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Determination of aluminium and its fluoro complexes in natural waters by ion chromatography

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ABSTRACT

Ion chromatography was applied to the determination of aluminium and its fluoro complexes in natural waters. The separation was carried out on a cation-exchange column. The aluminium species were detected by postcolumn reaction with Tiron followed by UV spectrophotometry. The method requires the adjustment of the pH and ionic strength of the sample to those of the mobile phase immediately prior to injection. Al^{3+}, AlF^{2+} and AlF_2^+ are eluted separately while all hydroxo complexes are readily dissociated and eluted along with Al^{3+} under these conditions. The sum of peak areas, which represents the total aluminium concentration, was conserved whatever the amount of fluoride in the sample. Linearity of calibration was observed over the range 20–2000 $\mu g\ l^{-1}$. Further, the speciation of fluoro–aluminium complexes as determined experimentally by ion chromatography is in good agreement with calculations based on complexation constants. The applications and limitations of the method are discussed.

INTRODUCTION

In its unique oxidized state, Al(III) is hydrolysed in aqueous media and forms hydroxo complexes. This phenomenon sometimes leads to dramatic decreases in pH and is therefore often involved in ecological concerns about acidic soils and hydrological systems. Recent studies have established the toxicity of aluminium to both fish [1–3] and plants [4]. However, this toxicity seems to be highly dependent on the chemical form of aluminium, the most dangerous form being assigned to the free cation, whereas fluoro and organic complexes tend to display only slight toxicity. It has been shown, for instance, that fish reproduction rates are enhanced in slightly acidic lake waters when complexing ligands (such as citrate or fluoride) are added [2]. To confirm such properties, a knowledge of total or free aluminium concentrations (as given by spectrofluorimetry [5–7] or ion-selective electrodes [8]) is no longer sufficient for an accurate description of the medium. Analytical methods that can account for the chemical speciation of this element are therefore necessary.

A controversial estimate of the distribution of inorganic, organic and polymeric species of aluminium in partially neutralized media is given by spectrophotometric methods that use the specific kinetic behaviour of each form [9–11]. In waters that contain little organic matter, OH^- and F^- are likely to form the major aluminium complexes. Some papers [12–18] have described the use of ion chromatography for the direct determination of Al(III) and the speciation of fluoride and organic complexes of aluminium in soils and aqueous solutions. The separation is based on slow kinetics of the decomplexation of the aluminium species. Most methods require a cation-

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exchange column to separate the different species and postcolumn reaction for their detection. This paper describes a chromatographic method for the determination of AlF_2^+, AlF^{2+} and Al^{3+} in natural waters.

EXPERIMENTAL

Reagents

All reagents were of analytical-reagent grade. Ammonium chloride, ammonium acetate and hydrochloric acid were purchased from Merck and Tiron (disodium 1,2-dihydroxybenzene-3, 5-disulphonate) from Sigma.

Aluminium and fluoride standard solutions were prepared by dissolving $AlCl_3$ (Merck) and NaF (Merck) in dilute HCl adjusted to the desired pH.

The water used throughout was deionized with a Milli-Q system (Millipore) and all solutions were filtered through 0.45-μm filters (Millipore) and degassed.

Apparatus and chromatographic conditions

A Model 2000i ion chromatograph (Dionex), featuring a DQP-1 pump and a 50-μl loop injector was equipped with a reagent delivery module (RDM) (Waters) and an Opti-Ion UV–Vis detector set at 310 nm (Dionex). The separation was performed with a CS2 cation-exchange column (Dionex) protected by a CG2 guard column (Dionex).

The mobile phase consisted of 0.5 *M* NH_4Cl–0.01 *M* HCl unless stated otherwise, at a flow-rate of 1.1 ml min^{-1}. The postcolumn reagent, $3 \cdot 10^{-4}$ *M* Tiron in 3 *M* ammonium acetate, was introduced into the eluent stream via a T-piece located at the outlet of the column, at a rate of 0.75 ml min^{-1}. The final pH of the effluent was 6.70.

RESULTS AND DISCUSSION

The separation of the different fluoro–aluminium complexes was carried out on the cation-exchange column. Each eluted complex was detected via addition of a postcolumn reagent, Tiron, chosen for its ability to give stable complexes that can further be quantified spectrophotometrically.

Postcolumn reaction for spectrophotometric detection

The addition of a reagent to the eluent stream to complex the solute for on-line detection of the final product by UV spectrophotometry is a method that requires the following: (i) complete dissociation of the eluted complexes (*i.e.*, AlF_n^{3-n}) and quantitative complexation of Al^{3+} by Tiron; this condition is of major importance for quantitative speciation of a component; (ii) rapid kinetics to allow complete dissociation and recomplexation of the aluminium species within the connection between the RDM and the detector (a few seconds); and (iii) limited absorptivity of Tiron at 310 nm, which is the wavelength of maximum absorption of the Al–Tiron complex, to avoid baseline disturbances created by the injection.

The absorbance of a solution of $1 \cdot 10^{-4}$ *M* Tiron is plotted in Fig. 1. The titration curve of a solution ten times this concentration is also

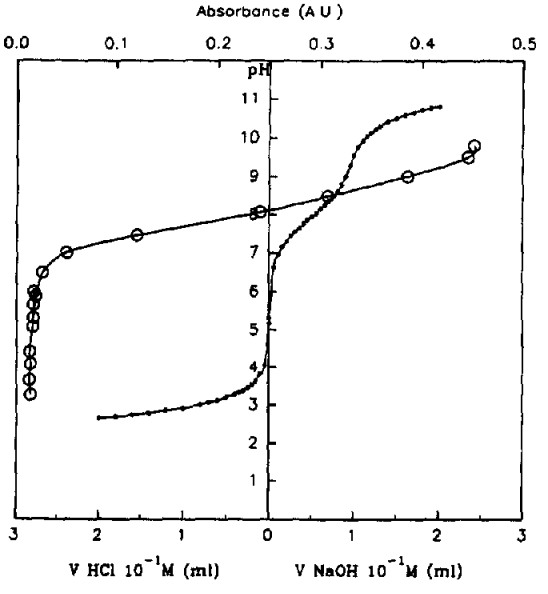

Fig. 1. Acid–base and spectrophotometric characteristics of Tiron. ● = Titration of $1 \cdot 10^{-3}$ *M* Tiron: pH *vs.* volume of reagent. ○ = pH *vs.* absorbance (310 nm) of $1 \cdot 10^{-4}$ *M* Tiron.

displayed for comparison ($pK_{a1} = 7.65$ and $pK_{a2} = 12.5$). Fig. 1 shows important alterations of the absorbance in the pH range 7.0–9.5. This range must be avoided to achieve both a steady baseline and a high signal-to-noise ratio. The best conditions are at pH 4–7, where the absorbance is low and independent of pH. The absorbance of the Al–Tiron complex is dependent on the pH: the more alkaline the medium, the higher is the absorbance of the complex. However, the signal-to-reference ratio is optimum around pH 6.7, which was chosen as a good compromise between no baseline offset but too low a signal and good sensitivity but too high a residual level. The molar absorptivity coefficients of Tiron and the Al–Tiron complex under such conditions were found to be 2000 and 18 000 l mol^{-1} cm^{-1}, respectively. The optimum pH value is in the range determined by Dean [17].

Chromatographic conditions

Although the postcolumn reaction conditions have previously been optimized to avoid perturbations of the baseline during the injection, a system peak occurs at the void volume when the injection solvent is water and interacts with the first-eluted peak. Changing the elution strength of the mobile phase had no perceptible effect on the capacity factor of this first peak as it is quasi-unretained on the CS2 column, whatever the conditions (see Fig. 2). The system peak disappears if the sample composition and pH are adjusted to those of the mobile phase. However, care should be taken to operate immediately prior to injections so that the equilibria be altered as little as possible, taking advantage of the slow kinetics of re-equilibration.

Fig. 3 shows some chromatograms of a solution containing $3.7 \cdot 10^{-5}$ *M* total aluminium and various amounts of fluoride in water. The relative evolution of the three peaks shows the following features. Fig. 3a displays a single peak that corresponds to Al^{3+} under the conditions of the injection; however, injections of alkaline samples containing aluminium in various $Al(OH)_m^{3-m}$ forms led to the same chromatogram, which suggests that $Al(OH)_m^{3-m}$ species are dissociated and eluted as Al^{3+}. Considering

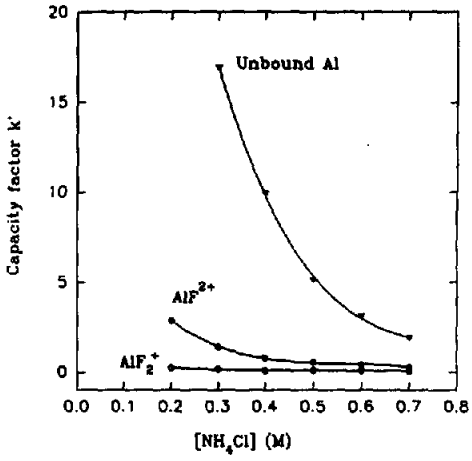

Fig. 2. Influence of the eluent strength of the mobile phase on the capacity factors (k') of the different fluoro–aluminium complexes. $[Al]_{Tot} = 3.7 \cdot 10^{-5}$ *M* and $[F]_{Tot} = 5.3 \cdot 10^{-5}$ *M*. Columns, CG2 + CS2; mobile phase, NH_4Cl–0.01 *M* HCl (flow-rate, 1.1 ml min^{-1}); postcolumn reagent, $3 \cdot 10^{-4}$ *M* Tiron in 3 *M* $CH_3CO_2NH_4$ (flow-rate, 0.75 ml min^{-1}); injection loop, 50 μl; detection wavelength, 310 nm.

the lability of hydroxo complexes, it is likely that they are decomplexed during pH adjustment of the sample. This phenomenon has been observed previously [15,16,19]. Peaks 1 and 2 were assigned to AlF_2^+ and AlF^{2+}, respectively, based

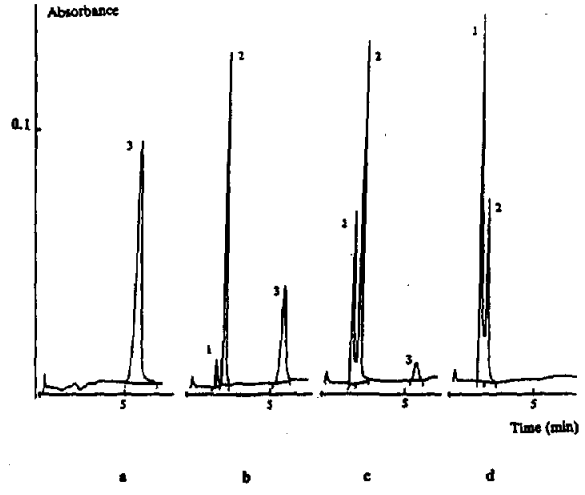

Fig. 3. Evolution of the distribution of fluoro–aluminium complexes as a function of total fluoride concentration. Chromatograms of standards containing $[Al]_{Tot} = 3.7 \cdot 10^{-5}$ *M* and (a) no fluoride, (b) $[F]_{Tot} = 2.6 \cdot 10^{-5}$ *M*, (c) $[F]_{Tot} = 5.3 \cdot 10^{-5}$ *M* and (d) $[F]_{Tot} = 10.5 \cdot 10^{-5}$ *M*. Mobile phase, 0.5 *M* NH_4Cl–0.01 *M* HCl; other conditions as in Fig. 2.

on their relative evolution in Fig. 3b, c and d and their charge. The calculations corresponding to the sample injected in Fig. 3d gave a share of 19% to the neutral species AlF_3. No peak can be observed for this species whereas peak 1 is increased by the corresponding amount to what is expected from the AlF_2^+ concentration; in this instance, the first peak accounts for both AlF_2^+ and AlF_3.

The quantitativity of the postcolumn reaction was also demonstrated: the sum of the areas of the three peaks representing the aluminium species is conserved whatever the amount of fluoride in the sample. This suggests that sufficiently rapid kinetics of AlF_n^{3-n} dissociation and Al–Tiron complex formation occur as these species successively react with Tiron before reaching the detector cell.

The influence of the concentration of NH_4Cl in the mobile phase on the capacity factors (Fig. 2), selectivity and resolution between the peaks of AlF_2^+ and AlF^{2+} was investigated. As expected, the higher the ionic strength, the lower were the capacity factors and the selectivity. The resolution presents a maximum value for NH_4Cl concentrations between 0.4 and 0.5 *M*. The latter was adopted throughout the study.

Calibration and performance

Linearity of the calibration for total aluminium was investigated over the range 20–2000 $\mu g\ l^{-1}$ ($7.4 \cdot 10^{-7}$–$7.4 \cdot 10^{-5}$ *M*). The calibration graph is shown in Fig. 4. For each aluminium concentration, distinction is made between standards containing only aluminium in water (injected in duplicate, open circles) and standards containing fluoride at various concentrations (namely, in mol l^{-1}, $[F]_{Tot} = 0.71[Al]_{Tot}$, $[F]_{Tot} = 1.42[Al]_{Tot}$ and $[F]_{Tot} = 2.84[Al]_{Tot}$) (closed circles). No statistical difference was observed between the

TABLE I

COMPARISON BETWEEN THE DISTRIBUTION OF THE FLUORO-ALUMINIUM COMPLEXES DETERMINED EXPERIMENTALLY BY ION CHROMATOGRAPHY AND CALCULATED BY MINEQL: INFLUENCE OF THE TOTAL ALUMINIUM CONCENTRATION OF THE SAMPLE

The standards were diluted in water; their final pH was between 4.5 and 5.1.

Sample		Al^{3+} (%)		AlF^{2+} (%)		AlF_2^+ (%)	
[F]/[Al]	$[Al]_{tot}$ (μM)	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.71	1.9	48.1	48.4	51.9	46.8	–	4.9
	3.7	34.0	42.8	59.0	51.4	7.0	5.8
	7.4	38.0	40.3	56.4	52.9	5.6	6.8
	18.5	35.3	38.0	59.5	54.5	5.2	7.4
	37.1	39.1	36.9	56.3	55.9	4.6	7.1
	74.1	33.5	36.9	61.3	55.7	5.2	7.4
1.42	1.9	16.5	19.8	67.0	61.1	16.5	19.0
	3.7	12.9	14.8	68.7	59.7	18.4	25.8
	7.4	12.4	10.2	68.3	57.5	19.3	31.8
	18.5	8.0	7.3	72.8	53.8	19.2	38.2
	37.1	7.1	7.3	61.7	50.0	31.2	41.9
	74.1	6.2	5.5	62.7	51.2	31.1	42.4
2.84	1.9	–	8.2	71.0	46.4	29.0	48.6
	3.7	5.3	1.5	52.6	34.5	42.1	63.1
	7.4	–	–	64.4	23.1	35.6	75.9
	18.5	–	–	40.6	12.1	59.4	87.3
	37.1	–	–	35.8	7.1	64.2	92.4
	74.1	–	–	32.7	4.1	67.3	94.9

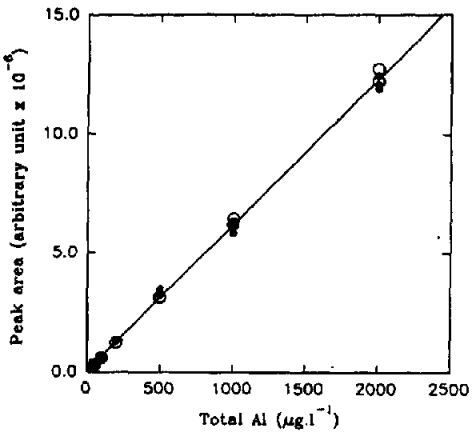

Fig. 4. Calibration graph and linear fit for total aluminium concentration in the range 20–2000 $\mu g\ l^{-1}$ ($7.4 \cdot 10^{-7}$–$7.4 \cdot 10^{-5}$ M). Conditions as in Fig. 3. ○ = $[F^-] = 0$; ● = $[F^-] \neq 0$.

two sets of data after linear regression. The final fit taking all the values into account yields $A = (6137 \pm 17)[Al] + (44\,860 \pm 15\,700)$.

The repeatability was tested by injecting the same standard containing $3.7 \cdot 10^{-5}$ M (1000 $\mu g\ l^{-1}$) aluminium seven times; the relative standard deviation was 5.3%.

The detection limit, determined as twice the average amplitude of the short-term noise, was 20 $\mu g\ l^{-1}$ for Al^{3+} and 9 $\mu g\ l^{-1}$ for both AlF^{2+} and AlF_2^+.

No interference was detected from Fe(III) at concentrations up to 10 mg l^{-1} but nitric acid induced baseline disturbances at the void volume.

Speciation

The influence of the composition of the samples ($[Al]_{Tot}$, $[F]_{Tot}$ and the sample matrix) was investigated in order to establish the feasibility and limitations of this method for accurate speciation determinations. Does the chromatographic process alter the relative concentrations of the aluminium species in the sample? In other words, is the chromatogram representative of the sample?

MINEQL software [20] was utilized in all theoretical calculations of solution equilibria. Thermodynamic constants were taken from ref. 21. Mixtures of aluminium and fluoride at different aluminium concentrations and [F]/[Al] ratios were prepared and analysed. Table I gives the result of speciation analysis; the experimental contribution of each species is deduced from the corresponding peak area and compared with the calculated value. Calculated values for Al^{3+} include labile hydroxo complexes which are dissociated into Al^{3+} prior to the chromatographic process.

Table I shows that the difference between the calculated and experimental values is not a function of total aluminium concentration but rather of that of total fluoride. The chromato-

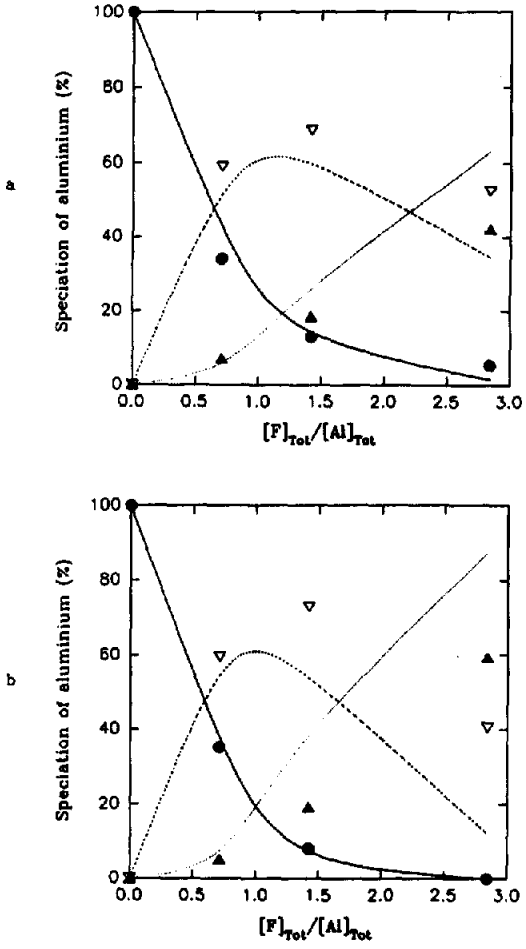

Fig. 5. Distribution of the fluoro–aluminium complexes in water as a function of the relative fluoride concentration. (a) $[Al]_{Tot} = 3.7 \cdot 10^{-6}$ M; (b) $[Al]_{Tot} = 18.5 \cdot 10^{-6}$ M. Conditions as in Fig. 3. Calculated: solid line = unbound Al; dashed line = AlF^{2+}; dotted line = AlF_2^+. Experimental: ● = unbound Al; ▽ = AlF^{2+}; ▲ = AlF_2^+.

graphic results for samples that contain little relative fluoride are in good agreement with the calculated values; at the highest fluoride concentrations, experimental speciation is no longer representative of the composition of the sample.

Further, peak 3 representing unbound aluminium seems to be less affected by the chromatographic conditions than peaks 1 and 2. Fig. 5 shows the experimental underestimation of AlF_2^+ simultaneously with the overestimation of AlF^{2+} and the correct estimation of unbound aluminium. This phenomenon is increased at high total fluoride concentrations and suggests a shift in the equilibrium $AlF_2^+ \rightleftharpoons AlF^{2+} + F^-$ in favour of AlF^{2+} during the chromatographic process: fluoride is not retained on the column and is eluted at the void volume whereas all cationic species are retained on the top of the column. This sudden lack of fluoride drives the complexes to react in order to provide for free fluoride. Further evidence for this exchange of fluoride between AlF_2^+ and AlF^{2+} is given by the shape of the chromatogram, where peaks 1 and 2 are separated by a plateau instead of displaying baseline resolution.

Table II shows the influence of the pH and the ionic strength of the sample on the accuracy of the speciation as determined by chromatography. Standards were prepared in dilute HCl or NaOH solution. Good agreement is obtained for acidic samples (pH ≈ 2), whatever the total fluoride concentration and the ionic strength. The agreement is still satisfactory at pH 4.7 for low fluoride contents.

In contrast, pH is a parameter of great influence at high values. In an alkaline medium, aluminium only exists as the species $Al(OH)_4^-$, whatever the total fluoride concentration. The chromatographic process with these standards should lead to a single peak 3. The existence of peaks 1 and 2 suggests a rapid alteration of the complexation equilibria to yield AlF_n^{3-n}, n depending on the relative fluoride concentration. This modification occurs during the adjustment of the sample matrix to the pH and ionic strength of the mobile phase prior to injection. It can be reasonably assumed that the higher the pH difference between the sample and the mobile phase and the ratio $[F]_{Tot}/[Al]_{Tot}$, the faster are the kinetics of the reactions

TABLE II

COMPARISON BETWEEN THE DISTRIBUTION OF THE FLUORO–ALUMINIUM COMPLEXES DETERMINED EXPERIMENTALLY BY ION CHROMATOGRAPHY AND CALCULATED BY MINEQL: INFLUENCE OF THE pH AND IONIC STRENGTH OF THE SAMPLE

$[Al]_{Tot} = 3.7 \cdot 10^{-5}$ *M*. MP = mobile phase.

Sample			Al^{3+} (%)		AlF^{2+} (%)		AlF_2^+ (%)	
[F]/[Al]	pH	Ionic strength	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
0.71	1.9	$1.3 \cdot 10^{-2}$	41.7	44.8	53.2	51.8	5.0	3.3
	4.7	$1.5 \cdot 10^{-4}$	37.4	36.9	59.2	55.9	3.3	7.1
	10.4	0.8	58.0	100.0	33.2	–	8.2	–
	2.0 (MP)	0.5	55.5	54.2	44.4	42.8	–	3.0
1.42	1.9	$1.3 \cdot 10^{-2}$	11.5	16.9	70.3	67.8	18.0	15.1
	4.7	$1.5 \cdot 10^{-4}$	5.0	7.3	66.6	50.0	28.3	41.9
	10.4	0.8	68.4	100.0	23.8	–	7.8	–
	2.0 (MP)	0.5	30.5	28.5	63.8	60.0	5.6	11.4
2.84	1.9	$1.3 \cdot 10^{-2}$	–	4.1	53.6	54.5	46.4	40.5
	4.7	$1.5 \cdot 10^{-4}$	–	–	33.5	7.1	66.4	92.4
	10.4	0.8	66.3	100.0	19.9	–	14.7	–
	2.0 (MP)	0.5	8.6	10.2	67.5	58.6	23.8	30.4

$$Al(OH)_4^- \rightarrow AlOH^{2+} \rightarrow Al^{3+}$$

$$Al^{3+} + F^- \rightarrow AlF^{2+}$$

$$AlF^{2+} + F^- \rightarrow AlF_2^+$$

On the column, rearrangement occurs between AlF_2^+ and AlF^{2+} during elution, as described previously. These modifications both in solution and on the column imply that, in contrast to what was observed for acidic samples, conservation of unbound aluminium is no longer verified.

The ionic strength of the sample, up to 0.5 *M*, did not seem to influence the accuracy of the experimental results.

CONCLUSIONS

The feasibility of ion chromatography for aluminium speciation in waters has been demonstrated. This method requires adjustment of the sample pH and ionic strength to match the mobile phase and limit interactions of system peaks with the first-eluted species. The total aluminium concentration can be measured by addition of the contributions of each aluminium complex; linearity of the calibration for total aluminium was observed over a wide range (20–2000 $\mu g\ l^{-1}$), whatever the fluoride content in the sample.

Provided that the sample pH is low (<4.5), ionic strength and total fluoride concentration have no significant influence on the accuracy of the experimental results; they are reliable estimates for aluminium speciation. With initial sample pH values higher than 5, acidification of the sample before injection favours rapid dehydroxylation followed by fluorination of Al^{3+}. The total aluminium concentration is still correctly deduced but the method is not suitable for speciation.

For natural samples, it is recommended that they be treated with HCl instead of HNO_3 in order to remove the system peaks on the chromatogram and to allow the quantification of AlF_2^+ and higher complexes.

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