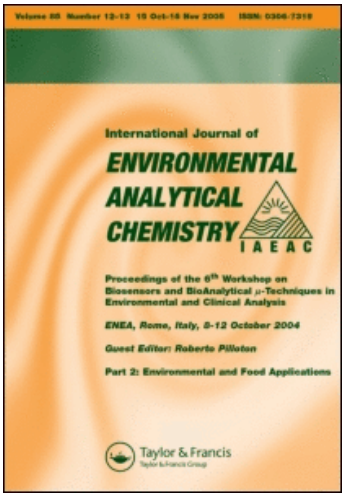

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Speciation of Aluminium in Environmental Water Samples Employing Microcolumn Chelating Ion-Exchange Chromatography - ETAAS

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SPECIATION OF ALUMINIUM IN ENVIRONMENTAL WATER SAMPLES EMPLOYING MICROCOLUMN CHELATING ION-EXCHANGE CHROMATOGRAPHY-ETAAS

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A microcolumn chelating ion-exchange chromatography-electrothermal atomic absorption spectrometry procedure (ETAAS) was developed for aluminium speciation at the nanogram per millilitre level in water samples from the environment. Chelex-100 resin (100-200 mesh, H^+ form) was filled into a micro column and connected to a peristaltic pump. Before analysis, the resin column was equilibrated to the pH of the particular sample analyzed. Sample was then pumped through the column at a flow rate of 0.5 cm^3 min^{-1}. Labile aluminium monomeric species were retained by the resin column and, after elution with 5 cm^3 of HCl (1 mol dm^{-3}), determined by ETAAS. At pH higher than 5.0, prewashing with 0.025 mol dm^{-3} HCl was applied prior to elution with 1 mol dm^{-3} HCl, to remove $Al(OH)_3$ adsorbed on the column resin. The distribution of aluminium species over a pH range from 3.0 to 8.0 in synthetic standard solutions was closely matched by the 8-hydroxyquinoline spectrophotometric method and reported calculated data. Good reproducibility of measurement (± 1.5%) was obtained (10 ng cm^{-3} of Al, pH 4.0). LOD (3σ) for separated aluminium species (50 cm^3 of sample) was found to be 0.3 ng cm^{-3}. The influence of some inorganic and organic complexing ligands as well as the effect of high salinity, nonionic surfactants and an excess of alkaline-earth ions on aluminium speciation was investigated. The technique was successfully employed in determination of aluminium species in various water samples from the environment.

Keywords: Aluminium speciation: micro column chelating ion-exchange chromatography-ETAAS; environmental water samples

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INTRODUCTION

Although aluminium is a very abundant element in the Earth's crust, it is normally very insoluble. Therefore, its concentrations in surface, drinking and ground water are commonly very low. However, the solubility of aluminium is significantly increased as a consequence of acid rain. Of the various inorganic and organic complexes of aluminium as well as its polymeric forms, the most toxic species to living organisms in the aquatic environment[1-4] have been found to be positively charged aquo- [$Al(H_2O)_6^{3+}$] and hydroxy- monomeric aluminium forms [$Al(OH)(H_2O)_5^{2+}$, $Al(OH)_2(H_2O)_4^{+}$]. Helliwell et al.[2] reported that as little as 5 ng cm^{-3} of labile aluminium hydroxy- monomeric forms at pH between 5.8 and 6.2 inhibited algal growth. Growing environmental concern over the presence of increased aluminium concentrations in soil solution and fresh waters resulted in the development of numerous analytical techniques for determination of aluminium species. Among various analytical techniques for speciation of aluminium, the procedures based on rates of reaction with complexing agents such us 8-hydroxyquinoline[5-8] and pyrocatechol violet[9] are frequently used. These procedures enable speciation of total monomeric aluminium. The Driscoll fractionation method[10] is a widespread technique[11,12] for determination of aluminium species. It combines three procedures: addition of a complexing agent followed by rapid extraction into an organic solvent, a cation-exchange column technique followed by analysis of separated aluminium species, and acid digestion, to differentiate between labile monomeric aluminium, non-labile monomeric aluminium and acid-soluble aluminium fractions. Chelating ion-exchange chromatography [13-17] is also a commonly applied technique for speciation of aluminium. Chelex-100 resin is used in Na^+, Ca^{2+} or H^+ forms. Batch[13-15] and column techniques[16,17] enable determination of total monomeric aluminium in the low μg cm^{-3} range. In order to lower the detection limits for determination of aluminium species in water samples, Fairman and Sanz-Medel[18] developed a flow injection fluorimetric detection system incorporated into the Driscoll fractionation method. Quintela et al.[19] reported an automatic flow injection method for aluminium speciation in waters based on a pyrocatechol violet ion-exchange method. Ion chromatography was employed in simultaneous determination of various aluminium forms in aqueous solutions[20] and drinking waters[21]. The technique developed by Jones and Paull[21] enables direct determination of aluminium species over a wide pH range, including the alkaline region. Inorganic monomeric aluminium species were separated from AlF^{2+}, AlF_2^{+} and organically bound aluminium.

Most of the procedures developed for speciation of aluminium in water samples have been used for the acidic pH region. There are some studies devoted to

speciation of aluminium from the acidic to weakly alkaline region in environmental samples e.g. waters[21] and soil extracts[17,22]. Most water samples from the environment (sea water, river water, tap water, percolating water, lake water) are close to neutrality and contain very low aluminium concentrations. There is still a lack of information on reliable analytical procedures for speciation of aluminium in such environmental samples. So, the aim of our work was to investigate the abilities of simple chromatographic procedure, which offers preconcentration and separation of aluminium species in water samples from the environment. For this purpose the parameters which influence aluminium speciation by microcolumn chelating Chelex-100 ion-exchange-ETAAS procedure were carefully investigated in the pH range 3.0 to 8.0 and compared to the commonly used 8-hydroxyquinoline spectrophotometric method[5] and reported calculated data[24].

EXPERIMENTAL

Instrumentation

The laboratory assembled system for the separation of aluminium species consisted of a microcolumn (Perkin Elmer) filled with Chelex-100 chelating resin, connected to a peristaltic pump (Ismatec MS4 Reglo). The aluminium species separated, as well as total aluminium, were determined off-line by electrothermal atomic absorption spectroscopy on an Hitachi Z-8270 Polarized Zeeman Atomic Absorption Spectrophotometer. The alternative sensitive techniques e.g. fluorimetry which allows on-line detection could be also applied, but in our laboratory we didn't have the equipment available. A Varian Cary Model 16 spectrophotometer adjusted to a wavelength of 395 nm was used for the determination of aluminium species separated by the 8-hydroxyquinoline spectrophotometric method[5]. A Norell Unifet Microprocessor pH meter with ISFET sensor was employed to determine the pH of the samples.

Reagents

Merck Suprapur acids and water doubly distilled in quartz were used for the preparation of samples and standard solutions. All other chemicals were of analytical reagent grade.

A standard aluminium stock solution (1000 μg Al cm^{-3} as $Al(NO_3)_3 \cdot 9H_2O$ in 0.5 mol dm^{-3} HNO_3) was obtained from Merck.

Aluminium citrate and oxalate complexes were made by mixing $Al(NO_3)_3 \cdot 9H_2O$ stock solution with an appropriate amount of ligand (3: 1 ligand to aluminium ratio)[23]. Merck aluminium sulphate 18-hydrate ($Al_2(SO_4)_3 \cdot 18H_2O$), aluminium chloride 6-hydrate ($AlCl_3 \cdot 6H_2O$), aluminium phosphate ($AlPO_4$) and aluminium fluoride 3-hydrate ($AlF_3 \cdot 3H_2O$) and Fluka nitrilotriacetic acid ($C_6H_9NO_6$) (NTA) were used in the study of the influence of inorganic and organic ligands on the speciation of aluminium. Merck sodium chloride (NaCl) was used in the study of the effect of salinity on aluminium speciation, and calcium and magnesium nitrate ($Ca(NO_3)_2$ and $Mg(NO_3)_2$ in HNO_3 0.5 mol dm^{-3}) stock standard solutions (1000 μg cm^{-3}) to study the effect of alkaline earth ions. Polyethyleneglycol 1000 ($HO(C_2H_4O)_nH$) (POLY) was used in the study of the influence of nonionic surfactants on aluminium speciation.

Merck potassium hydrogen-phthalate ($C_8H_5KO_4$) (10.2 g dissolved in 1 dm^3 of doubly distilled water) buffer solution with addition of an appropriate amount of Merck nitric acid (HNO_3) or potassium hydroxide (KOH) were used to adjust the pH in the range 3.0-6.5. Merck imidazole ($C_3H_4N_2$) (3.405 g dissolved in 1 dm^3 of doubly distilled water) buffer solution with addition of an appropriate amount of nitric acid was used to adjust pH in the range 6.5-8.0.

Chelating resin, Chelex-100, Na^+ form, 100-200 mesh, was obtained from Bio-Rad, and converted to H^+ form prior to analysis.

Merck butyl acetate ($C_6H_{12}O_2$) and 8-hydroxyquinoline (C_9H_7NO) were used. Sartorius cellulose nitrate membrane filters of 25 mm diameter and 0.45 or 0.1 μm pore size were used in the filtration procedure.

Sample Preparation and Determination of Aluminium and Separated Aluminium Species

To avoid contamination by extraneous aluminium all laboratory ware was of polyethylene. Plastics were treated with 10% HNO_3 for 24 h and rinsed with an adequate amount of doubly distilled water before use. Separation of aluminium species and determination of aluminium were carried out at room temperature under clean-room conditions (class 10 000).

Synthetic standard solutions: For the study of the distribution of aluminium species over a wide pH range the following procedure was applied for preparation of standard solutions. Buffer solution was adjusted to the required pH. 95 $cm^3$of buffer solution was then transferred to a 100 cm^3 polyethylene volumetric flask and an appropriate amount of stock standard solution of aluminium added and the flask filled to the mark with buffer solution. Samples were immediately filtered through 0.45 μm membrane filters, following by filtration through 0.1 μm filters[17]. The speciation of aluminium was investigated in filtered (0.1 μm) standard solutions.

Environmental water samples: Samples were stored in closed polyethylene bottles at 277 K and analyzed within ten hours of sampling. Before analysis samples were filtered through a 0.45 μm membrane filter, followed by further filtration through a 0.1 μm filter. Aliquots of filtered (0.1 μm) samples were used for the determination of total aluminium by ETAAS and various aluminium species employing the microcolumn chelating ion-exchange chromatography-ETAAS and 8-hydroxyquinoline spectrophotometric methods. One aliquot of filtered (0.1 μm) sample was used for determination of pH and the other one for determination of total organic carbon (TOC) by a Dohrmann analyzer (high temperature combustion oxidation method).

Microcolumn Chelating Ion-Exchange Chromatography-ETAAS Procedure

A previously developed system for separation of aluminium species in soil extracts[17] employing column Chelex-100 chelating ion-exchange chromatography-ICP-AES was modified to a microcolumn technique with off-line ETAAS detection to obtain an order of magnitude lower detection limits. Chelex-100 (Na^+ form, 100-200 mesh) was converted to H^+ form (2 mol dm^{-3} HCl). Resin was slurried with water and transferred with a polyethylene pipette to the microcolumn (volume 50 mm^3) which was connected to a peristaltic pump. Before analysis, the resin column was equilibrated with the buffer solution at the pH of the particular sample analyzed (flow rate 1.0 cm^3 min^{-1}). 5-50 cm^3 of sample was then pumped through the column at a flow rate of 0.5 cm^3 min^{-1}. Labile aluminium monomeric species were retained by the resin and were eluted with 5 cm^3 of HCl (1 mol dm^{-3}) into a plastic cup at a flow rate of 1.0 cm^3 min^{-1} (and if necessary diluted) before determination of aluminium by ETAAS. The same procedure was applied to the blank solution. At pH higher than 5.0, application of 10 cm^3 of 0.025 mol dm^{-3} HCl was applied prior to elution with 1 mol dm^{-3} HCl to remove $Al(OH)_3$ adsorbed on to the resin column, and the eluate discarded[17]. It was confirmed that 0.025 mol dm^{-3} HCl dissolved only $Al(OH)_3$ on the basis of excellent agreements with results obtained by spectrophotometry and reported calculated data[17]. The chelating ion-exchange resin column was used for 20 consecutive separations, and after that the column was refilled with fresh resin. The measurement parameters for determination of aluminium by ETAAS at 309.3 nm when injecting 10 mm^3 of sample into a graphite cuvette are presented in Table I. Matrix modifier was not used in ETAAS determinations, since by apllying the selected measurement conditoins (Table I), sensitive and reproducible determinations of aluminium in all particular sample matrices were obtained.

TABLE I Measurement parameters for determination of aluminium by ETAAS

Stage No.	*Stage*	*Temp. (°C) Start*	*Temp. (°C) End*	*Time (s) Ramp*	*Time (s) Hold*	*Gas Flow (cm^3 min^{-1})*
1	Dry	60	90	5	5	200
2	Dry	90	100	10	5	200
3	Dry	100	150	10	0	200
4	Ash	150	1000	10	40	100
5	Atomization	2700	2700	0	4	0
6	Clean	2800	2800	0	4	200
7	Cool	/	/	0	5	200

8-Hydroxyquinoline Spectrophotometric Method

Labile monomeric aluminium species were determined by the procedure of James et al.[5], with the exception that the samples were filtered (0.1 μm). Separations were carried out in sealed glass tubes (100 cm^3). To 40 $cm^3$of sample 5 cm^3 of Na-acetate (1 mol dm^{-3}) and 5 $cm^3$of mixed reagent (20% hydroxylamine hydrochloride + 1% 8-hydroxyquinoline in 2.5% glacial acetic acid, 1:4 ratio; pH 5.0) were added and the sample was shaken for exactly 15 s. After that, 5 cm^3 of butyl acetate were added and the sample was immediately shaken for 15 s. After separation of the aqueous and organic phases, the aluminium species were immediately determined in the organic phase by spectrophotometric detection at 395 nm.

RESULTS AND DISCUSSION

Parameters Influencing Aluminium Speciation

Influence of pH on the Distribution of Aluminium Species

A standard solution of 10 ng Al cm^{-3} ($Al(NO_3)_3 \cdot 9H_2O$) was employed to investigate the distribution of aluminium species in the pH range 3.0-8.0. The filtered sample (0.1 μm) was divided in two aliquots: 50 cm^3 was used for speciation of aluminium by microcolumn chelating ion-exchange-ETAAS and 40 cm^3 for determination of aluminium species by the 8-hydroxyquinoline spectrophotometric method. The results of this study are presented in Table II. From data on the distribution of monomeric aluminium species in aqueous solutions[24], calculated on the basis of thermodynamic equilibrium constants at 25°C and an ionic strength of 0.16, it follows that at pH <3.5 aquo- Al^{3+} is alone present, at pH

TABLE II Influence of pH on speciation of aluminium (10 ng Al cm^{-3}, $Al(NO_3)_3 \cdot 9H_2O$) employing microcolumn chelating ion-exchange chromatography-ETAAS (50 cm^3 of sample) and the 8-hydroxyquinoline spectrophotometric method (40 cm^3 of sample). Results represent the percentage of labile monomeric aluminium species in synthetic filtered (0. 1 μm) samples, n = 3

pH	*Microcolumn chelating ion-exchange chromatography-ETAAS (%)*	*8-hydroxyquinoline spectrophotometric method (%)*
3.0	100	101
4.0	98.7	103
5.0	76.9	81.5
6.0	49.8	46.3
6.5	3.5	<LOD
7.5	<LOD	<LOD
8.0	<LOD	<LOD

3.5-5.0 aquo- Al^{3+}, hydroxy- $Al(OH)^{2+}$ and $Al(OH)_2^+$ are present, while at pH 5.0-6.2 a mixture of aquo- Al^{3+}, hydroxy- $Al(OH)^{2+}$ and $Al(OH)_2^+$, $Al(OH)_3$ and $Al(OH)_4^-$ species coexist. At pH > 6.2 the prevailing aluminium species is $Al(OH)_4^-$. It has been demonstrated in our previous investigations[17,22], by comparing the data of filtered and unfiltered synthetic aqueous solutions of aluminium, that filtration efficiently removed voluminous hydrated species on which $Al(OH)_4^-$ is adsorbed, while the small colloidal molecule $Al(OH)_3$ passed through the filter. In 8-hydroxyquinoline spectrophotometric determinations $Al(OH)_3$ does not influence the determination of positively charged monomeric aluminium species[17]. When chelating ion-exchange chromatography is applied, $Al(OH)_3$ is removed (pH higher than 5.0) by prewashing of resin with 0.25 mol dm^{-3} HCl[17]. So, employing the recommended procedures, the sum of positively charged monomeric aluminium species is determined by both techniques. Data in Table II indicate that at a pH below 5.0 positively charged monomeric aluminium species exist. At pH higher than 5.0 a substantial decrease of labile monomeric aluminium species is observed due to the appearance of $Al(OH)_3$ and $Al(OH)_4^-$. Comparison between the two methods investigated indicates good agreement of data, which are also in correlation with our previous work applying to aluminium in the μg cm^{-3} concentration range[17], and with the reported calculated data on the distribution of monomeric aluminium species in aqueous solutions at various pH[24].

Reproducibility of Measurements and Limits of Detection

The reproducibility of the measurements was tested in six parallel determinations of aquo- Al^{3+} standard solution (10 ng Al cm^{-3}($Al(NO_3)_3 \cdot 9H_2O$) at a pH of 4.0, applying both techniques. The results are presented in Table III. It is evident from

TABLE III Reproducibility of measurements for aluminium speciation at pH 4.0 (10 ng Al cm^{-3}, $Al(NO_3)_3 9H_2O$) by microcolumn chelating ion-exchange chromatography-ETAAS (50 cm^3 of sample) and the 8-hydroxyquinoline spectrophotometric method (40 cm^3 of sample). Results represent the percentage of labile monomeric aluminium species in synthetic filtered (0.1 μm) samples

Method	*Preconcentration factor*	*Labile monomeric aluminium species pH = 4.0 (%)*	*Reproducibility of measurement (%)*
Microcolumn chelating ion-exchange chromatography-ETAAS	10	98.2 98.8 101 ($\bar{x}$ = 100) 102 101 99.3	± 1.5
8-hydroxyquinoline spectrophotometric method	8	97.0 105 101 ($\bar{x}$ = 102) 107 98.4 105	± 4.0

this Table that the reproducibility of these measurements was found to be ± 1.5% applying microcolumn chelating ion-exchange chromatography-ETAAS and ±4.0% by the 8-hydroxyquinoline spectrophotometric method. Both techniques exhibit linearity of measurement up to 500 ng cm^{-3} of aquo- Al^{3+}, while the LOD (35) was found to be 0.3 ng cm^{-3} (50 cm^3 of sample) for microcolumn chelating ion-exchange chromatography-ETAAS and 2.5 ng cm^{-3} (40 cm^3 of sample) for the 8-hydroxyquinoline spectrophotometric method.

Influence of Inorganic and Organic Complexing Ligands, the Effect of High Salinity, Non-Ionic Surfactants and an Excess of Alkaline Earth ions on the Speciation of Aluminium

The influence of inorganic and organic ligands, which may occur in the aquatic environment, as well as the effect of high salinity, non-ionic surfactants and an excess of alkaline earth ions was investigated on the speciation of aluminium. Microcolumn chelating ion-exchange chromatography-ETAAS and the 8-hydroxyquinoline spectrophotometric method were applied. Standard solutions of various aluminium compounds (10 ng Al cm^{-3}) were examined at a pH of 4.0 and 6.5. Samples were filtered through 0.1μm filters before analysis and ana-

lyzed under the recommended procedures. The data from this investigation on the speciation of aluminium as compared to pure aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$ are summarized in Table IV. The data in Table IV indicate that high salinity and an excess of alkaline earth ions cause severe negative interference effects on aluminium speciation by the microcolumn chelating ion-exchange chromatography-ETAAS due to the partial change of the form of the ion-exchange resin (from H^+ to Na^+ or Ca^{2+} and Mg^{2+}). This effect is observed at both pH in the presence of an excess of alkaline earth ions and at pH 4.0 in the presence of an excess of NaCl. At pH of 6.5 an excess of NaCl in the solution of Al-nitrate, exhibits weak influence of chloride ion on aluminium speciation, resulting in slightly higher concentrations of separated aluminium species. In contrast high salinity and an excess of alkaline earth ions do not interfere with aluminium speciation by the 8-hydroxyquinoline spectrophotometric method at either pH studied. Non-ionic surfactants have no influence on the determination of aluminium species by microcolumn chelating ion-exchange chromatography-ETAAS at both pH examined, while in the 8-hydroxyquinoline spectrophotometric method, positive interferences are observed at both pH's, probably due to surface tension effects and the influence of high molecular weight organic polymers. NTA forms strong negatively charged complexes with aluminium at both pH studied. These negatively charged aluminium species are not retained by the chelating resin microcolumn, nor do they react with 8-hydroxyquinoline, as is clearly evident from the data of Table IV.

Al-chloride and Al-sulphate exhibit behaviour similar to Al-nitrate at pH 4.0 with both techniques. At pH of 6.5 little influence of chloride ion is evident by employing the microcolumn chelating ion-exchange chromatography-ETAAS and a greater contribution of positively charged species from Al-sulphate. This is, in the latter case, due to the presence of the positively charged sulphato-aluminium complex[25].

Al-phosphate is less soluble than $Al(OH)_3$, and exists as a non-charged species[24], so it is not retained by the chelating resin microcolumn and does not react with 8-hydroxyquinoline at either pH, as is evident from the data of Table IV.

Al-fluoride exhibits different behaviour for the two techniques. At pH 4.0 about 90% and at pH 6.5 about 40% of aluminium is determined as positively charged species by the microcolumn chelating ion-exchange chromatography-ETAAS. These data are in good agreement with data reported for the distribution of positively charged aluminium fluoro-complexes in aqueous solutions[24], and with the observations of Campbell et al.[13] who at pH 5.0 determined all aluminium complexed to fluoride as positively charged species when employing a batch (60 min) chelating ion-exchange procedure. On applying the

TABLE IV Influence of high salinity, an excess of alkaline earth ions, a non-ionic surfactant and some inorganic and organic ligands on aluminium speciation (10 ng Al cm^{-3}) by microcolumn chelating ion-exchange chromatography-ETAAS (50 cm^3 of sample) and the 8-hydroxyquinoline spectrophotometric method (40 cm^3 of sample) at pH 4.0 and 6.5. Results are given as percentage of labile monomeric aluminium species in synthetic samples, n = 3

Al compound	*Microcolumn chelating ion-exchange chromatography – ETAAS*		*8-hydroxyquinoline spectrophotometric method*	
	pH = 4.0 (%)	*pH = 6.5 (%)*	*pH = 4.0 (%)*	*pH = 6.5 (%)*
Al-nitrate	98.7	3.5	103	<LOD)
Al-nitrate + NaCl (0.5 mol dm^{-3})	40.8	12.4	96.4	<LOD
Al-nitrate + NaCl (1.0 mol dm^{-3})	33.0	11.0	94.0	<LOD
Al-nitrate + Ca (20 mg dm^{-3}) + Mg (2 mg dm^{-3})	17.4	<LOD	103	<LOD)
Al-nitrate + POLY (10 mg dm^{-3})	100	<LOD	124	62.8
Al-nitrate + POLY (100 mg dm^{-3})	96.9	<LOD	152	35.7
Al-nitrate + [NTA]:[Al] = 1:1	6.7	3.4	<LOD	<LOD
Al-nitrate + [NTA]:[Al] = 2:1	4.2	<LOD	<LOD	<LOD)
Al-chloride	93.6	6.7	101	<LOD
Al-sulphate	97.3	51.3	102	41.6
Al-phosphate	<LOD	<LOD	<LOD	<LOD
Al-fluoride	90.7	39,4	<LOD	<LOD
Al-oxalate	47.8	20.6	56.0	55.8
Al-citrate	101	3.8	102	<LOD

8-hydroxyquinoline spectrophotometric method positively charged aluminium fluoro-complexes do not react with 8-hydroxyquinoline at both pH values. These data are in good agreement with the findings of James et al.[5].

Al-oxalate, which at lower pH's exists partially as positively charged complex species and at higher pH predominantly as a negatively charged complex[25], exhibits moderate influence on the determination of positively charged monomeric aluminium by the microcolumn chelating ion-exchange-ETAAS technique at pH 4.0 and 6.5. A slightly greater influence is observed when employing the 8-hydroxyquinoline spectrophotometric method at both pH values, due to the competition of 8-hydroxyquinoline for aluminium bound on organic ligands.

At pH lower than 4.0 Al-citrate exists as positively charged ionic species, at pH 4.0 partially as a neutral complex and at pH's higher than 5.0 in the form of strong negatively charged complexes[24]. Therefore, at pH 6.5 it does not influence the determination of positively charged monomeric species by either technique. At a pH of 4.0 it is determined as a positively charged monomeric

aluminium species by both techniques. When the microcolumn chelating ion-exchange-ETAAS procedure is applied, partial adsorption of neutral Al-citrate species on the resin column contributes to amount of positively charged aluminium species retained, and when the 8-hydroxyquinoline spectrophotometric method is used the competition of 8-hydroxyquinoline for aluminium bound to organic ligands resulted in 100% recovery of aluminium species at pH 4.0.

Analysis of Environmental Water Samples

In order to evaluate the ability of the two methods for the speciation of aluminium in water samples, various water samples from the environment were selected and analyzed for total aluminium and its species. Total aluminium was determined by ETAAS, while separated aluminium species were analyzed by both the microcolumn chelating ion-exchange-ETAAS and the 8-hydroxyquinoline spectrophotometric methods. Samples were filtered (0.1 μm) and pH and total organic carbon (TOC) determined. Aliquots of filtered samples (5-50 cm^3) were used for speciation of aluminium by both techniques. The results of these measurements are summarized in Table V. It is evident that the concentration of total aluminium in different samples varies from the low ng cm^{-3} up to the μg cm^{-3} range. The 8-hydroxyquinoline spectrophotometric method is not sensitive enough for speciation of aluminium in most of the samples analyzed. The LOD in water samples from the environment was found to be 5.0 ng cm^{-3}, while for microcolumn chelating ion-exchange chromatogaphy-ETAAS it was found to be 0.3 ng cm^{-3}. Data from Table V indicate that when the content of TOC is low, there is agreement between the two techniques for speciation of aluminium in percolating water samples (sample No.1). When percolating water samples contain a higher amount of TOC (samples No. 5 and 6) much higher results for labile monomeric aluminium species are obtained by the 8-hydroxyquinoline spectrophotometric method. The difference between two speciation techniques, which is evident particularly in percolating water No. 6, represents aluminium bound to organic matter (humic and fulvic acids). 8-hydroxyquinoline competes more strongly for aluminium than do organic ligands, so the most of aluminium bound to organic molecules is determined by spectrophotometric technique. On the contrary fulvic and humic acids strongly inhibit adsorption of aluminium on the chelating resin Chelex-100[13], so the results obtained by microcolumn chelating ion-exchange-ETAAS are much lower than those by 8-hydroxyquinoline spectrophotometric method. Percolating water No.3 corresponds to a sand soil with a high content of fluoride (540 μg g^{-1}). On the basis of our study on the influence of fluoride on determination of alumnium species (Table IV) it is evident that spectrophotometry excludes determination of alumnium fluoride complexes,

TABLE V Determination of aluminium species in filtered (0.1 μm) environmental water samples by microcolumn chelating ion-exchange chromatography-ETAAS and the 8-hydroxyquinoline spectrophotometric method, n = 3

Sample	*pH of sample*	*TOC (mg cm^{-3})*	*Concentration of total aluminium (ng cm^{-3})*	*Microcolumn chelating ion-exchange chromatography–ETAAS* (ng cm^{-3})*	*8-hydroxyquinoline spectrophotometric method** (ng cm^{-3})*
Percolating water 1 (acid clay soil)	4.2	9.5 ± 0.1	355 ± 5	288 ± 13	329 ± 3
Percolating water 2 (clay soil)	7.0	23.9 ± 0.2	8.07 ± 0,13	0.38 ± 0.03	<5.0
Percolating water 3 (sand soil)	6.5	16.3 ± 0.1	160 ± 3	50.9 ± 2.1	<5.0
Percolating water 4 (sand soil)	7.8	25.5 ± 0.2	9.04 ± 0.18	0.59 ± 0.09	<5.0
Percolating water 5 (peat soil)	4.0	36.6 ± 0.3	223 ± 2	41.5 ± 4.1	149 ± 19
Percolating water 6 (acid forest soil)	5.0	2454 ± 1	3350 ± 19	42.1 + 3.1	2307 ± 16
Tap water 1	8.1	2.4 ± 0.1	13.2 ± 0.8	0.98 ± 0.17	<5.0
Tap water 2	7.7	2.0 ± 0.1	88.5 ± 0.4	2.94 ± 0.26	9,15 ± 0.47
Sea water	8.0	2.3 ± 0.1	44.4 ± 0.5	<0.3	<5.0
Stream water (Besnica)	6.0	4.1 ± 0,1	1.94 ± 0.12	<0.3	<5.0

*sample volume 5-50 cm^3
**sample volume 5-40 cm^3

while these species are determined by microcolumn chelating ion-exchange chtomatography. For this reason aluminium species which were determined by the 8-hydroxyquinoline spectrophotometric method were below the LOD, and those which were determined by microcolumn chelating ion-exchange-ETAAS represent aluminium bound to fluoride. Speciation of aluminium in tap water No.2 gave lower results by microcolumn chelating ion-exchange-ETAAS than by the 8-hydroxyquinoline spectrophotometric method. Since this tap water has a high content of calcium and magnesium, these observations agree with the study on the interference effects of high concentrations of calcium and magnesium (see Table IV). Concentrations of labile monomeric aluminium species in sea and stream water were found to be below the LOD for both speciation techniques.

CONCLUSIONS

A procedure has been developed for speciation of alumnium in environmental water samples of various pH, employing microcolumn chelating ion-exchange chromatography-ETAAS. In comparison to a previously developed column technique[17] this procedure gave an order of magnitude lower detection limit for separated aluminium species (0.3 ng cm^{-3}). Chelex 100 resin in H^+ form was preconditioned with a buffer solution to the pH of the sample. In synthetic aqueous solutions, aquo- and positively charged monomeric hydroxy-aluminium species were retained by the resin column and eluted with 1 mol dm^{-3} HCl. Separated aluminium species in the eluate were determined by ETAAS.

A comparative study was made by employing the conventionally used 8-hydroxyquinoline spectrophotometric method. Good agreement between the two techniques and with reported calculated data was obtained for speciation of aluminium in synthetic aqueous solutions in the pH range 3.0-8.0.

On the basis of a study of the influence of some inorganic and organic complexing ligands, high salinity, the effect of an excess of alkaline earth ions and non-ionic surfactants on the speciation of aluminium, it was found that employing microcolumn chelating ion-exchange chromatography-ETAAS positively charged monomeric aquo- and hydroxy-aluminium species plus sulphato- and fluoro-aluminium complexes were determined. Applying the 8-hydroxyquinoline spectrophotometric method, positively charged monomeric aquo- and hydroxy-aluminium species plus sulphato- and most of labile organic aluminium species were determined. High salinity and an excess of alkaline earth ions cause severe negative interference effects on aluminium speciation by the microcolumn chelating ion-exchange chromatography-ETAAS method, but do not interfere with aluminium speciation by the 8-hydroxyquinoline spectrophotometric method. On the other hand, non-ionic surfactants have no influence on determination of aluminium species by the microcolumn chelating ion-exchange chromatography-ETAAS, but cause positive interference effects when the 8-hydroxyquinoline spectrophotometric method is employed.

Both techniques were employed in the speciation of aluminium in percolating waters, tap waters, sea and stream waters of various total aluminium content and pH. The 8-hydroxyquinoline spectrophotometric method was not sensitive enough for most of the samples analyzed, while the microcolumn chelating ion-exchange chromatography-ETAAS was adequate for almost all samples examined. Data on analysis of water samples from the environment agreed with the findings of the study on the influence of inorganic and organic complexing ligands, high salinity, the effect of an excess of alkaline earth ions and non-ionic surfactants on the speciation of aluminium.

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