Utilization of Chelating Ion Exchange for Aluminium Speciation*

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The utilization of chelating ion exchange by the method based on binding strength and kinetic discrimination was studied for aluminium speciation in natural waters. Two chelating ion exchangers Iontosorb Oxin and Iontosorb Salicyl, cellulose resins containing covalently bound 8-hydroxyquinoline and salicylic acid functional groups, were used for the determination of reactive aluminium by batch technique. For detection of aluminium species flame atomic absorption spectrometry was used.

The toxicity of aluminium [1] is strongly dependent on its distribution among various forms or species coexisting in their environment. The published studies [2] indicate that the species primarily responsible for the toxicity of aluminium include the cationic monomeric forms (Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$). Generally, these fractions defined operationally according to the method of speciation are termed reactive or labile aluminium [2] and their ratio increases with decreasing pH value of the environment.

In the present work the sorption properties of chelating resins Iontosorb Oxin and Iontosorb Salicyl in the pH range 2.5—6.0 are examined in the synthetic solutions containing aluminium as Al nitrate and acetate buffer. The distribution of monomeric aluminium at pH 4.0 is investigated in the synthetic solutions containing some inorganic and organic ligands. The effect of potential interfering ions on the sorption of aluminium at pH 4.0 is also studied.

EXPERIMENTAL

Iontosorb Oxin (IO) and Iontosorb Salicyl (IS) (Iontosorb, Ústí nad Labem, Czech Republic), cellulose resins containing covalently bound 8-hydroxyquinoline and salicylic acid functional groups with the capacity 0.2 mmol and 0.5 mmol of active groups per 1 g of dry resin (IO and IS, respectively) and the water content 84 %, were used.

The contents of Al were determined by flame atomic absorption spectrometry (FAAS) using the Perkin—Elmer Model 5000 atomic absorption spectrometer (a wavelength of 309.3 nm, nitrous oxide—acetylene flame). The other elements were detected by FAAS using the Perkin—Elmer Model 1100 at
absorption spectrometer.

Reactive Al in the filtered samples was determ
after its sorption on the resin by the batch techn
in polyethylene bottles. Portion of the filtrate
stirred with a magnetic stirrer at room tempera
in the presence of the resin (10 g of damp resin
50 cm^3 of solution). At appropriate intervals sti
was stopped momentarily and an aliquot (8 cm
the supernatant after centrifugation was remove
analyzed for Al. The concentration of reactive A
measured as difference between concentration of
the solution before and after sorption [3].

Sampling of acid surface waters was perform
the area of Šobov (near Banská Štiavnica in the
tral Slovakia) where ecological crash is observed
acidification of environment comes from the sulfi
idation in the quartzite mine dump). Further inf
tion about the area has been summarized by *Šu*
al. [4]. Four samples were collected with differen
tance from the mine dump, 200 m above (the s
5) this waste deposit and 10 m, 140 m, 400
low (the samples *8*, *21*, *24*), respectively. The sa
were stored in closed polyethylene bottles and fi
before analysis under low vacuum in a polysulfo
tration apparatus with a cellulose nitrate mem
filter of nominal pore size 0.4 μm.

RESULTS AND DISCUSSION

The effect of pH on the sorption of Al was
ined in the synthetic solutions containing 0.5
as aluminium nitrate and 10 cm^3 of 0.1 mol dm
etate buffer. Aluminium in this form reacts wit

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Table 1. Composition of Water Samples

Sample	$\rho_i/(\text{mg dm}^{-3})$						
	Na	Ca	Mg	Fe	Mn	Zn	Cu
5	11.06	59.2	16.4	7.88	4.32	0.992	0.179
8	5.19	284.0	260.0	1428	34.16	4.12	3.04
21	12.78	187.8	92.6	32.87	20.82	1.78	0.570
24	15.34	189.2	68.8	6.11	22.31	2.80	0.370

resins quickly for 1 min at pH 4.0—6.0. Under pH 3.0 the capture of Al on both resins is very slow and insufficient; only 60 % of Al is captured for 10 min at pH 2.5. It appears that Iontosorb Salicyl has better exchange kinetics than Iontosorb Oxin.

The influence of some inorganic and organic ligands frequently occurring in the terrestrial and aquatic environment on the sorption of Al at pH 4.0 was investigated. Aluminium nitrate and aluminium sulfate exhibit a similar behaviour for both resins. Both the aluminium forms are exchanged readily (almost 100 % exchange after 1 min) and they belong to the mostly reactive and toxic species of Al. In both the cases this is due to the presence of cationic monomeric hydroxoaluminium complexes, and in the latter case it is also due to the formation of the positively charged aluminium sulfato complex [5]. Aluminium fluoride ([Al]:[F] = 1:2), mainly cationic mono and difluoro complexes, is captured by both resins in less extent than the previous species (above 70 % exchange after 1 min). They prove to be nontoxic [1]. Tartaric acid ([Al]:[TartAcid] = 1:3) exhibits moderate influence on the determination of the reactive Al (almost 50 % exchange after 1 min for both resins). At pH lower than 4.0 aluminium citrate exists as positively charged ionic species, at pH 4.0 partially as a neutral complex [5]. After 1 min only 40 % and 50 % of complex ([Al]:[CitrAcid] = 1:3) was retained on resins. At lower pH aluminium oxalate occurs partially as the positively charged complex [5] and this one ([Al]:[OxalAcid] = 1:3) exhibits slightly greater influence on the sorption of reactive Al (above 30 % exchange after 1 min). Nitrilotriacetic acid and ethylenediaminetetraacetic acid ([Al]:[NTA], [EDTA] = 1:3), which represent very strong complex ligands, form the negatively charged complexes with Al (about 10—15 % exchange for both resins). Fulvic acid forms with Al kinetically inert complexes. This one strongly inhibits sorption of Al (about 10 % exchange for both resins). From these facts it is evident that organic matter complexes the reactive Al and decreases its toxicity.

The effect of major (Na, Ca, Mg, Fe, Mn) and minor (Zn, Cu) elements and acetate buffer on the sorption of reactive Al at pH 4.0 was studied. The concentrations of potential interfering ions were chosen with regard to their expected contents in real samples.

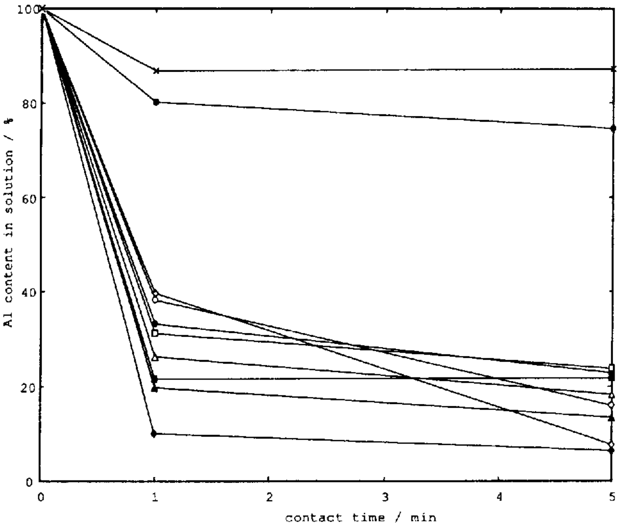

Fig. 1. Exchange of Al in water samples. IS: ■ *5*, ♦ *8*, ● *21*, ▲ *24*, ⊗ *24* + FA; IO: □ *5*, ◇ *8*, ○ *21*, △ *24*, × *24* + FA.

Only iron and manganese at concentrations 10—50 mg dm^{-3} for both resins affect negatively the exchange of Al (drop in recovery of Al exchange about 15—30 % and 15—20 % for IS and IO, respectively). Neither other elements nor acetate buffer affect the recovery of reactive Al. The contents of major components in samples are listed in Table 1. It is evident that only the content of iron in original sample *8* is much higher than the concentration in the interference study. But all the samples except *5* were diluted and the content of reactive Al in sample *8* is the highest (about 90 % of total Al content). From this it results that iron does not interfere or interferes only in the small extent.

From the above-mentioned details and Fig. 1 it is obvious that 1 min time for sorption of reactive Al in the water samples was chosen. All the diluted samples exhibit similar behaviour for both resins except the difference between sorption curves for sample *8* (about 60 % exchange for IO *vs.* about 90 % for IS). It is affected by better exchange kinetics of IS at pH 3.0. The reactive Al was determined as the average from two values of exchange recoveries for IO and IS (except the one value of exchange recovery for IS and sample *8*) in the intervals 60—80 % and 70—90 % for IO

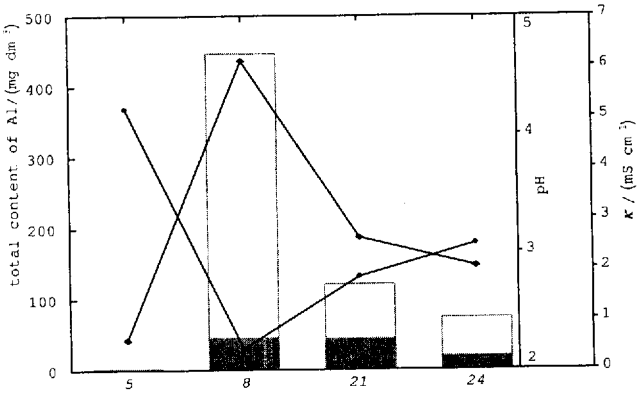

Fig. 2. Distribution of total Al in water samples. ☐ Reactive Al, ▨ nonreactive Al, ■ Al retained on filter, ◆ κ, ● pH.

and IS, respectively. In the presence of added fulvic acid the rate of Al exchange was reduced (sample *24*). The dilution of samples can change the distribution of aluminium species, this fact will be counted on in the another research.

The determined content of reactive Al in water samples ranges from 1.16 to 401.3 mg dm^{-3} (Fig. 2). The content of Al retained on filter is negligible or equal to zero. From this it follows that no organic compounds (humic and fulvic acid) [6] and polymeric inorganic Al species with high molecular mass were present in the samples.

CONCLUSION

The proposed method for speciation of aluminiu in the water samples with the utilization of chelati ion exchange is relatively simple without the need high-cost instrumentation, and some procedures c be performed in the field (instead of polyethylene b tle the plastic syringe with filter unit can be use The determined ratio of reactive Al in the water sa ples was relatively high – from 64.2 % (sample 2 to 89.9 % (sample *8*) of total Al content. It is caus by extremely low original pH of water samples, hi original κ (conductivity), and the absence of orga matter in water samples.

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