SIMULTANEOUS SORPTION OF CHELATES OF ELEMENTS WITH ORGANIC REAGENTS ON AMBERLITE XAD-2 AS A PRECONCENTRATION STEP FOR THE EMISSION SPECTROMETRIC DETERMINATION OF THE ELEMENTS

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The macroporous hydrophobic sorbent Amberlite XAD-2 proved to be well suited to the preconcentration of minority amounts of Al, Au, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Sn, Ti and V in the form of their chelates with organic reagents. From among 14 reagents tested, 8-hydroxyquinoline and diethyldithiocarbamate appeared most suitable for the quantitative sorption up to a level of 1 $\mu g\ l^{-1}$ of analyte. Emission spectrometry served as the analytical finish; the nitrous oxide–acetylene flame, electric arc and inductively coupled argon plasma were chosen according to the nature of the element. The procedure is convenient for the determination of the minority analytes in waters.

Conventional methods for the preconcentration of elements include their extraction in the form of complexes with organic reagents or of ionic associates, coprecipitation onto a low soluble compound, and sorption on conventional or chelating ion exchangers. Procedures based on the sorption of chelates or ionic associates of metals with organic reagents on nonpolar sorbents such as activated carbon, modified silica gel and synthetic resins have also been developed recently; as against the use of chelating ion exchangers, such methods offer a wider choice of functional groups of the modifying reagents and of the sorption conditions. According to the method chosen, reagents with different selectivity then can be employed. The use of a nonselective reagent in conjunction with a method allowing multicomponent determination is a general trend. A review comparing the potential of preconcentration of metal complexes by sorption on ion exchangers and on nonpolar sorbents has been presented by Marina, Gonzales and Rodriguez[1].

As compared to activated carbon and modified silica gel, macroporous hydrophobic sorbents such as the Amberlite XAD type offer a cleaner work, easier handling and higher variability of the sorption and elution conditions. Such sorbents have been applied, in addition to the trapping of organic substances, also to the investigation of element species in waters and to the chromatographic separation of metal complexes with reagents[2]. Their application to the preconcentration of traces of metals in the form of their 1,10-phenanthroline complexes has been the concern of Nevoral[3]. The feasibility of fixing the reagent to the sorbent prior to introducing the analyte has also been studied and the dynamic and static modes have been compared using various eluting agents[4]. A comparison of the sorption of metal complexes with various organic reagents on activated carbon and on Amberlite XAD-4 has been presented by Yang and Jackwerth[5], who also compared the sorption properties of the XAD-4 and XAD-7 types with respect to the sorption of halo complexes and ionic associates[6].

The sorption of elements on Amberlite XAD-2 modified by a number of nonselective reagents was the concern of the present work. The dynamic variant was chosen as technically more convenient, using the reagent either added to the solution or fixed to the sorbent. In this procedure the hazard of sample contamination is considerably lower than in the extraction or coprecipitation methods. Emission photometry in the acetylene–nitrous oxide flame, arc spectrography and ICP-OES were used as the analytical finish.

EXPERIMENTAL

Apparatus

A homemade photometer comprising a GDM-1000 monochromator (Zeiss, Jena) and a photomultiplier and interfaced to a recorder was used[7] for the flame photometric measurement in the acetylene–nitrous oxide flame. The burner length was 5 cm. The nebulizer chamber was taken from a Perkin–Elmer Type 306 AAS spectrometer.

Arc spectrographic measurements were performed on a PGS-2 spectrograph (Zeiss, Jena): grating 650 grooves per mm, 1st order of the spectrum (blaze 320 nm); the instrument involved a three-lens imaging system and a three-step filter, and photographic detection was applied.

The ICP-OES measurements were carried out on a PU 7000 spectrometer (Pye–Unicam, U.K.).

UBI-1 arc generator (RFT, Germany), alternating arc 15 A; SU 380 carrier electrode, SU 202 counterelectrode, SU 602 graphite powder (Elektrokarbon, Slovakia). ORWO WU-3 spectral plates 9 × 24, ORWO MH-28 developer. MD 100 microphotometer (Zeiss, Jena), magnification 20 ×, P-transformation subtraction. An OP 208/1 digital pH-meter fitted with an OP 0808P combined electrode (Radelkis, Hungary). Finnpipette adjustable pipettes (Finland).

Chemicals and Solutions

Standard solutions of Al, Au(III), Cu, Fe(III), Ga, Mg, Ni, Pt(IV), Sn(II) and Ti(III) were prepared by dissolving the metals of spectral purity in concentrated HCl or in a HCl–HNO_3 mixture. Solutions of Mo(VI), V(V), Cr(III,VI), Co(II), Pd(II), Mn(II), Ge, Ca, Na and Cd were prepared from chemicals of reagent grade purity and, except for Na, Cr(VI) and Ge, standardized chelometrically. The resulting metal concentration was 10 mg ml^{-1}.

The following buffers were used: borate buffer (pH 6 – 9); 1,1,1-tris(hydroxymethyl)aminomethane–HCl or NaOH buffer (pH 6 – 9); acetate buffer (pH 4 – 5); and phthalate buffer (pH 3). Their concentration was 1 mol l^{-1}.

All the reagents used were chemicals of reagent grade purity supplied by Lachema, except for APDC (Merck, Darmstadt) and thiooxine (Soyuzkhimeksport, C.I.S.). Chromazurol S, Eriochromcyanine R, 1-(2-pyridylazo)-2-naphthol (PAN), 4-(2-pyridylazo)resorcinol (PAR), 1-(2-thiazolylazo)-2-naphthol (TAN), 1-(2-thiazolylazo)resorcinol (TAR), 1-(2-quinolylazo)-2-naphthol (QAN), 2-(2-thiazolylazo)-4-methoxyphenol (TAM), 2-mercaptobenzothiazole, thionalide, sodium diethyldithiocarbamate (NaDDC), ammonium pyrrolidine dithiocarbamate (APDC), 8-hydroxyquinoline (oxine), sodium 8-mercaptoquinolinate (thiooxine). Their solutions in water (thiooxine, NaDDC, APDC, PAR, Eriochromcyanine R, Chromazurol S) and in methanol (PAN, TAN, TAR, QAN, TAM, thionalide, mercaptobenzothiazole, oxine) were used at a concentration of 0.5%.

Hydrochloric acid in acetone (0.1 mol l^{-1}) served as the eluent. Solution of reference elements and matrix modifiers for emission spectrography contained Ge (0.1 mg ml^{-1}), Pd (0.37 mg ml^{-1}), Ca (1.0 mg ml^{-1}) and Mg (0.1 mg ml^{-1}).

HNO_3 p.p., HCl p.a., NaCl p.a., NaOH p.a., methanol p.a., argon 99.94%.

The reagents and chemicals used were checked for purity by spectral analysis.

Sorbents

Amberlite XAD-2 and XAD-4 (Merck, Darmstadt), which are macroporous sorbents based on a styrene–divinylbenzene copolymer, grain size 0.32 – 0.50 mm. The sorbents were decanted with methanol and dried under an infralamp prior to their first use. A glass column 8 × 90 mm was packed with 1 g of the dry sorbent. In the column, the sorbent was washed with methanol, which was allowed to act in the column for a day. Subsequently the sorbent was washed with water, HNO_3 (6 mol l^{-1}), HCl (0.1 mol l^{-1}) in acetone, and water again, and was stored in water.

Determination of the Analytes by Flame Emission Spectrometry

The behaviour of the reagents on the sorbents was examined using a system comprising Fe, Cu, Mn, Ga and Cr, which were determined by flame photometry[8,9]. The effect of acetone on the emission of all of the analytes and the poor reproducibility of the copper line background were eliminated by calibration using the standard addition method.

Conditions: acetone flow rate 4.1 l min^{-1} for calibration and 3.9 l min^{-1} for measurement, nitrous oxide flow rate 8.7 l min^{-1}, slit width 0.05 mm, height 20 mm, emission measurement in the 3rd order for Cu and Fe and in the 2nd order for Mn and Cr.

Eluate from the column was collected in a 25 ml volumetric flask and analyzed by the standard addition method. The solutions contained spectral buffer (NaCl) and HNO_3 in concentrations of 1 mg ml^{-1} Na and 0.5 mol l^{-1}, respectively. The emission of copper was measured against a solution containing HNO_3 (0.5 mol l^{-1}), Na (1 mg ml^{-1}), buffer (2 ml) and acetone (4 ml) in 25 ml. The analytical parameters of the determination are given in Table I.

Determination of the Elements by Emission Spectrography

For TAR, PAR, NaDDC, APDC and oxine the blend of elements was extended with Au, Al, Cd, Co, Mo, Ni, Pb, Pt, Sn, Ti and V, which then were quantitated by emission spectrography with arc excitation. For Al, Cd, Cr, Cu, Fe, Mo, Ni, Pb, Sn, Ti and V the procedure was partly based on the previous work[10,11]; for some elements, however, different spectral lines were selected with regard to the different excitation parameters. Platinum was determined according to ref.[12], for Co, Au and Ga the lines were chosen so that the conditions of excitation should be the same as for the remaining elements. Sufficient sensitivity and a low background were the principal criteria for the selection of the lines. Ge and Pd proved to suit well as the reference elements for the regions of 260 – 300 and 300 – 330 nm, respectively, based on the linearity of their calibration dependences.

An 15 A alternating arc was employed; electrode spacing 3 mm, exposure 51 s without presparking, slit width 0.02 mm. Plate blackening was evaluated by P-transformation, correction was made for background and blank[11]. Background had to be subtracted for lines measured at the 50% and 100% filter transmission, correction for the blank was applied to Al, Fe and Cu. The analyte content of sample was determined based on the calibration plots.

Calibration was performed by adding 5 ml of concentrated HNO_3, 1 ml of solution of internal standards and matrix modifiers and the appropriate amounts of the standard solutions of analytes to 150 mg of graphite, evaporating the dish content to dryness and grinding it thoroughly with 100 mg of solid NaCl, and filling the this mixture into the electrodes.

The eluate from the column was collected in a Teflon dish containing 150 mg of graphite, and evaporated to dryness under an infralamp. The evaporation residue was worked up by the same procedure as the samples for calibration (without adding the analytes). The parameters of determination are given in Table II.

Determination of the Analytes by ICP-OES

Natural water samples were analyzed in an inductively coupled argon plasma. The operating conditions of the source were optimized for the determination of the analytes in the eluate. The spectral lines were selected and the optical conditions optimized following the manufacturer's recommendations. Some data of the determination are given in Table III.

Parameters: generator power 1.4 kW, cooling argon, plasma argon and sample flow rates 18, 0.2 and 1 l min^{-1}, respectively. The results were processed by a computer in the on-line mode.

Eluate from the column was collected in a 25 ml volumetric flask and evaporated to a volume of approximately 5 ml under an infralamp. After diluting to the mark, the solution was directly analyzed.

RESULTS AND DISCUSSION

The behaviour of the reagents was examined in the sorption of 50 μg of Mn, Cr(III) and Ga at pH 5, 7 and 9. The dynamic variant with the reagent added to the solution was

TABLE I
Parameters of analyte determination by flame photometry

Analyte	λ, nm	Detection limit μg ml^{-1}	RSD[a], %	Linear region of calibration μg ml^{-1}
Cu	324.754	0.3	3.5	0.5 – 100
Cr	425.435	0.004	3.5	0.1 – 100
Fe	371.994	0.1	3.5	0.5 – 100
Ga	417.206	0.02	1.5	0.1 – 100
Mn	403.076	0.009	3.4	0.1 – 100

[a] Relative standard deviation for 15 measurements, criterion: 3s(p), analyte concentration 5 μg ml^{-1}; calibration plot regression coefficient was from 0.9984 to 0.9999.

chosen. For some low soluble reagents which also give low soluble complexes (PAN, QAN, thionalide), the mode of fixing the reagent to the sorbent was employed.

The column containing 1 g of sorbent was washed with 5 ml of the buffer of choice (tenfold diluted), after which the sample was allowed to pass through the column at a flow rate of 1 to 2 ml min^{-1}; 50 ml of sample contained 5 ml of buffer, 1 ml of reagent solution and the appropriate amount of analyte. Prior to the sorption, the pH was precisely measured. After the sorption the column was washed with 5 ml of the dilute buffer and eluted with 8 ml of HCl (0.1 mol l^{-1}) in acetone. The eluate was collected in a 25 ml volumetric flask for the quantitation by flame photometry or ICP-OES, and in a Teflon dish for the quantitation by arc spectrography.

If the reagent was to be fixed, the sorbent was prepared by washing with 10 ml of 2% reagent solution in methanol or in a buffer at pH 5 (NaDDC, APDC, thiooxine). The free reagent fraction was removed by elution with 50 ml of water or buffer at pH 5. The sorption procedure was as above, without addition of reagent to the sample.

TABLE II
Parameters of analyte determination by emission spectrometry

Analyte	λ, nm	Detection limit $\mu g\ ml^{-1}$	RSD[b], %	Linear region of calibration[a,c] $\mu g\ ml^{-1}$	Reference element[d]
Al	308.216	0.13	5.5	7 – 130	Pd
Au	267.595	4.0	5.3	7 – 130	Ge
Cd	298.063	6.0	13.2	7 – 130	Ge
Co	304.401	0.5	6.1	3 – 80	Pd
Cr	302.156	0.5	8.5	2 – 70	Pd
Cu	327.396	0.4	7.8	3 – 35	Pd
Fe	304.760	0.7	5.9	8 – 170	Pd
Ga	294.364	0.3	9.6	1 – 17	Ge
Mn	280.106	0.7	11.4	1 – 130	Ge
Mo	317.035	0.4	8.3	1 – 70	Pd
Ni	305.082	0.6	5.7	1 – 75	Pd
Pb	283.307	0.7	18.9	7 – 130	Ge
Pt	265.945	6.0	15.0	13 – 70	Ge
Sn	283.999	3.3	7.1	2 – 70	Ge
Ti	319.087	0.6	8.4	2 – 70	Pd
V	318.341	3.3	9.6	2 – 70	Pd

[a] Concentration in μg per g of graphite; [b] relative standard deviation for 16 determinations, criterion: 3s(p), analyte content of graphite: 30 μg g^{-1}; [c] regression coefficient was from 0.9927 to 0.9999; [d] Ge: 265.118 nm, 10% filter transmission; Pd: 325.164 nm, 50%; Al, Cu, V: 10%; Mn, Mo, Ti: 50%; remaining elements: 100% filter transmission.

For the majority of reagents the degree of sorption of the analytes was lower than 40%. Thiooxine proved unsuitable due to its rapid oxidation both in solution and on the sorbent. Only NaDDC, TAM, TAR and oxine brought about sorption higher than 80%. For oxine the results are consistent with those of ref.[5]. Therefore, these reagents were used to measure the dependence of the degree of analyte sorption on pH over the region of pH 3 – 11 for Cu, Cr(III), Fe, Ga and Mn. The dependences using oxine and NaDDC are shown in Figs 1 and 2, respectively. The two reagents are optimal with respect to the sorption efficiency and applicable pH region. Further work was therefore aimed at optimizing the method for them. Since the sorption exceeds 90% within the region pH 7 – 8.5 with NaDDC and within the region of pH 8 – 9.5 with oxine (except for chromium), sorption with a mixture of both was also examined. The assumption that the applicable pH region will broaden did not prove true; instead, the system behaved as in the presence of oxine solely.

The optimum pH ranges are pH 9 – 10 for the sorption of 8-hydroxyquinolinates and pH 7 – 8 for NaDDC; flow rates of 1 – 10 ml min^{-1} appeared suitable for sample as well as eluent.

For a preferential fixing of the reagent on the sorbent layer the column was prepared by rinsing with 20 ml of the reagent solution (1% solution of NaDDC in buffer at

TABLE III
Parameters of analyte determination by ICP-OES

Analyte	λ, nm	Detection limit, μg ml^{-1}	RSD[a], %
Al	309.271	0.023	1.4
Au	242.795	0.017	1.2
Cd	214.436	0.003	2.3
Co	228.616	0.007	3.1
Cr	206.149	0.006	2.2
Cu	324.754	0.005	1.3
Fe	259.940	0.006	2.7
Ga	417.206	0.066	6.1
Mn	257.610	0.002	1.4
Mo	202.030	0.008	2.1
Ni	231.604	0.015	2.1
Pb	220.353	0.042	2.7
Pt	265.956	0.081	3.4
Sn	189.926	0.070	3.5
Ti	334.941	0.0004	1.9
V	310.230	0.006	3.6

[a] Relative standard deviation for 6 parallel measurements at a concentration of 5 μg ml^{-1}.

pH 5, 1% solution of oxine in methanol). The sorption was accomplished with 50 ml of sample which contained 50 μg of the analytes. In this case the efficiency of sorption of Al and Mn did not change, it was the same as in the mode where the reagent was present in solution. For Cr, Ga and Cu the sorption decreased approximately 20 to 25%. Hence, in this case the fixed reagent mode has no advantages over the mode where the reagent is added to sample.

Matrix Effect

Attention was paid to the effect of Ca, Mg and Na as macrocomponents which are commonly present in natural water. Their effect on the sorption of Cu, Mn, Cr(III) and Ga (50 μg) is demonstrated in Table IV. The values given are the relative changes in the sorption as compared to solutions from which the macrocomponents are absent. Each of the macrocomponents causes an increase in the sorption of the minority component, this increase being the more pronounced the lower is the degree of sorption in the absence of the matrix. In real natural water samples (except for mineral waters) the concentrations of the interferents are lower by orders of magnitude and so the above effect causing increased sorption will not be apparent. In the sorption with oxine, however, elevated quantities of magnesium (starting from 20 mg l^{-1}) interfere, causing a decrease in the permeability of the column due to the precipitation of the hydroxyquinolinate. These facts are consistent with those reported in refs[3,5].

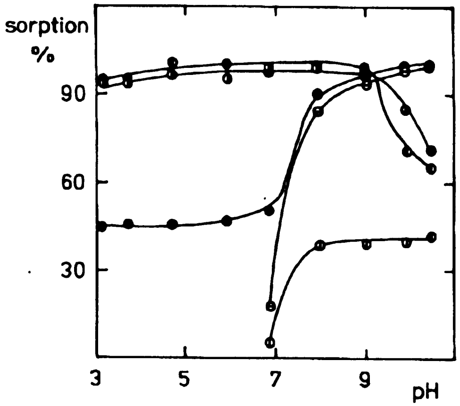

FIG. 1

pH-dependence of the degree of sorption of metal complexes with oxine; metal concentration 1 μg ml^{-1}, 1 ml of 0.5% oxine solution in 50 ml of dilute buffer (0.1 mol l^{-1}), flow rate 1 to 2 ml min^{-1}. ◐ Cu, ◑ Fe, ⊖ Mn, ⦶ Cr(III), ● Ga

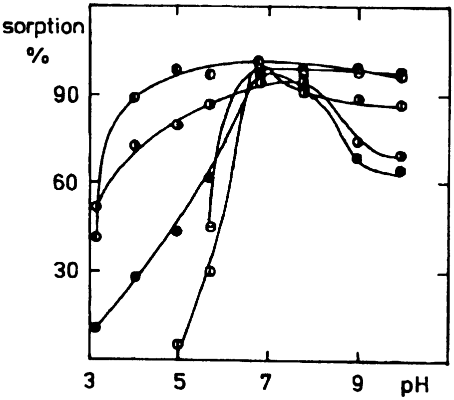

FIG. 2

pH-dependence of the degree of sorption of metal complexes with NaDDC; metal concentration 1 μg ml^{-1}, 1 ml of 0.5% solution of NaDDC in 50 ml of dilute buffer (0.1 mol l^{-1}), flow rate 1 to 2 ml min^{-1}. ◐ Cu, ◑ Fe, ⊖ Mn, ⦶ Cr(III), ● Ga

The effects of sample microcomponents must also be taken into account with respect to the applicability of the method to the analysis of natural water. It is particularly fluoride and phosphate that are present. However, in concentrations of 1 and 10 mg l^{-1}, their effect on the sorption of Cu, Fe, Al, Cr(III), Ga and Mn with NaDDC was not statistically significant.

The two oxidation states of chromium (Cr(III) and Cr(VI)) exhibit different chemical behaviour and, in particular, different toxicity. The sorption of Cr(VI) was found to be mere 40 to 50% as compared to the sorption of Cr(III), for NaDDC as well as for oxine (50 μg Cr). After boiling for 3 min, the sorption of Cr(III) as well as Cr(VI) with NaDDC dropped to below 5% whereas with oxine the sorption of Cr(III) increased to 84% (from the initial 73%) while the sorption of Cr(VI) remained unchanged at 35%.

Since the sorption of Cr(III) and Al(III) with NaDDC is high although these elements do not form stable complexes with NaDDC (Cr(III), only on heating), the possibility of sorption of Al, Cr(III), Ga, Mn and Cu hydrolyzates was investigated. The results are

TABLE IV
Matrix effect on the chelate sorption

Element	ρ, mg l^{-1}	Change in sorption degree[a], rel. %			
		Cu	Mn	Ga	Cr(III)
		Chelates with NaDDC[b]			
Ca	500	+6	+7	+13	+8
	750	+6	+9	+17	+8
	1 000	+15	+20	+26	+40
Mg	250	+1	+1	+5	+5
	500	+1	+5	+2	+9
Na	2 500	0	+6	+3	+2
	5 000	+4	+5	+4	+11
		Chelates with oxine[c]			
Ca	115	+11	0	+2	+102
	230	+22	+4	+3	+102
Mg	120	0	0	0	+106
	240	0	+4	+3	+130
Na	2 500	0	+3	0	+55
	5 000	0	+3	0	+77

[a] 50 μg of analyte, average of 8 determinations; [b] pH 8; [c] pH 10.

given in Table V, indicating that in the case of Al and Cr(III) the sorption rather involves their hydrolyzates and is promoted by the cosorption of other elements.

The sorption efficiency was also compared for Amberlite XAD-2 and XAD-4, which differ in their physical properties such as the specific surface area, degree of crosslinking and pore size. No statistically significant difference in the degree of sorption was observed between the two types in the sorption of Mn, Ga and Cr(III) with NaDDC.

Group Sorption of Al, Au, Cd, Co, Cr, Cu, Fe, Ga, Mn, Mo, Ni, Pb, Pt, Sn, Ti and V

The analytes were quantitated by emission spectrometry with arc excitation. The systems with NaDDC and with oxine were used at pH 8 and pH 10, respectively. The results are given in Table VI. NaDDC appears to be a suitable reagent for Al, Au, Cr, Cu, Fe, Co, Mn, Ni and Pb, whereas oxine is suitable for Al, Au, Cu, Fe, Ga, Mn, Pb and Ti. Out of the two, NaDDC is superior to oxine in the higher degree of sorption for a higher number of elements and also in a better reproducibility of the course of sorption. Oxine is only applicable to samples with low magnesium contents, because the forming magnesium oxinate is insoluble and reduces appreciably the permeability of the column.

For some elements the relative standard deviation of the entire process is lower than that of the arc spectrographic determination alone. This concerns Cd, Ga and Mn when using oxine, and Ga, Mn, Pb, Sn and V when using NaDDC. The improved reproducibility is probably due to a better atomization of the elements from the complexes sorbed on graphite than from graphite itself.

Determination of Minority Elements in Surface Water Samples

The minority elements in surface water were determined by ICP-OES following preconcentration on Amberlite XAD-NaDDC. The standard addition was applied prior to sorption. This technique eliminates the possible effects of the organic components of the matrix, humic acids in particular, on the sorption, as well as the nonquantita-

TABLE V
Degree of sorption (%) of analyte hydrolyzates[a]

pH	Al	Cr	Ga	Mn	Cu
8	92.7	89.2	37.1	75.0	19.9
10	51.4	38.5	39.3	54.1	63.3

[a] 50 μg of analytes in 50 ml of sample, free of reagent.

TABLE VI
Degree of sorption of chelates

Analyte	Degree of sorption, %	RSD[a], %	Degree of sorption, %	RSD[a], %
	NaDDC		Oxine	
Al	91.8	12.3	79.3	9.9
Au	102.8	5.4	86.4	17.1
Cd	26.1	14.4	65.3	9.8
Co	78.9	9.3	67.9	15.5
Cr	88.2	9.2	73.4	13.8
Cu	99.8	8.7	91.5	15.4
Fe	78.8	12.1	94.0	8.9
Ga	64.3	6.3	102.6	6.7
Mn	93.9	5.9	100.7	8.4
Mo	5.5	20.5	12.3	17.4
Ni	95.3	7.0	73.6	10.9
Pb	93.6	6.6	93.6	19.5
Pt	50.9	26.8	50.3	19.9
Sn	55.4	5.4	42.9	8.7
Ti	40.4	21.0	101.6	10.1
V	39.6	7.8	69.9	12.9

[a] Relative standard deviation commonly for sorption and determination; 16 parallel sorptions of 5 μg amounts of metals, criterion: 3s(p).

TABLE VII
Analysis of samples of water I and II[a]

Analyte	Added	Found		Analyte	Added	Found	
		I	II			I	II
Al	–	44.0	51.2	Au	20	26.4	24.2
Cd	20	13.6	14.6	Co	20	20.4	17.8
Cr	20	20.2	19.0	Cu	20	17.8	20.2
Fe	–	251.4	259.6	Sn	20.6	34.2	30.4
Mn	–	81.2	72.0	Ni	20	23.0	22.0
Ti	20	21.6	21.4	Pb	20	8.4	6.8
V	20	28.2	25.6				

[a] Data in μg l^{-1}, quantitation by ICP-OES, sorption of NaDDC complexes; Pt, Mo and Ga were below their detection limits.

tiveness of sorption of some elements. Since the sample did not contain the analytes followed (except for Fe, Al and Mn), these were added in amounts of 10 μg per 500 ml of sample.

Nitric acid was added as a preservative in a quantity of 2 ml per 1 000 ml of sample; prior to the sorption, the acid was neutralized with a solution of NaOH (2 mol l^{-1}) to pH 7 – 9. To 500 ml of sample were added 15 ml of buffer (pH 8) and 10 ml of reagent. A standard addition of 10 μg of the metals was also pipetted to one of the samples. The sample was allowed to pass through the column at a flow rate of 5 – 10 ml min^{-1} and the sorbed substances were eluted with 8 ml of HCl (0.1 mol l^{-1}) in acetone. The contents observed are summarized in Table VII.

The results give evidence that the method is also applicable to concentrations lower than 20 ppb, even if the analyte sorption does not reach 95%. The values found agree with the amounts added for the majority of analytes; the quantitation of Mo is dubious due to the low degree of sorption (below 10%), and for Ga and Pt the content of 20 ppb is below the detection limit. The deviations for Pb and Sn are due to the fact that the quantitation was near the detection limit and the background was rather complex. The determination of Fe, Cu and Al is limited by the blank value.

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