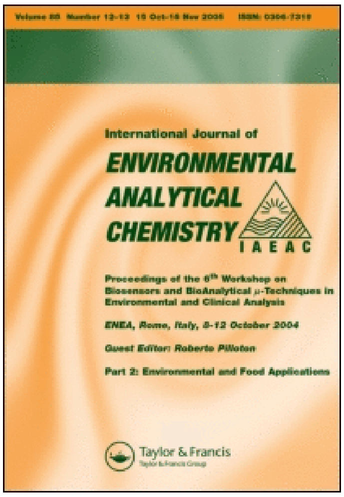

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Detata-Filters for Metal Preconcentration and Multielement Determination in Natural Waters

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DETATA-FILTERS FOR METAL PRECONCENTRATION AND MULTIELEMENT DETERMINATION IN NATURAL WATERS

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New sorption filters containing conformationally flexible amino-carboxylic groups were proposed for preconcentration of metals. Quantitative recovery of metals was achieved in a dynamic regime at a solution flow rate up to 4 $ml \cdot min^{-1} \cdot cm^{-2}$ in a pH range 3–8 from solutions with high salt content and in the presence of natural complexing agents. The dynamic capacity of DETATA-filters of the heavy metals was investigated. XRF and ICP-AES methods of heavy metals determination after preconcentration on the filters were developed.

KEY WORDS: Preconcentration, sorption filters, heavy metals, ICP-AES, X-ray fluorescence analysis.

INTRODUCTION

Contents of most heavy metals in surface waters of all types and in rain are very low, therefore the preconcentration stage is necessary even when the most sensitive modern multielemental determination methods, such as atomic emission spectrometry with inductively coupled plasma (AES-ICP), are used. Cellulose filter application with inoculated

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complex-forming groups makes the preconcentration simple and effective for both studying the background of trace elements in natural waters and monitoring water pollution[1–3]. The method is also effective for the preconcentration of trace elements in underground and waste waters. Using a cascade of membrane filters and sorption filters in dynamic conditions allows to separate suspended substances and to preconcentrate trace elements from solution in a single operation. The possibility of quantitative desorption of elements from filters permits to carry out the determination not only "in situ" by X-ray fluorescence, but also after elution from filters by acids by means of atomic emission with ICP and atomic absorption spectrometry (AAS). Some sorption filters, containing aminocarboxylic groups, selective to heavy metals, have been described[1–3].

In a previous work[4] we discussed the advantages and shortcomings of these sorbents and suggested our own approach to the synthesis of highly effective sorbents, containing conformationally flexible aminocaboxylic groups (DETATA). Synthesized sorbents possess much greater dynamic capacity with respect to heavy metals, they can be obtained in the form of thin-layer filters (DETATA-filters).

The aim of this work was to investigate the sorption properties of DETATA-filters, the influence of natural waters inorganic macrocomponents and dissolved organic substances on trace elements sorption and to develop X-ray fluorescence and AES-ICP methods for heavy metals determination in water after preconcentration on DETATA-filters. The application of these methods for analysis of rainfalls and different natural waters is also described.

EXPERIMENTAL

Reagents

Stock solutions were prepared by dissolving the metal salts in 0.1 M HCl. Concentration of metals was determined by flame atomic absorption using standard reference solutions (Physico-Chemical Institute, Ukrainian Academy of Sciences). Ashless preparations of fulvic acids were extracted from highly coloured water of Moskva-river head by adsorption chromatography on active carbon after preconcentration of fulvic acids by freezing[5]. Fulvic acid concentration in the stock solution corresponds to the water colority 2275° according to the platinum-cobalt scale.

DETATA-filters (Chemistry Department, Moscow State University) were used in the NH^+_4-form with a capacity of 0.7–0.8 mM/g of DETATA-groups and filtering surface diameters equal to 22 mm.

Procedures and equipment

Sorption properties of DETATA-filters were investigated in dynamic regime by passing the solution through a single filter and through a cascade of two or three filters, placed into the holders (Byospektr, Sankt-Petersburg), by means of a peristaltic pump PP-1-0.5 (Zalimp, Poland), and also under the conditions of free filtration. A set of model solutions containing either chlorides of test trace elements or chloride solutions was prepared in the presence of inorganic macrocomponents of waters, namely sodium, calcium, potassium, magnesium and fulvic acids. The pH values of the pattern solution were adjusted within the limits of 5–6. Model solutions were sustained for 1–3 days after mixing, then were filtered through a 0.45 µm membrane filter. The filtrate was used in dynamic experiments.

Recovery of metals on the filters was determined by their amount in filtrate fractions (volume of 10–50 ml) by AES-ICP (ICAP 9000, Jarrell Ash Corp.) or AAS (Perkin-Elmer 403) and also radiometrically by residual specific radioactivity of solution (^{60}Co, ^{54}Mn, ^{65}Zn, ^{152}Eu were used) on γ-spectrometer (NRG-603, Czechoslovakia). The same methods were used to determine metals in the solution after desorption from filters.

Determination of V, Mn, Fe, Co, Ni, Cu, Zn, Pb and Cd on DETATA-filters was carried out by energy-dispersive X-ray fluorescence, constituted by a (Si-Li)-semiconductor detector with a 180 eV resolution at 5.9 keV (Mn K_α), a X-ray tube with Ag-anode (side-window tipe, Kevex), a spectrometric section (Link Analytical) and a microcomputer. Measurement conditions for the determination of V, Mn, Fe, Co, Ni, Cu, Zn, Pb were—45 kV, 0.5 mA, filter Ag-of 0.177 mm thickness, exposition time—400 s. For the determination of cadmium an ^{241}Am source of $3.7 * 10^9$ s^{-1} activity was used, with an exposition time of 500 s.

RESULTS AND DISCUSSION

Trace metals sorption and desorption

Sorption of trace concentrations of Mn(II) and Zn on DETATA-filters was studied using radiotracers depending on the concentrations of basic salt components in natural waters (Figure 1). Sorption was carried out at pH 5, optimum for extraction of a wide range of metals by aminocarboxylic sorbents[6]. Mn and Zn were recovered quantitatively at high concentrations of salts, that are considerably higher than their concentrations in natural waters of basic types[7]. Using radiotracers the possibility of preconcentration of trace metals from river and sea waters was examined (Table 1). Data of metals recovery on the DEN-filters are given for comparison[8].

Mn(II), Co, Zn and Eu(III) are quantitatively desorbed in 30 min by 2 M HNO_3 or HCl under static conditions without filter destruction, that provides the possibility of their regeneration. The extent of metal recovery does not change after 5 cycles of sorption-desorption-regeneration.

Dynamic capacity of sorption filters

Dynamic capacity is an important parameter, defining the possibility of sorbent usage for metal preconcentration under dynamic conditions. It depends upon specific filtering surface, density of functional group arrangement, complex-formation kinetics, composition of solution and a number of other factors. Cellulose fibrous materials, containing aminocarboxylic groups, possess high dynamic capacity[4]. Besides, higher conformational

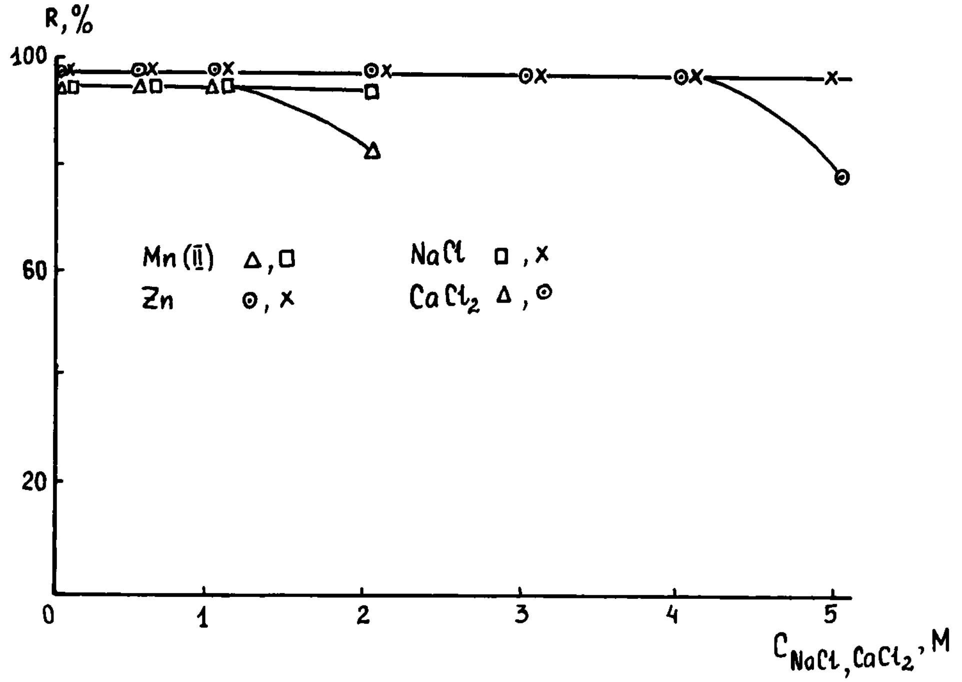

Figure 1 Effect of NaCl and CaCl2 concentration on the recovery of manganese (II) and zinc on the DETATA-filters. $C_{Mn} = 3.6 \cdot 10^{-9}$ M; $C_{Zn} = 1.5 \cdot 10^{-10}$M; V = 100 ml; v = 1 ml·min^{-1}·cm^{-2}; pH 5

flexibility of DETATA-groups provides their availability for metal complex-formation.

Figure 2 displays dynamic curves of Cu(II), Zn and Cd sorption on DETATA-filters under the following initial conditions: $C_{Cu} = 10$ µg/ml, pH = 5.7, $C_{Zn} = 10$ µg/ml, pH = 5.7, $C_{Cd} = 20$ µg/ml, pH = 5.4; flow rate is 8–10 ml/min. One may see that the three curves are practically identical. Capacity of DETATA-filters was the following: 0.46 mM/g for Cu(II), 0.43 mM/g for Zn, 0.51 mM/g for Cd; and also the capacity for "breakthrough": 0.14 mM/g for Cu(II), 0.13 mM/g for Zn, 0.15 mM/g for Cd. Thus, the capacity for "breakthrough" of DETATA-filters for all three elements is about 30% of the total capacity.

One must mention that full balance of trace elements in these experiments was achieved—discrepancy of introduced and found amount of trace elements in liquid fractions

Table 1 Recovery of metals (%) from waters on the amino- (DEN) and aminocarboxylic (DETATA) filters $C_{Mn} = 3.6 \cdot 10^{-9}$M; $C_{Co} = 6.8 \cdot 10^{-10}$M; $C_{Zn} = 1.5 \cdot 10^{-10}$M; $C_{Eu} = 2.0 \cdot 10^{-9}$M; V=250 ml; pH 5; v=1 ml·min^{-1}cm^{-2}

	Distilled water				*Sea water*				*River water*			
Filter	*Mn(II)*	*Co(II)*	*Zn*	*Eu(III)*	*Mn(II)*	*Co(II)*	*Zn*	*Eu(III)*	*MnII*	*Co(II)*	*Zn*	*Eu(III)*
DEN	95	97	100	78	8	84	84	95	31	85	96	100
DETATA	99	99	99	99	100	99	98	99	99	97	96	99
DETATA*	-	-	-	-	98	98	97	98	98	97	97	98

*v=3 ml·min^{-1}·cm^{-2}

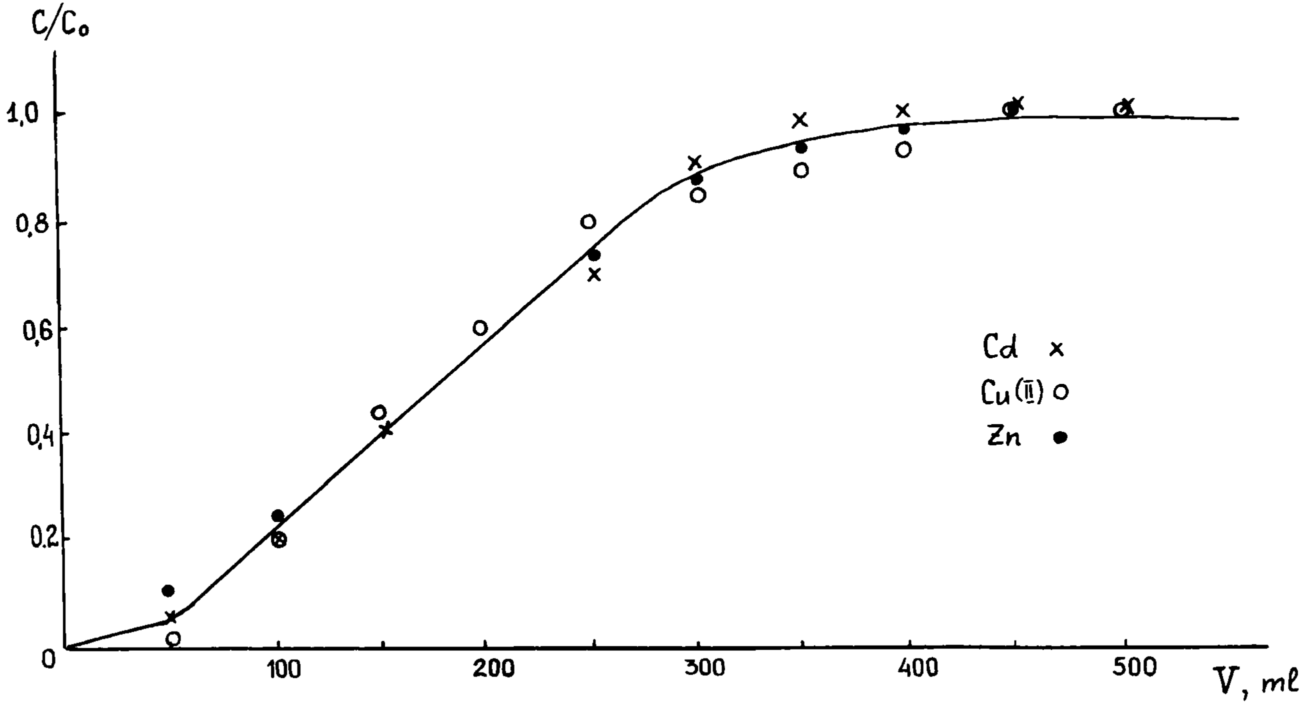

Figure 2 Dynamic curves of metal recovery on the DETATA-filters. $C_{o(Cu)} = 10\ mg \cdot l^{-1}$, pH 5.7; $C_{o(Zn)} = 10\ mg \cdot l^{-1}$, pH 5.7; $C_{o(Cd)} = 20\ mg \cdot l^{-1}$, pH 5.4; v = 8–10 $ml \cdot min^{-1}$

and on filters was not higher than 0.2–0.3%. The contribution of suspended forms, separated during filtration through a membrane filter of 0.45 μm, was not higher than 0.05–0.17%.

Inorganic macrocomponents influence

Studies of the influence of potassium, sodium, calcium and magnesium ion on copper (II), zinc and cadmium sorption were carried out in a wide range of macrocomponent concentrations (from 0 to 100 mg/l), covering sufficiently the normal characteristics of surface natural waters. Model solutions of 500 ml each with initial concentrations of copper, 3.5–4.0 μg/ml, and cadmium, 4–5 μg/ml and increasing concentration of each macrocomponent were filtered through DETATA-filters. The total contents of microelements in the filtrates were determined, and also the microcomponent amounts recovered on DETATA-filters. The corresponding results are represented in Figures 3 and 4.

Potassium ions do not greatly affect copper and cadmium sorption. The influence of other tested macrocomponents on microelement sorption was as follows Mg > Ca > Na. The influence of magnesium was the greatest when its concentration in the solution was 100 mg/l, the recovery of copper(II) was reduced from 83% for solutions without magnesium to

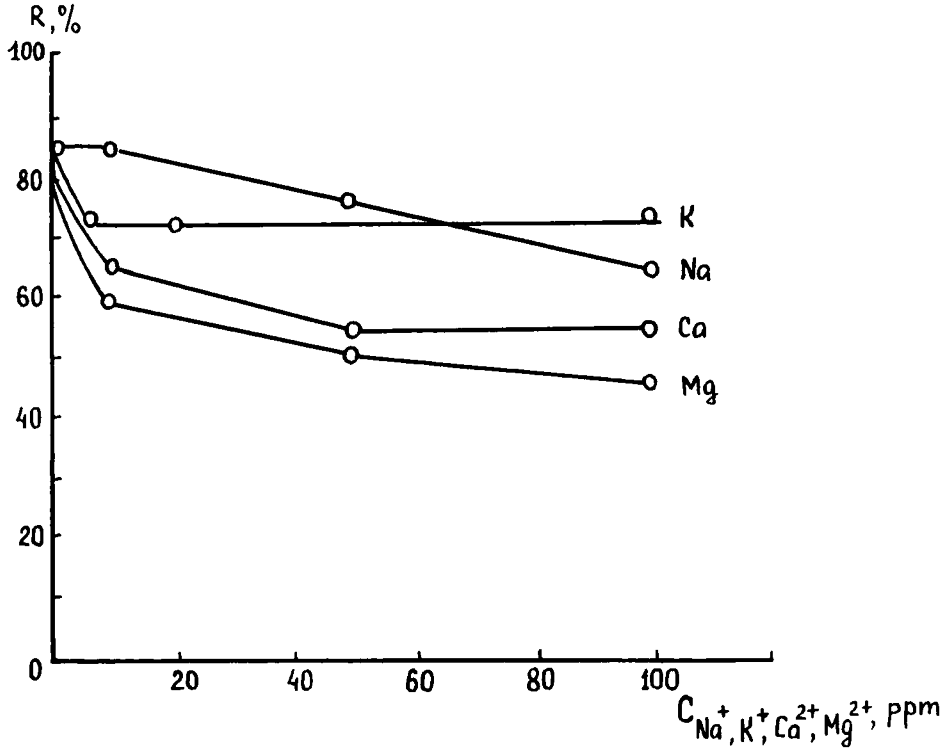

Figure 3 Effect of sodium, potassium, calcium and magnesium chlorides concentration on the recovery of copper(II) on the filters. $C_{Cu} = 3.5$–4.0 mg·l^{-1}; pH 5.7; v = 8–10 ml·min^{-1}.

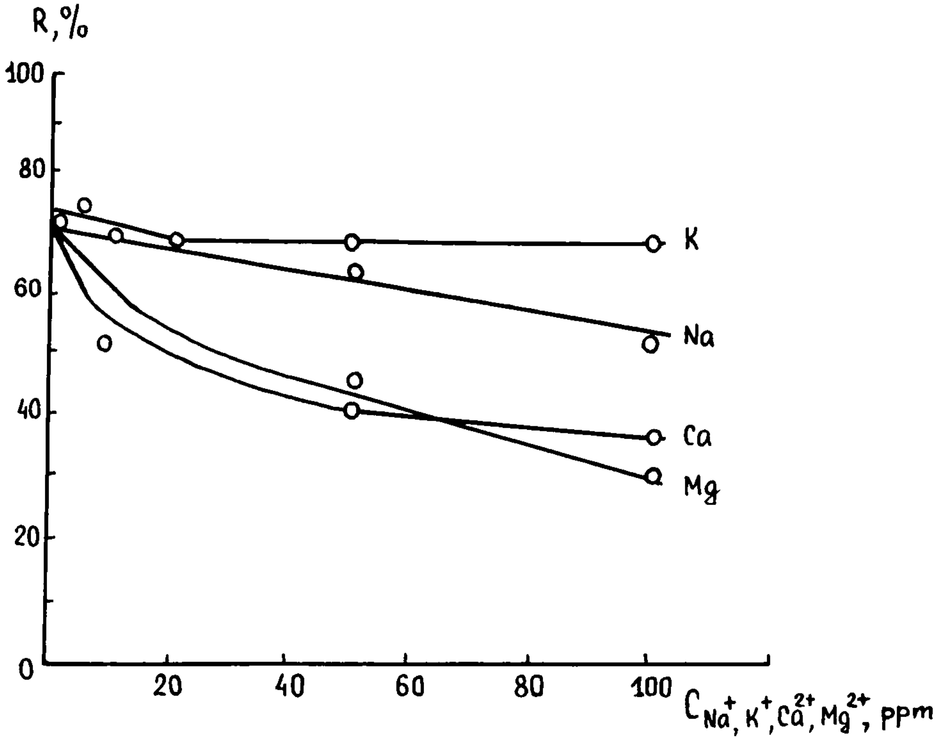

Figure 4 Effect of sodium, potassium, calcium and magnesium chlorides concentration on the recovery of cadmium on the filters. C_{Cd}= 4–5 mg·l^{-1}; pH 5.5; v= 8–10 ml·min^{-1}.

45% with magnesium, and recovery of cadmium—from 70 to 30%. These tests were carried out under metal concentrations near to full filter saturation on microcomponents, and just under such conditions the influence of inorganic macrocomponents was significant.

The research of the trace components recovery depending on their own concentration in the solution demonstrated that, if total microcomponent content on the filter is not higher than 15% of the capacity of DETATA-filters, trace elements are extracted quantitatively (90–95%).

Comparison of data, given in Figures 1, 3 and 4, shows the different behaviour of very low and microgram amounts of heavy metals during sorption in the presence of inorganic macrocomponents of natural waters. Macrocomponent influence on sorption is high only at high degree of filter capacity filling with heavy metals. This factor may be found important for the analysis of thermal waters, underground waters near ore deposits, industrial waste waters and other kinds of waters enriched in heavy metals. On the other hand, the high extraction degree of heavy metals in very low concentrations from the solutions in the presence of Na, K, Ca, Mg in a wide range of concentrations allows to recommend DETATA-filters for the analysis of different types of natural waters, from snow waters to sea waters.

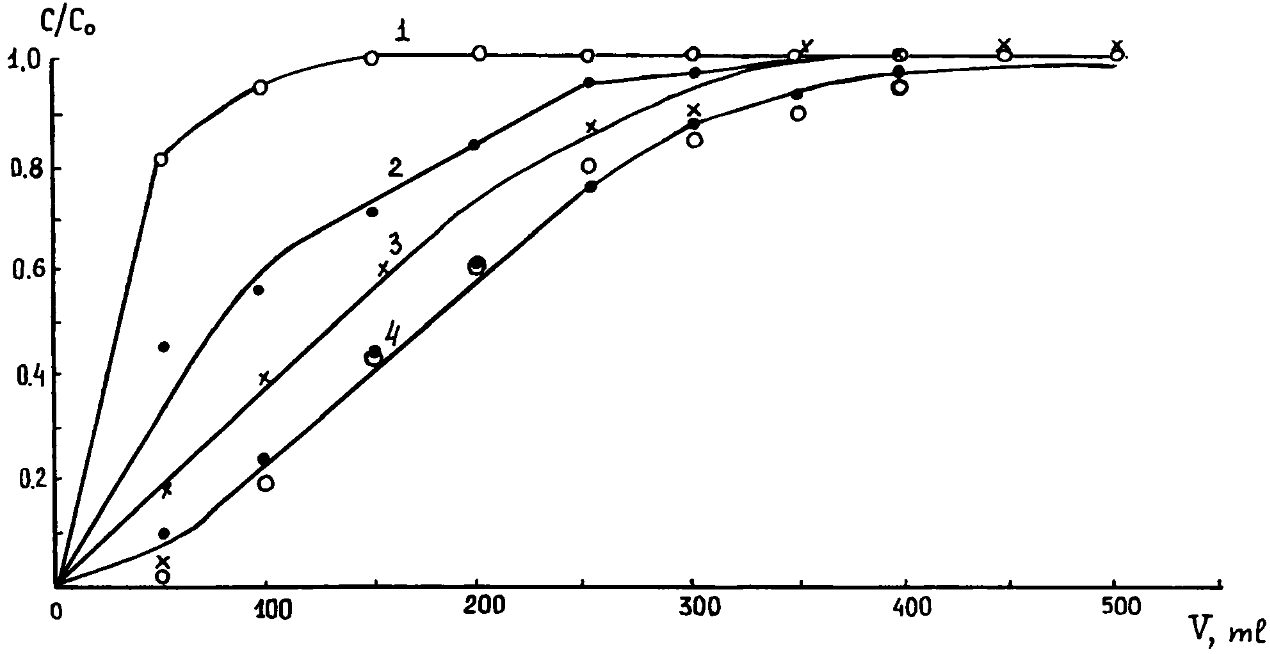

Figure 5 Dynamic sorption curves of metals on the DETATA-filters in the presence of fulvic acids. Sorption of Cu (1), Zn (2), Cd (3); colority of 250° (Pt-Co scale); metals sorption in the absence of fulvic acids (4). $v = 8\text{–}10\ \mathrm{ml{\cdot}min^{-1}}$; pH 5.5–5.7; $C_{Me} = 4\text{–}10\ \mathrm{mg{\cdot}l^{-1}}$.

The influence of the dissolved organic substances in natural waters

Other components affecting on the heavy metal sorption on DETATA-filters are dissolved organic substances of natural waters. They are represented (60–80%) by fulvic acids, polydispersed polyfunctional natural ligands, forming strong complexes with heavy metals. Mainly carboxylic and phenoxy groups of fulvic acids[9] take part in complex-formation. It is known that fulvic acids are well recovered by anion-exchange cellulose[10]. Tertiary aminogroups in high concentration are also contained as fragments of DETATA-groups.

The influence of competing formation of heavy metal complexes with dissolved organic substances on metal sorption by DETATA-filters is well illustrated by the separation of metals from model solutions with a fulvic acid content of 50 mg/l and color 250° Pt-Co scale (Figure 5). The dependence of copper(II) and cadmium recovery on model solution colority was also investigated (Figure 6[11]). One may see, that colority, typical for continental surface waters, does not greatly affect the recovery of cadmium on DETATA-filters, as cadmium forms unstable complexes with fulvic acids ($\lg \beta_{11} = 3.0$–4.0[12]). The recovery of copper(II), forming sufficiently stable complexes with fulvic acids ($\lg \beta_{11} = 6.5$[13]) is reduced from 85 to 65%.

However, under real concentration conditions of surface waters the content of a great number of metals is lower by an order of 3–5[7], than in the given model experiments. At the

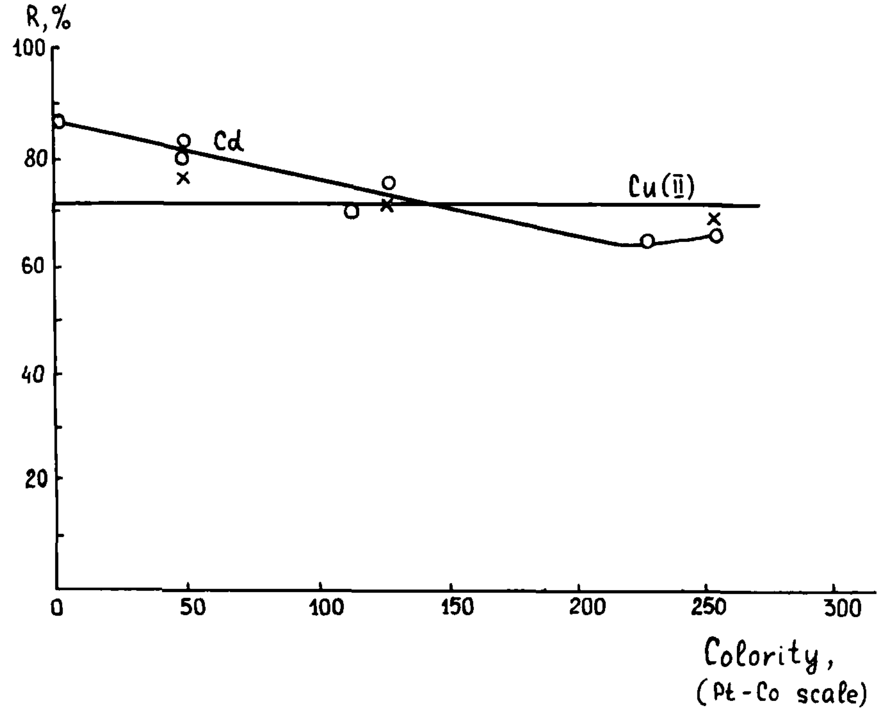

Figure 6 Effect of fulvic acids concentration in solution on Cd and Cu(II) recovery on the DETATA-filters. C_{Me}= 4–5 mg·l^{-1}; v = 8–10 ml·min^{-1}; pH 5.5–5.7.

same time the high recovery of heavy metals in trace concentrations is provided both by a great excess of free functional groups and by sorption of anion complex compounds of metals with associates of fulvic acids on nitrogen-containing DETATA-groups.

The influence of solution flow rate

The increase of solution filtration rate through the cascade of two filters up to 4 ml·min^{-1}·cm^{-2} (14 ml·min^{-1} through the holder with the diameter of 25 mm) does not result in metal losses during preconcentration (Figure 7). Figure 8 shows the dependence of X-ray fluorescence signal intensity on nickel and copper concentrations, obtained at solution flow rates of 1 and 4 ml·min^{-1}·cm^{-2}. Metals were determined in each cascade filter, the analytical signal representing the sum of values measured apart. It is necessary to note that at the flow rate of 1 ml·min^{-1}·cm^{-2} metals are basically concentrated on the first cascade filter, at the rate of 4 ml·min^{-1}·cm^{-2} the contribution of the second filter is significant. Calibration curves, obtained at different solution flow rates, practically coincide, demonstrating the reliability

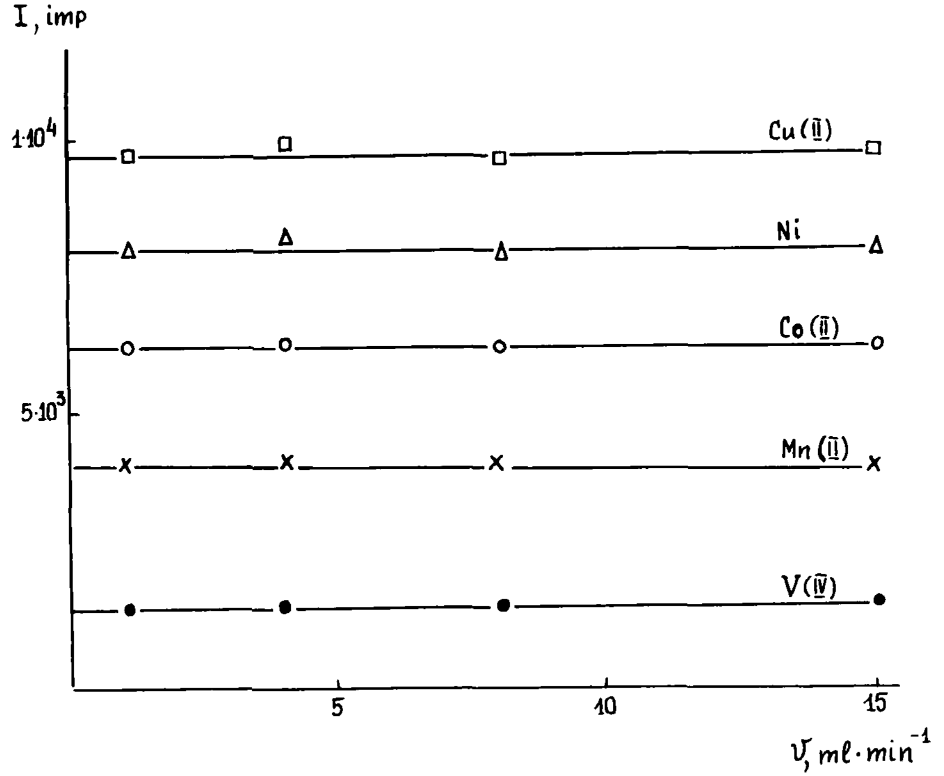

Figure 7 Effect of solution flow rate on the X-ray fluorescence signal intensity. C_{Me} = 50μg; V = 100 ml; pH 5.

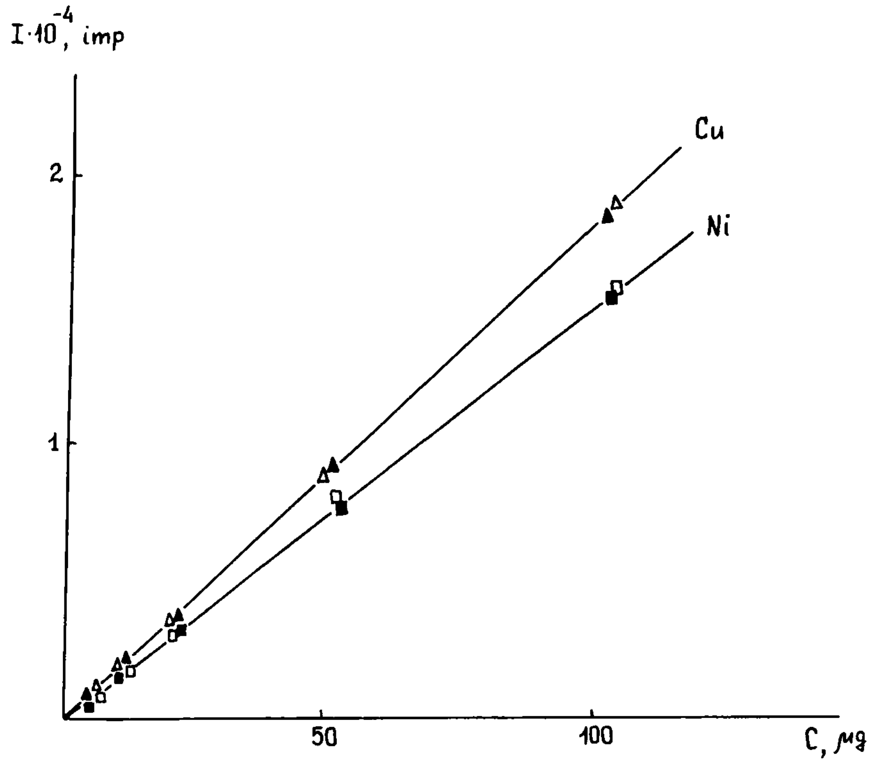

Figure 8 Effect of metal concentration on the X-ray fluorescence signal intensity for copper(II) and nickel on the DETATA-filters. V = 100 ml; v = 1 (△, □); 4 (▲, ■) ml min^{-1} cm^{-2}; pH 5

of the metal preconcentration. Metal preconcentration from water sample of 500 ml on 25 mm DETATA-filters requires a little more than 30 min. A preconcentration extent of 1.2 * 10^4 is achieved.

Flow rate of 1–1.5 ml ml·min^{-1}·cm^{-2} through the cascade of two DETATA-filters can be achieved under conditions of free filtration. Higher flow rates are possible only with the use of pumps.

Metal desorption from the filters

It was shown earlier[4] that quantitative desorption of trace heavy metals from DETATA-filters is achieved by 2 M HCl. In the present work the heavy metal desorption was investigated, depending on the temperature and the time of the process. It was found, that V, Mn, Ni, Cu, Zn, Pb, Cd were quantitatively desorbed by 2 M HCl at room temperature during 1 hour. At the same time about 20% of iron and cobalt was lost. Quantitative desorption of all metals was observed at double fold treatment of DETATA-filters by 2–3 ml of 2 M HNO_3 under 50–60°C under static conditions.

In accordance with the data obtained the conditions were proposed for heavy metal determination in natural waters in a wide range of compositions, from ultra-fresh to sea waters.

Preconcentration and determination of metals in natural waters

Samples of 0.1–1.0 l were filtered through membrane filters with pore diameters of 0,4–0,5 μm. The filtrate pH was adjusted in the range of 4–7 by means of double filtrated through DETATA-filters acetate-ammonia buffer solution. The sample was pumped through the cascade of two DETATA-filters with the help of a peristaltic pump with a flow rate of 10–14 ml·min^{-1} (holder diameter, 25 mm) or under conditions of free filtration with a rate of 4–5 ml·min^{-1}. Filters were pulled out of the cells and dried out between the sheets of filter paper. Metals were determined directly on the filters by X-ray fluorescence method (XRF). Standard samples were prepared by filtering of certified metal solutions through the cascade of two DETATA-filters.

Optimum conditions for XRF determination were chosen on the samples, containing 5 and 10 μg of each metal (Figure 9). XRF analysis includes three steps: measuring-recording of spectrum, spectrum manipulation (smoothing, background substraction, taking into account the superposition of analytical lines, receipt of "pure" analytical signal) and calculation of element concentrations using the value of the analytical signal. All the procedures were carried out on the basis of a software developed at the Analytical Centre of Geological Institute[14].

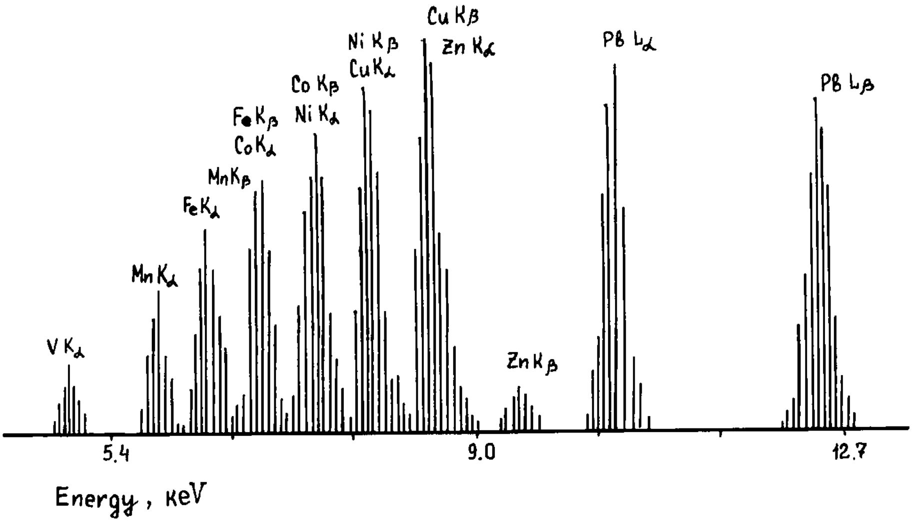

Figure 9 Spectrum of the sample containing 10 μg of each metal. 45 kV; 0,5 MA; F = 0,177 mm; τ = 400 s.

One of the main problems of the energy dispersive XRF analysis is the calculation of matrix effects and interelement influences. In the case of the uniform content matrix (cellulose filters) and low concentrations of the analyte elements (1–100 µg) the intensity of the analytical signal of each identified element is proportional to its concentration in the sample[15]. Effects of selective absorption and excitation in the sample in this case can also be ignored. It has been found, that the analytical signal intensity of the analyte element in the concentration range 5–100 µg depends only on its atomic number and has a linear character (Figure 10). In this case, the calculation of the concentration of the elements only requires the solution of simple linear equations.

For metal determination by AES-ICP, wet filters-concentrates were removed from the cells, placed in flasks of 50 ml and filled with 2–3 ml of 2 M HNO_3. The solution was heated to 50–60°C and filtered through a small filter for the separation of fibres of DETATA-filters into the measuring test-tube of 10 ml volume. The treatment procedure of filter by 2 M HNO_3 was repeated. The flask and filters were washed with few ml of distilled water and the solution volume was brought up to 10 ml in the measuring test-tube. The metal concentration in the solution was determined by AES-ICP.

AES-ICP and XRF determination of metals in snow waters after sorption preconcentration

Snow waters are widely used in estimation of land pollution by heavy metals. Heavy metal concentration in these ultrafresh waters is usually in the range of 0.1 to 30 µg/l, depending on the element nature and pollution level of snow cover. At such concentrations the majority of heavy metals cannot be determined directly by the modern multielement instrumental methods.

Accuracy of the sorption-AES-ICP method developed was determined by the method of metal spikes to snow water sample, collected at Vorob'evy Gory in Moscow. Spikes of Cu(II), Ni, Zn, Co(II), Cd and Mn(II) from 10 to 500 µg were added to 500 ml of water, pre-filtered through a 0.45 µm membrane filter at the natural pH value of this water, 7.02. After addition of spikes and standing for 24 hours, the sample was filtered through a membrane filter and then through the cascade of two DETATA-filters. After desorption, the metal quantity was determined on each filter separately, and also in the resulting filtrate (Table 2). In all spikes investigated a good balance (83–100%) of element amount, found in all components of the system, was observed. After metal sorption no more than 2–10% of introduced amount was found in the solution.

Significant breakthrough was noticed only during sorption from solutions, containing 500 µg of each metal, i.e. under conditions close to full filter saturation. Thus, errors introduced into the analysis by the preconcentration step do not make a considerable contribution into the total error of element determination in waters at the concentration levels of 10^{-5} -10^{-7}M. Though the main quantity of trace elements is recovered on the upper DETATA-filter, the use of two filters in cascade would be appropriate because it increases the reliability of preconcentration.

Overall, the sorption-AES-ICP method developed provides the possibility of the simultaneous determination of up to 16–22 trace elements in natural waters with detection limits of 0.01–0.1 µg/l. Table 3 gives the results of AES-ICP and sorption-AES-ICP determination

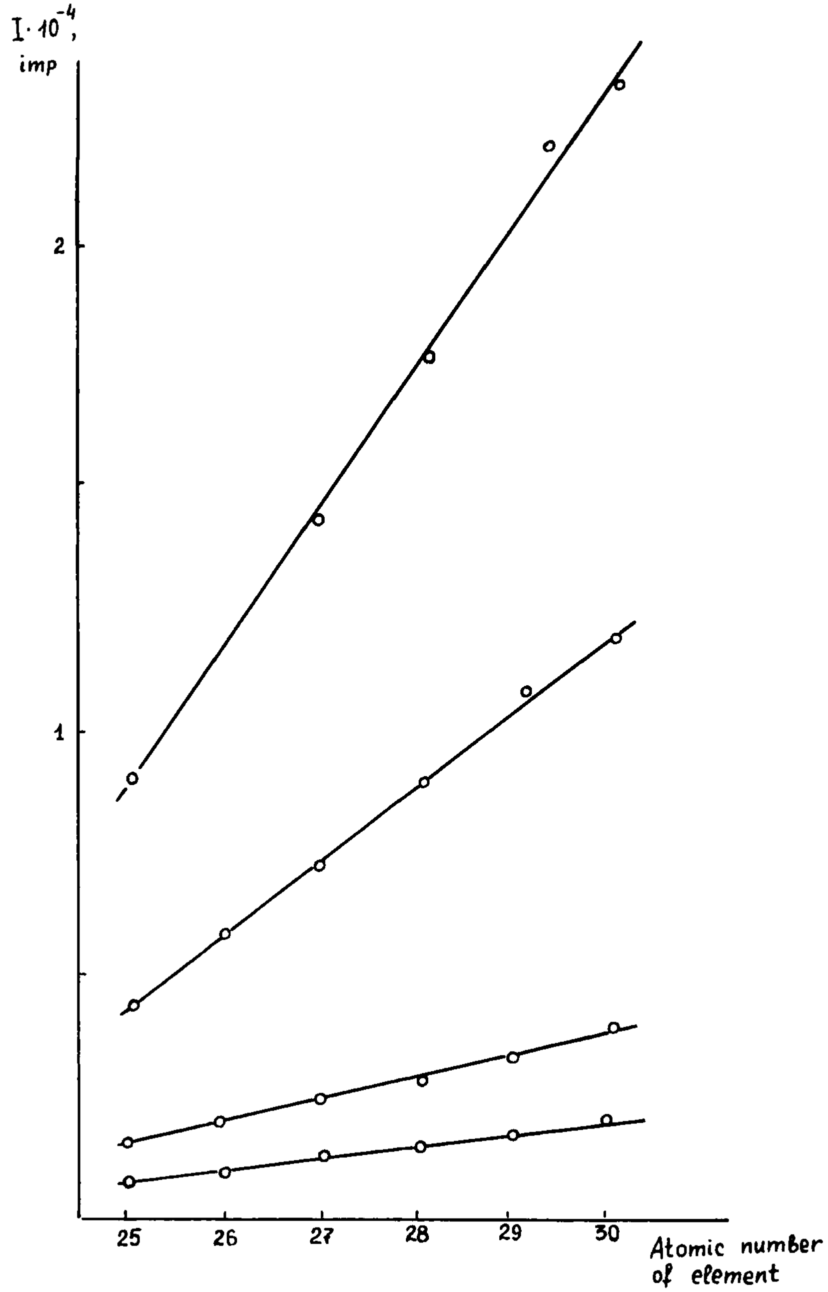

Figure 10 Effect of element atomic number on the X-ray fluorescence signal intensity. C_{Me}= 10 (1); 20 (2); 50 (3); 100 (4) μg.

Table 2 Results of metals distribution in Moscow snow water (v = 8–10 ml·min $^{-1}$; pH 7.02)

Metal	*Added,*	*Found, % from the added amount*				
	µg	*On the membrane filter*	*On the upper DETATA filter*	*On the lower DETATA filter*	*In the resulting solution*	*Balance*
Cu	10	1.1	65.2	4.9	23.3	95
	20	0.9	73.5	5.9	14.4	95
	50	13.5	62.9	3.2	4.1	84
	200	8.3	67.2	5.3	3.6	84
	500	2.6	54.3	7.4	2.2	90
Ni	20	0.3	80.5	12.9	1.9	96
	50	2.7	85.2	8.2	1.0	97
	100	5.1	69.6	8.0	3.9	87
	200	1.9	71.6	9.5	2.6	86
	500	6.0	64.4	17.7	9.0	97
Cd	20	0.1	81.7	13.3	7.8	103
	50	0.2	87.2	10.8	4.4	103
	100	1.6	72.6	10.7	2.8	88
	200	0.2	72.6	13.5	5.3	92
	500	0.5	56.9	23.7	19.4	101
Mn	20	0.3	89.5	17.5	3.2	111
	50	3.4	69.1	27.4	5.0	105
	100	6.6	53.6	23.3	4.9	88
	200	9.8	47.3	22.7	11.0	91
	500	20.7	20.9	17.7	39.8	99
Zn	35	2.5	67.7	8.5	7.7	86
	55	1.6	68.7	12.3	5.4	88
	115	1.7	76.0	12.0	2.8	93
	215	4.9	60.8	10.1	3.0	79
	415	0.1	65.5	12.8	4.0	82
	1015	1.3	51.7	22.6	17.1	93
Co	10	0	79.0	8.1	3.0	90
	20	0	80.2	13.1	2.3	96
	50	2.5	86.2	12.3	1.2	102
	100	5.5	70.1	12.1	2.3	90
	200	2.1	72.4	13.9	3.1	92
	500	6.3	53.8	24.4	18.4	103

of trace elements in snow water samples, collected in Moscow, demonstrating the high efficiency of the developed method. Instead of 3–4 trace elements determined by AES-ICP without preconcentration, the suggested method allowed to determine the content of 16 trace elements. The application of this method for the analysis of snow waters increases the significance of these samples in pollution monitoring studies.

Table 4 gives the results of a number of metal determinations in snow waters (collected in the region of Leninogorsk), carried out by XRF after sorption preconcentration, and also by direct AES-ICP and AAS methods. Results confirm the absence of systematic errors in metal determinations by the suggested XRF method.

Table 3 Results of ICP-AES determination of elements in Moscow snow water before and after preconcentration on the DETATA-filters
Enrichment factor of 100

Element	*Determined, (μg·l⁻¹)*	
	Before preconcentration	*After preconcentration*
Al	<25	4.12
Ba	30.2	33.5
Ca	3250	1440
Cd	<2	0.10
Cu	2.7	1.93
Mg	375	210
Mn	3.7	5.0
Ni	<10	2.37
Sr	8.0	6.42
V	4.9	2.37
Zn	88.7	82.6
Co	<3	0.08
Na	156	48.8
B	<4	1.42

Table 4 Results of four elements determination (mg/1) in snow water by ICP-AES, ETAAS and sorption-XRF methods (V = 100 ml; n = 4; P = 0.95)

Cu			*Fe*			*Zn*			*Pb*		
XRF	*ICP-AES*	*ETAAS*	*XRF*	*ICP-AES*	*ETAAS*	*XRF*	*ICP-AES*	*ETAAS*	*XRF*	*ICP-AES*	*ETAAS*
0.21±0.03	0.24	0.20	0.15±0.05	0.17	0.20	0.11±0.02	0.13	0.13	0.001	<0.5	0.005
0.14±0.02	0.13	0.13	0.25±0.05	0.27	0.30	0.28±0.02	0.32	0.30	0.06±0.01	<0.5	0.07
0.08±0.01	0.08	0.09	0.20±0.03	0.29	0.20	0.42±0.03	0.47	0.45	0.07±0.02	<0.5	0.07
0.07±0.01	0.07	0.05	0.08±0.02	0.06	0.05	4.7 0.2	4.9	5.0	0.15±0.02	<0.5	0.14

XRF determination of heavy metals in river and sea waters

The absence of standard samples of natural waters did not give the opportunity to characterize the accuracy of metal quantification by the most correct method. Therefore, recovery of metal spikes to natural waters was tested. One may suppose that for 10–30 days of standing, metal additions change into complex forms, close to natural. The method of spikes for waters of the river Oka (middle stream) gives the possibility to determine eight metals in fresh waters (Table 5). Results display practically quantitative recovery of spikes.

Table 5 Results of sorption -XRF determination of metals (μg) in river water
(V=100 ml, n=5, P=0.95; 50 μg of metals were added)

Metal	*Found*	*RSD*
V	47±2	0.04
Fe	50±2	0.04
Co	47±1	0.02
Ni	47±1	0.01
Cu	48±1	0.02
Zn	50±2	0.04
Pb	48±2	0.02
Cd	51±2	0.02

Table 6 Results of ICP-AES and sorption-XRF determination of metals (mg·l^{-1}) in sea water (V=100 ml, n=5, P=0.95)

Metal	*Found* *ICP-AES*	*XRF*	*RSD*
V	-	0.055±0.006	0.12
Mn	0.105	0.098±0.003	0.03
Co	0.120	0.101±0.001	0.01
Ni	0.100	0.098±0.002	0.03
Cu	0.086	0.082±0.006	0.07
Zn	0.134	0.138±0.002	0.02
Pb	-	0.071±0.003	0.04
Cd	0.100	0.098±0.002	0.02

Another approach was used for metal extraction from sea waters. The high pH values of sea water (7–8) and also relatively low concentrations of organic complex-forming substances (waters, selected at a distance of 200 km from archipelago Bismark, were used as a model) result in great hydrolysis of introduced metal spikes. Therefore, after standing with metal spikes the samples were refiltered and, before preconcentration, the metal concentration was determined by an independent method [16]. Results given in Table 6 confirm the opportunity to use the method developed for metal determination in sea waters as well.

The assessment of the reproducibility of metal determinations by XRF method was carried out in different waters (Table 7). The test was planned according to the scheme of

Table 7 The total root-mean-square deviation of metals determination in waters by sorption-XRF method

Metal	*Metal concentration, μg·l^{-1}*	*Root-mean-square deviation* *calculated*	*allowed*
V	<10	0.06	0.30
	10–49	0.06	0.15
	>50	0.04	0.10
Mn	<50	0.07	0.30
	50–99	0.06	0.15
	>100	0.04	0.10
Fe	<200	0.04	0.30
	>200	-	0.10
Co	<50	0.07	0.30
	50–99	0.05	0.15
	>100	0.04	0.10
Ni	<50	0.07	0.30
	50–490	0.04	0.15
Cu	<50	0.07	0.30
	50–490	0.04	0.15
Zn	<50	0.07	0.30
	50–490	0.04	0.15
Pb	<20	0.06	0.30
	>20	0.04	0.10
Cd	<10	0.07	-
	10–49	0.05	-
	50–100	0.02	-

dispersion analysis[17]. The total root-mean-square deviation and its constituents, related with the sample preparation, short-term and long-term drifts, were calculated. The analysis showed that factors linked with short-term drift make the principle contribution into the total error of identification. Total error constituents linked with sample preparation and long-term drifts were negligible.

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