At. Spectrom.* 10 (1995) 371–379.
- [21] K.E. Jarvis, A.L. Gray, R.S. Houk, *Handbook of Inductively Coupled Plasma-Mass Spectrometry*, Blavkie, Glasgow, 1992.
- [22] S. Nakashima, R.E. Sturgeon, S.N. Willie, S.S. Berman, Determination of trace metals in seawater by graphite furnace atomic absorption spectrometry with preconcentration on silica—immobilized 8-hydroxyquinoline in a flow-system, *Fresenius J. Anal. Chem.* 330 (1988) 592–595.
- [23] S.C. Pai, P.Y. Whung, L.R. Lai, Preconcentration efficiency of Chelex-100 resin for heavy metals in seawater. Part 1. Effects of pH and salts on the distribution ratios of heavy metals, *Anal. Chim. Acta* 211 (1988) 257–270.