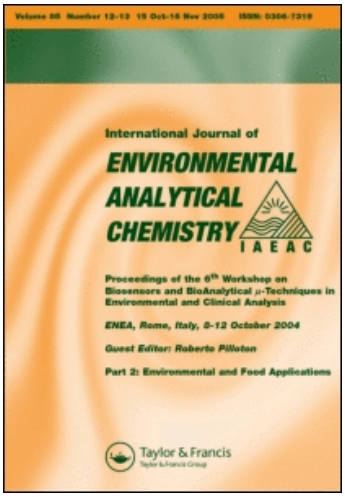

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The Determination of Quickly Reacting Aluminium in Natural Waters by Kinetic Discrimination in a Flow System

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To cite this Article Clarke, N. , Danielsson, L. G. and Sparén, A.(1992) 'The Determination of Quickly Reacting Aluminium in Natural Waters by Kinetic Discrimination in a Flow System', International Journal of Environmental Analytical Chemistry, 48: 2, 77 — 100
To link to this Article: DOI: 10.1080/03067319208027043
URL: http://dx.doi.org/10.1080/03067319208027043

Intern. J. Environ. Anal. Chem., Vol. 48, pp. 77–100
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THE DETERMINATION OF QUICKLY REACTING ALUMINIUM IN NATURAL WATERS BY KINETIC DISCRIMINATION IN A FLOW SYSTEM

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(Received 21 February 1991; in final form 25 October 1991)

Different aluminium species react with oxine at different rates, a behaviour that we have used as the basis of an analytical method. The reaction is performed in a FIA system and is terminated by extraction of the excess oxine, together with the aluminium trioxinate formed, into chloroform. The reaction time is 2.3 sec, much shorter than that used normally. After separation, the amount of aluminium trioxinate in the organic phase is determined spectrophotometrically.

The system has been validated using model substances with known complexation constants. Al^{3+}, $AlOH^{2+}$, probably $Al(OH)_2^+$, aluminium sulphato complexes and, to some extent, some of its weakest organic complexes are included in the measured fraction, whereas fluoro complexes, citrato complexes and $Al_{13}O_4(OH)_{24}^{7+}$ are excluded. Complexes with fulvic and humic acid cause a reduction of the signal. The detection limit is at best about 5 μg/L (ca. 0.2 μM), and we can make 60 measurements per hour. Results from measurements made on natural waters are presented.

KEY WORDS: Aluminium, speciation, natural waters, flow injection, oxine, kinetics

INTRODUCTION

Aluminium is the third most abundant element in the Earth's crust, and the most abundant metal.[1] In rocks it occurs primarily in aluminosilicate minerals, such as feldspars, micas and clay minerals, and as hydroxide minerals, for example in bauxites and laterites.[2] In natural waters it occurs in many different forms, including hexaaquaaluminium ions ($Al(H_2O)_6^{3+}$ or Al^{3+}), and hydroxo-, fluoro-, sulphato- and organic complexes as well as carbonato-, silicato- and phosphato- complexes.[3–5] Some of these are shown in Figure 1.

The solubility of aluminium increases with decreasing pH, so that acid waters tend to have higher aluminium concentrations than neutral waters. Laboratory experiments suggest that an increased concentration of aluminium is poisonous to fishes,[6–9] marine bacteria[10] and algae.[11] Birds that are dependent on aquatic insects as prey can lay eggs with thinner shells,[12] which leads to unsuccessful breeding. Increased concentrations of aluminium in soil solutions may be poisonous to plants.[13,14] Certain human illnesses are or may be connected with aluminium.[12,15] However, the toxicity of aluminium depends on the form in which it occurs.[6,8,10] As it is important

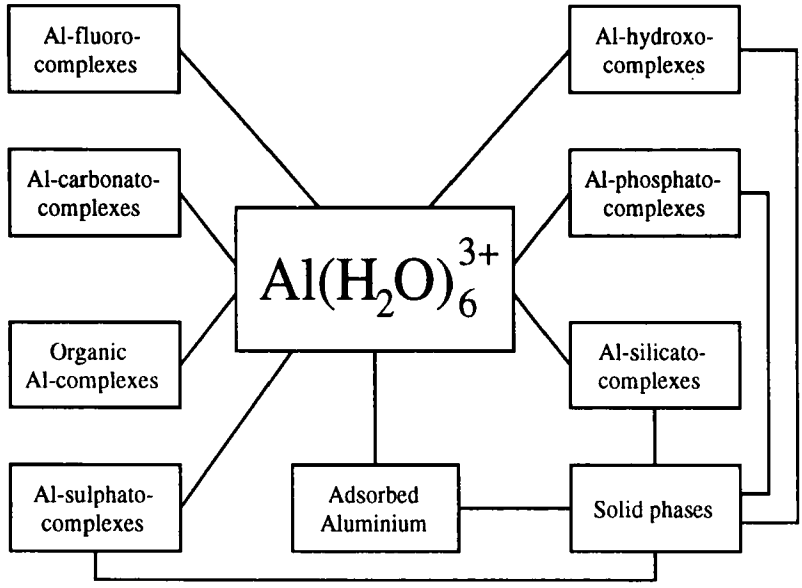

Figure 1 A schematic representation of the main groups of aluminium species in natural waters. The sketch may not be complete.

to know the concentrations of the various aluminium species and not just the total concentration, we need to develop methods to estimate these concentrations.

We have developed a method using flow injection analysis (FIA[16,17]) to measure the most quickly reacting forms of aluminium in natural waters. The method involves the reaction of aluminium with 8-hydroxoquinoline (Hox, oxine) to form aluminium trioxinate, $Al(ox)_3$, which is then extracted into chloroform. The reaction time is about 2.3 sec, which is much shorter than that used normally. The detector is a UV-visible spectrophotometer. Like FIA methods in general, ours is fast, simple to operate and gives good control of the reaction time. Although we have until now only used the method in the laboratory, it should also be possible to use it as a field method.

We have presented parts of this work earlier in poster form at the conference 'Kemistdagar i analytisk kemi' in Lund, Sweden, in June 1990, and at the International Conference on Acidic Deposition, Its Nature and Impacts, in Glasgow, UK, in September 1990.

METHODS OF ALUMINIUM SPECIATION

Metal speciation is a difficult problem to tackle: *Any* treatment is liable to change the sample, affecting the equilibria between the species, and thus the speciation. One might conclude that true speciation is impossible, but, as the White Queen said, "sometimes I've believed as many as six impossible things before breakfast."[18]

A number of authors have presented various analytical methods for speciating aluminium in water solutions.[19–32] We have neither the intention of covering all methods, nor of criticizing specific papers. We would rather discuss some general ideas on aluminium speciation and highlight some important methods. For a more complete review we refer to the work by Hanning[30] which, although rather critical, is fairly comprehensive.

A general problem in the field of aluminium speciation is the operational definition of almost all proposed methods. This makes it difficult to compare results from different investigations. A very important task when developing a new method is to verify the results by, for example, equilibrium calculations. Another approach is to compare the results from different speciation methods. Such comparisons have occupied a lot of authors.[29,33–40]

Extending the classification of Hodges,[36] one could claim that the methods for aluminium speciation are based on the following principles:

—The *rate of reaction* of Al^{3+} with a selective complexing agent; in most cases oxine,[20–26,28–30,34,36] pyrocatechol violet[33,38,41] or ferron.[6,42]

—The removal of charged species by their sorption on *cation-exchange resins.*[19,28,36,37]

—The separation of various aluminium species by *ion chromatography.*[31]

—*Size exclusion* of large complexes, e.g. by filtration or dialysis.[29,34,37–39]

—Reduction of $[F^-]$ through complex formation with Al^{3+},[28,29,36] i.e. an indirect measurement of Al by the *fluoride electrode.*

—The *mobility* of ions *in an electric field.*[32]

In the middle fifties, Japanese researchers presented the first attempts to speciate aluminium in water solutions. Tanaka[19] proposed an ion-exchange method for separating ionic aluminium from non-ionic forms of the metal, while Goto, Okura and co-workers[20,21] further developed the extraction procedure for determining total aluminium proposed by Gentry and Sherrington.[43] The idea of Goto, Okura and their co-workers was to let the aluminium sample react with oxine for a very short time and then extract it into an organic solvent (chloroform). The extracted aluminium trioxinate was detected spectrophotometrically. In this manner they could determine aluminium in true solution in the presence of colloidal forms of aluminium, but they did not strictly know which aluminium species were included in the measured parameter. They allowed a pH between 4.5 and 9.5.

Turner[22] used filtration in combination with the method proposed by Goto *et al.* when dividing the aluminium-containing species into three fractions. Like Goto *et al.*, Turner stuck to synthetic solutions.

In 1975 Barnes[23] presented a method for the speciation of aluminium in natural waters, based on the work of Goto *et al.*, Okura *et al.* and Turner. Her basic idea was very similar to the original idea of Goto *et al.*, i.e. a kinetic discrimination. The main differences from Goto's method were the pH of extraction, for which 8.3 was chosen so as to reduce interferences that might occur in natural water samples, and

the choice of organic phase, methyl isobutyl ketone, that made detection by atomic absorption possible and thus enhanced the selectivity. The result of the method was an operationally defined value, called *dissolved and readily reactive species of aluminium.*

About ten year later, Driscoll[28] extended the method of Barnes by combining it with cation exchange. Driscoll divided his sample into three fractions; two parts were analyzed according to Barnes, with and without prior acidification. Those two parts were called *acid reactive* and *monomeric aluminium* respectively. The last part of the sample was run through a cation-exchange column, which was used to retain the inorganic forms of aluminium and to let the organic forms through. The organic complexes that passed through the column were then analyzed with the Barnes method, giving the *non-labile monomeric aluminium.* By subtracting the non-labile monomeric aluminium from the total monomeric, Driscoll obtained the *labile monomeric aluminium*, i.e. the sum of Al^{3+} and the inorganic aluminium complexes (sulfato-, fluoro- and hydroxo-complexes). Dristoll also evaluated his method by comparing the results with those obtained by measuring free fluoride[44–46] and indirectly calculating the aluminium speciation. The method of Driscoll has been widely used for field work.[47–49]

LaZerte[29] slightly modified the Barnes method, aiming at speeding up the extraction procedure and thus improving selectivity and precision. He also compared the method with equilibrium dialysis and the free fluoride method and concluded that the modified Barnes method measures *inorganic monomeric and organic aluminium.*

Bloom *et al.*[24] measured aluminium trioxinate after extraction into butyl acetate using fluorescence as well as UV-visible spectophotometry. The reaction of aluminium and oxine took place at pH 5. They used a reaction time of 15 min before extraction, but suggested that immediate extraction could be used to prevent the reaction of much of the organically complexed aluminium with oxine. James *et al.*[26] used a UV-visible spectrophotometric method similar to that of Bloom *et al.*, but reduced the reaction time to 15 sec. Lalande and Hendershot[34] separated aluminium into operationally defined classes, based on 15 sec reaction time at pH 5.0, 15 sec reaction time at pH 8.3 and 60 min reaction time at pH 8.3. They compared their results with results obtained from dialysis using LaZerte's method.

May *et al.*[25] tried to improve the detection limit for the oxine extraction method. The key to improvement was to use a very small volume of toluene as the extracting agent. The detection limit reached 0.2 μg Al/L (ca. 7.4 μM) which was a ten-fold improvement compared with that reported by Barnes.

Few authors have tried the possibility of applying a flow system to aluminium determination, even though the advantages seem apparent, e.g. ease of operation, a better control and reproducibility of the reaction and extraction times and an increased sample throughput.[30] We would like to wind up this short review by mentioning some of the attempts to determine aluminium in a flow system, including the ones that do not deal with aluminium speciation.

Röyset[50] determined *total aluminium* in a FIA system and compared four different chromogenic reagents. In a later study,[51] he optimized the method for pyrocatechol violet, based on the earlier work by Anton,[52] Wilson and Sergeant[53] and Dougan

and Wilson.[54] Röyset also described a method using eriochrome cyanine R and cetyl trimethyl ammonium bromide.[55] Valcárcel and Gallego[56] used a FIA system for determining total aluminium in synthetic solutions by the method of Gentry and Sherrington.[43] They especially studied the enhancement of selectivity in a flow system in comparison with a manual procedure. Kinetic methods of aluminium determination in a flow system include that of Zöltzer and Schwedt.[57] They measured kinetically labile aluminium in continuous flow and flow injection systems using chromazural S. However, they did not specify which species were included in kinetically labile aluminium.

Rögeberg and Henriksen[41] automated a combination of the Dougan and Wilson method[54] and the Driscoll ion-exchange procedure.[28] They determined *total monomeric Al* in a continuous flow system using pyrocatechol violet as the complexing agent and *non-labile monomeric Al* using an ion-exchange column connected to the flow system. Henshaw *et al.*[58] and Lexén and Borg[40] used similar systems, comparing them with variations of Barnes'[23] method. Campi and Ingle[59] developed a kinetic method using the formation of a fluorescent complex between Al^{3+} acid alizarine garnet R. Chung and Ingle[60] adapted this method to a FIA system. Unlike Campi and Ingle, Chung and Ingle did not test their method on a natural water sample. Hanning[30] did a lot of the basic theoretical and practical work for applying the manual oxine extraction method to a FIA system. His thesis has been the foundation upon which we have leant when stumbling along the path of mechanizing a kinetic method for aluminium speciation, remembering continuously the words of Hamlet: "Science is out of joint; O cursed spite, That ever I was born to set it right!"[61]

METHOD AND MATERIALS

Chemicals

Oxine (May and Baker) was recrystallised from methanol. Nordic Reference Humic and Fulvic Acids[62,63] were provided by the National Swedish Environmental Protection Board (SNV) and used as obtained. These acids have been isolated using the method of Thurman and Malcolm,[64] using adsorption chromatography followed by size-exclusion chromatography, hydrogen saturation by ion exchange and lyophilization. All other chemicals were from Merck; they were of analytical reagent grade and were used without further purification. To prepare solutions of cations, Titrisol (Merck) standard solutions were used and water which had been passed through either a Milli-Q or a Milli-RO system, both from Millipore.

Standard solutions at pH 2.5 were used for calibration. At this pH, nearly all aluminium should exist as Al^{3+}. The pH cannot be lower than 2.5, as the system can not sufficiently buffer solutions with lower pHs. Hydrochloric acid was used to adjust the pH. Solutions of known composition were used to determine which species react. 10 mM glycine was used as a pH buffer between pH 2.5 and 4, and 10 mM acetate/acetic acid between pH 4 and 6. The ionic strength of these solutions was adjusted to 0.1 M with $NaNO_3$.

All solutions were stored in acid-soaked polyethylene containers.

Equipment

FIA System:

—*Pumps:* Two Gilson Minipuls 2 peristaltic pumps with Tygon pump tubes from Technicon.

—*Injector:* A Model 7040 valve with a Model 5701 pneumatic actuator and a Model 7163 solenoid valve, all from Rheodyne.

—*Separator:* A membrane separator of the type described by Bäckström *et al.*,[65] with a 13 mm diameter 0.2 μm Fluoropore filter and a 13 mm Teflon-coated filter support screen, both from Millipore.

—*Reaction coils:* Teflon tubes from Tecator of variable lengths and with inner diameters of 0.35, 0.5 or 0.7 mm.

—*6-port valve:* Model 7060, with a Model 5703 pneumatic actuator and a Model 7163 solenoid valve, all from Rheodyne.

—*Displacement bottle* from Tecator.

—*Spectrophotometers:* A Hitachi L-4200 UV-Vis or an LKB 2151 Variable Wavelength Monitor.

—*Readout:* A Spectra-Physics SP 4270 integrator.

—*Automatic sample changer:* A Gilson Model 222.

—*Computer control:* Possible through the Labnet interface (Spectra-Physics).

GFAAS: An AA-1275 spectrophotometer and a GTA-95 graphite tube analyzer, both from Varian.

ICP-OES: An ARL 3520 B ICP Analyzer.

Outline of the method

Our apparatus, which is largely the same as Hanning's,[30] is shown in Figure 2. The flow rates and residence times normally used are shown in Table I. The samples are injected into a carrier stream of water. The injection volume is about 250 μl.

It is necessary to buffer the sample before oxine is added, as the reaction kinetics are dependent on pH.[30] As different samples have different pHs, it wouldn't be possible to compare them (or to compare natural water samples with standard solutions) without buffering. A 0.1 M mixture of acetic acid and sodium acetate to buffer to pH 5.0 was used. This pH is the same as that used by Hanning.[30] Since many natural waters have a pH of about 4-6, the disturbance to the sample caused by buffering will be kept to a minimum.

The buffer solution also contains 0.5 M hydroxylamine and 10 mM 1,10-orthophenanthroline. These prevent the reaction of iron and other interfering cations with oxine, when these cations are present in the concentrations normally found in natural waters. The method is based on that for determining iron developed by Saywell and Cunningham[66] and applied to a flow system by Mortatti *et al.*[67] Hedlund[68] worked on the application of this method to Hanning's[30] system. The hydroxylamine reduces

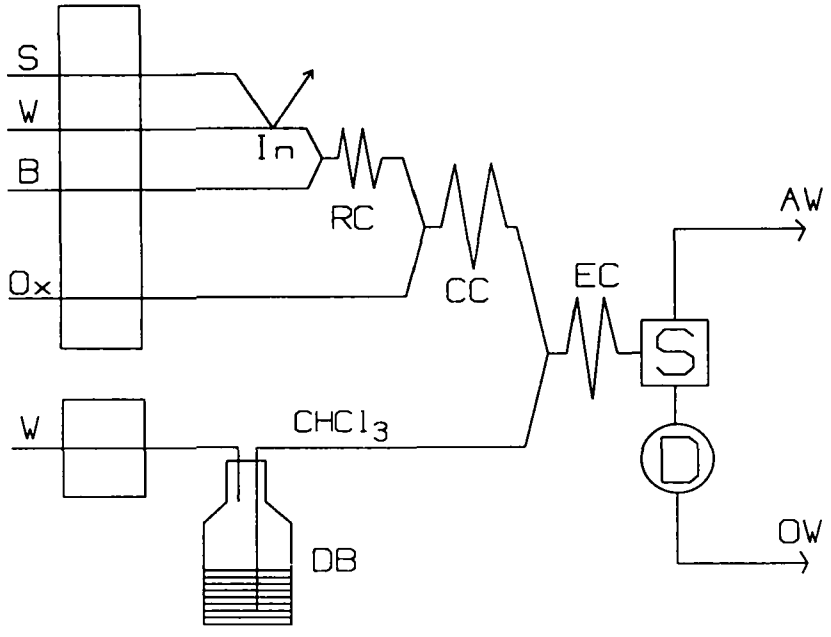

Figure 2 A schematic representation of the flow injection setup. S = Sample, W = Water, B = pH5-buffer, Ox = Oxine, In = Injector, RC = Reduction Coil, CC = Complexation Coil, EC = Extraction Coil, D = Spectrophotometric Detector, S = Phase Separator, DB = Displacement Bottle, OW = Organic Waste, AW = Aqueous Waste.

Table 1 Flow rates, volumes and residence times normally used in the FIA system

Stream	*Flow rate (ml/min)*
Sample	1.1
Carrier stream	1.1
pH 5 buffer	0.6
Oxine	0.9
Chloroform	0.9

Coil[a]	Length (m)	Volume (*μl*)	Residence *time (s)*
Injection coil	1.0	250[b]	—
Reduction coil	0.14	30	1.0
Complexation coil	0.50	100	2.3
Extraction coil	1.50	300	5.1

[a] I.D., 0.5 mm.
[b] Including 50 *μl* couplings

Fe^{3+} to Fe^{2+}, which forms a complex with the orthophenanthroline. 1,10-Orthophenanthroline also forms complexes with other cations.[69] This means that it can be used to mask them too. The residence time in the reduction coil is about 1.0 sec. To improve mixing, we use a knotted coil.[70]

After buffering, the sample stream is mixed for about 2.3 sec with a 4 mM solution of oxine in a 10 mM acetic acid/acetate buffer at pH 5.0. Both the oxine and the aluminium trioxinate are then extracted rapidly into chloroform. This is necessary, as aluminium trioxinate is fairly insoluble in water. Extraction accomplishes several other things: (1) Extraction of the oxine stops the reaction; (2) Many natural waters contain hydrophilic substances which absorb light strongly at 390 nm. Extraction prevents most of these from interfering; (3) The sample can also be made more concentrated by extracting it from a larger volume of water to a smaller volume of chloroform. This will improve the detection limit.

An advantage with chloroform is that much is known about its use as an extractant and the spectra of relevant substances dissolved in it.[43,71–84] A disadvantage is that chloroform can attack the pump tubes. To protect these, and to reduce pulsations, we use a displacement bottle to provide the chloroform flow.

The extraction time used is fairly short (5.1 sec), but nevertheless it effects some 97% extraction. The phases are then separated, and the concentration of aluminium oxinate is measured at a wavelength of 390 nm.

RESULTS AND DISCUSSION

Complexation kinetics

The basis of the proposed method is a strict control of the reaction time between Al^{3+} and oxine. By making this sufficiently short, it is possible to discriminate between quickly reacting aluminium forms and species that react more slowly.[20–22] One of the drawbacks with the presented manual methods is a lack of precise control of the reaction times. In a FIA system, it is possible to obtain repeatable reaction times in the range of a split second to some 30 sec, depending on the choice of the lengths and inner diameters of the tubes and on the total flow rate.

We have studied the reaction kinetics for the complexation between Al^{3+} and oxine. Hanning[30] assumed that the complexation reaction follows pseudo-first-order kinetics, as it takes place with a large excess of oxine. The reaction at pH 5.0 in a 0.5 mm inner diameter Teflon tube has reached 75% of its maximum after 3.3 sec, 90% after 6 sec and is complete within 15 sec. The results from one run are shown in Figure 3 and the parameters calculated from a non-linear curve-fitting are given in Table 2. Of course, the results obtained are due to a mixture of reaction kinetics and mixing within the flow system. We have made no attempts to separate the two of them, but experiments with different inner diameters of the reaction tube indicate that mixing is indeed an important parameter for understanding the reaction kinetics in a flow system.

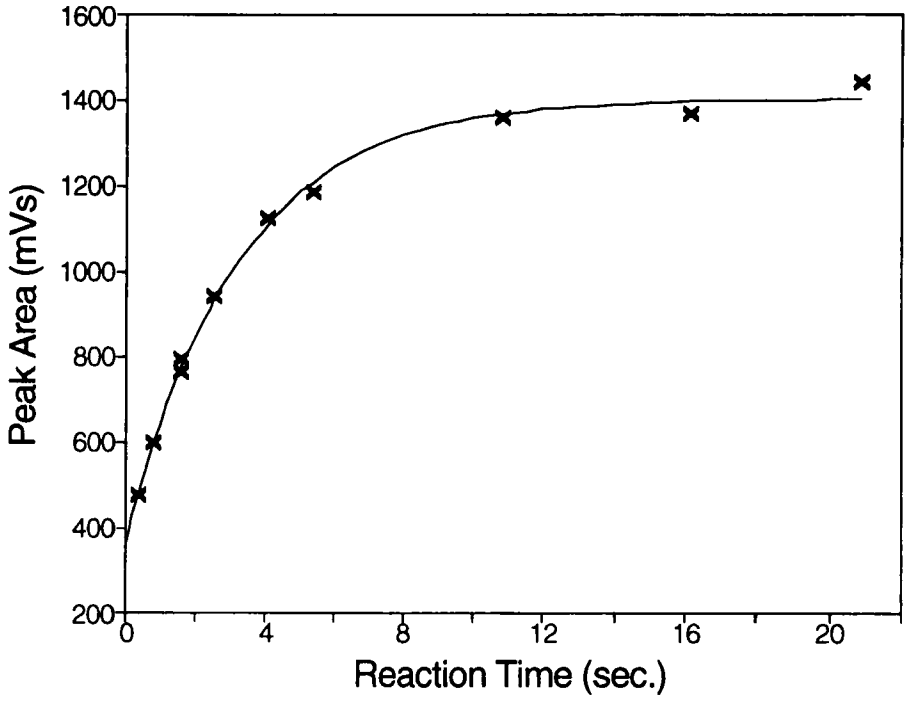

Figure 3 The reaction kinetics of Al^{3+} and oxine in a FIA system at pH = 5.0. Sample: $[Al]_{tot}$ = 25 μM, pH = 2.6. ×, measured values; —, fitted curve.

Extraction kinetics

Extraction in a FIA system was first proposed by Karlberg and Thelander.[85] As is the case with the reaction time, a flow system allows one to use a very short and reproducible extraction time.

The extraction process in a flow system is assumed to follow first-order kinetics.[86] We have studied the rate of extraction in a two channel FIA system according to Nord *et al.*,[86] and we found that the extraction of oxine into chloroform is very fast.

Table 2 Parameters of non-linear fitting to the curve of the reaction of Al^{3+} and oxine at pH5[a]

Constant	*Value*	*SD*
A (mVs)	1403	16
B	0.26	0.02
C (s^{-1})	0.315	0.02

[a] $[Oxine]_{tot}$ = 4.0 mM before mixing. Sample: $[Al]_{tot}$ = 25 μM, pH = 2.6 before mixing. Function: $Y = A*(B + (1 - B)*(1 - EXP(-C*t_r)))$. t_r, the residence time. Correlation coefficient, r, 0.9998.

At an extraction pH of 5.0, with an inner diameter for the tubing of 0.5 mm, an aqueous flow rate of 1.0 ml/min and an organic flow of 0.5 ml/min, 75% of the oxine had been extracted into the organic phase after 1.6 sec. After about 3 sec, 90% of the oxine had been extracted and the whole extraction procedure was complete within approx. 8 sec.

Problems connected with buffering

pH buffering will of course disturb the sample's equilibria, but this appears not to be a serious problem at pH values above about 3.5. Not many natural waters have such a low pH, although mine waters may have.[87] Samples with a pH between 2.5 and 3.5, and with a ligand which forms a strong complex with aluminium (for example, citrate), may give a lower signal than expected. This may depend on an increased formation of the complex due to the increase in pH. However, this problem does not affect our standard solutions at pH 2.5, as they contain no such ligand.

Acetate forms a weak complex with aluminium.[88–93] To check whether the formation of this complex affects our results, we compared the results obtained with an acetate buffer with those obtained with non-complexing buffers of hydroxylamine and hexamethylene tetramine. The only difference was that we got a larger signal with an acetate buffer, which could depend on a catalytic effect of the acetate similar to that described by Turner and Sulaiman.[94] Our conclusion is that the acetato-complex is not formed in amounts sufficient to affect the results. There may not be enough time for the complex to be formed before oxine is added.

Interferences

Oxine forms complexes with a number of cations.[95,96] Several of the metal oxinates are extractable into chloroform and absorb strongly around the absorption maximum of aluminium trioxinate.[72] Among these we find the oxinates of iron, copper, manganese, zinc, nickel and cobalt.[43,72,79,81,97] Iron can be quite abundant in natural waters, while the other elements are normally present only in trace amounts.[98] To check whether some of the cations present in natural waters would interfere with the determination of aluminium, a fractional factorial design study on eight cations was made. These were Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, K^{+} and Na^{+}. All of them except Na^{+} and Ca^{2+} were present in concentractions much greater than those normally found in natural waters. Figure 4 shows that only Cu^{2+} and Fe^{3+} affected the signal. We can to a large extent mask the reaction of Fe^{3+} and Cu^{2+} with oxine using hydroxylamine and 1,10-orthophenanthroline. Figure 4 shows that the presence of these reagents reduces the effect of the cations on the signal considerably.

Further experiments showed that one can tolerate non-complexed copper in concentrations up to 2.5 μM. This greatly exceeds the levels of total copper found in most natural waters, which several authors have recently estimated to be less than 30 nM.[99–101] Iron can be present in quite high concentrations in natural waters, although under oxidizing conditions it is mostly complexed or in colloidal form. The

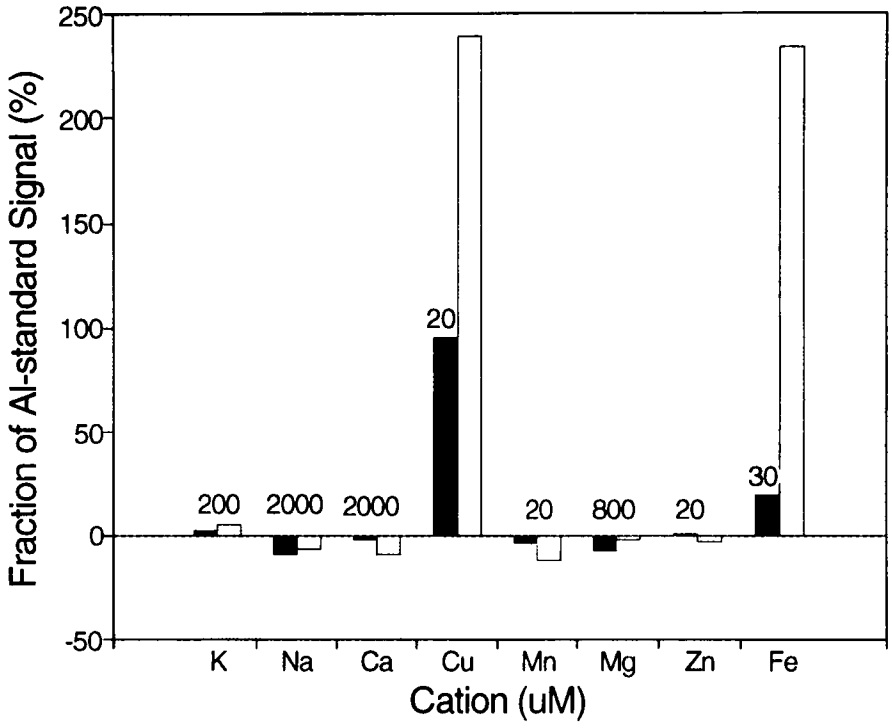

Figure 4 The main interfering effects of various cations on the determination of quickly reacting aluminium in a FIA system. All samples: $[Al]_{tot}$ = 10 μM, pH = 2.6. The total cation concentrations (μM) are indicated in the figure. All coupled effects have been neglected. Filled bars: Masking reagent present. Empty bars: No masking reagent present.

proposed method can tolerate non-complexed iron in concentrations up to about 2 mg/L (36 μM).

It is possible that strongly complexed or colloidal iron affects the signal despite the presence of hydroxylamine and 1,10-orthophenanthroline, as it could take more time for the iron to react with the hydroxylamine than the sample spends in the reduction coil. Thus there is a possibility that some reactive iron is formed after the sample has come into contact with oxine. To test this, we measured iron concentrations in the chloroform layer with graphite furnace AAS after extraction from natural water samples using our system. The iron concentrations found were below the detection limit. It was also necessary to check whether the water samples contained iron that would be measured if no masking agents were used. This we did by simply leaving out hydroxylamine and 1,10-orthophenanthroline from the pH 5.0 buffer solution. Measurable amounts of iron trioxinate were formed. These results confirmed that the masking agents do indeed prevent the iron from reacting with the oxine.

Natural water samples may contain substances which can be extracted into chloroform and which may absorb light at 390 nm. This potential problem will probably be larger for strongly coloured waters. We have detected such substances

by scanning the collected organic phase. In the present method, however, this does not normally lead to any serious interference, since the additional absorbance, if it occurs, is generally below the detection limit.

Choice of complexation time

Our intention was to choose as short a complexation time as possible, in order to avoid the dissociation of certain aluminium complexes, especially organic ones. However, it is not advisable to use too short a reaction time, as the signal-to-noise ratio would then decrease due to incomplete reaction between aluminium and oxine. As a compromise, a standard residence time in the complexation coil of about 2.3 sec was chosen, which is equivalent to a 0.5 m × 0.5 mm I.D. coil. This time includes both the mixing time and the reaction time, which of course overlap.

The pH of extraction

Hanning[30] buffered the solution to pH 8.0 with 1 M triethanolamine before extraction. At pH 8.0, the reaction of the aluminium fluoro-complexes with oxine was faster than at pH 5.0. He suggested that this kinetic difference could depend on the higher concentration of the oxinate anion at pH 8.0. Using his system, we found that, when we extract at pH 8.0, part but not all of the aluminium fluoro- and citrato-complexes react with oxine. In order to obtain a clear separation of the fluoro- and citrato-complexes from the hydroxo-complexes, we chose not to buffer the sample to pH 8.0 before extraction. This has the additional advantage that the system is simpler than Hanning's.

Which species are measured with our method?

Hanning[30] rejected the use of a single, necessarily arbitrary, reaction time to determine quickly reacting aluminium. Instead, he proposed an initial rate method. However, this method necessitates measuring each sample several times with complexation coils of different lengths, which makes it time-consuming. We have therefore decided to use a single reaction time, and as far as possible to determine which species are measured using this time.

The residence time in the complexation coil is 2.3 sec. We have also looked at the effect of other residence times on the speciation. The use of a 3.0 m × 0.5 mm I.D. complexation coil gave a residence time of about 14 sec. In some experiments, a 6-port valve was used to change between six different coil lengths, giving residence times between 0.6 and 16 sec. This was possible without stopping the experiment.

To determine which species react, synthetic solutions with various ligands, various aluminium concentrations and various pH values at a constant ionic strength of 0.1 M were used. At this ionic strength, differences and changes in speciation causing small variations in the ionic strength should not affect the equilibrium constants very much. We calculated the speciation in the solutions with a modified version (V87.02) of HALTAFALL,[102] using equilibrium constants from the literature. Öhman and

co-workers have obtained a large number of internally consistent constants. As far as possible, i.e. for hydroxo-,[103] citrato-[104,105] and acetato-complexes,[91] we have used their results. Other constants were obtained from Dyrssen[106] (hydroxo- and fluoro-complexes), Lindsay[107] (amorphous $Al(OH)_{3(s)}$, fluoro- and sulphato-complexes), Bjerrum *et al.*[108] (HF, HSO_4^-), Djurdjevic and Jelic[109] (glycinato-complexes), Stumm and Morgan[110] (iron complexes) and Wagman *et al.*[111] (iron complexes). Normally, we have ignored the carbonate system. The carbonato-complexes of aluminium may be neglected in slightly acid solutions except when the partial pressure of carbon dioxide is high.[4,112,113] The constants for the carbonate system, where these have been used, were taken from Stumm and Morgan,[110] and Hedlund *et al.*[4] All constants chosen were valid for 25°C. If necessary, the equilibrium constants for the ionic strength of the solutions were corrected using the Güntelberg and Davies approximations.[110] We then compared our results with these calculations.

Synthetic solutions are of course chemically much simpler than natural waters. However, it is necessary to look at simple chemical systems of known composition first. Then, when one understands how these behave, one can go on to more complicated chemical systems.

In stored solutions, except at low pH, part of the aluminium can be adsorbed on the container walls, especially in the absence of strong complexing ligands such as citrate (see Figs. 5 and 7). In our synthetic solutions, adsorption appeared to occur quickly, mostly within 1.5 h of preparation. To correct our results for this, the total dissolved aluminium was measured with ICP-OES.

The results show a larger decrease of the signal for synthetic solutions at around pH 5 than can be explained by adsorption on container walls (see Figure 5). This may be due to adsorption within the FIA system, which is indicated by the existence of carry-over effects for those solutions when followed by more acidic samples. This is an annoying problem, but probably not a serious one, since we have not normally found the phenomenon with natural water samples and since we compare these with standards of pH 2.5.

The species which react fastest are Al^{3+}, $AlOH^{2+}$ and the sulphato-complexes. These complexes take less than 15 sec to react completely. Their rates of reaction with oxine in our system appear to be about the same. This means that if, for example, 90% of the signal is due to hydroxo-complexes and 10% due to sulphato-complexes with a reaction time of 14 sec, *the same proportions will apply with a reaction time of 2.3 sec.*

According to the equilibrium calculations, the summed mononuclear hydroxo-complexes $Al(OH)_2^+$, $Al(OH)_{3(aq)}$ and $Al(OH)_4^-$ are less than 5% of the aluminium present at the concentrations and pH values used. Therefore, we cannot say with certainty how they react in our system. Hydrolysis equilibria are fast, and it is extremely likely that $Al(OH)_2^+$ reacts as quickly as $AlOH^{2+}$. When performing equilibrium calculations, we have assumed that these species react in the same way, but that $Al(OH)_{3(aq)}$ and $Al(OH)_4^-$ hardly being to react. If this assumption is wrong, the error will, however, be small. Likewise, we have assumed that polymeric hydroxo-complexes hardly begin to react with the oxine. This is certainly the case for large polymers, but it may not be true for very small cationic polymers. However,

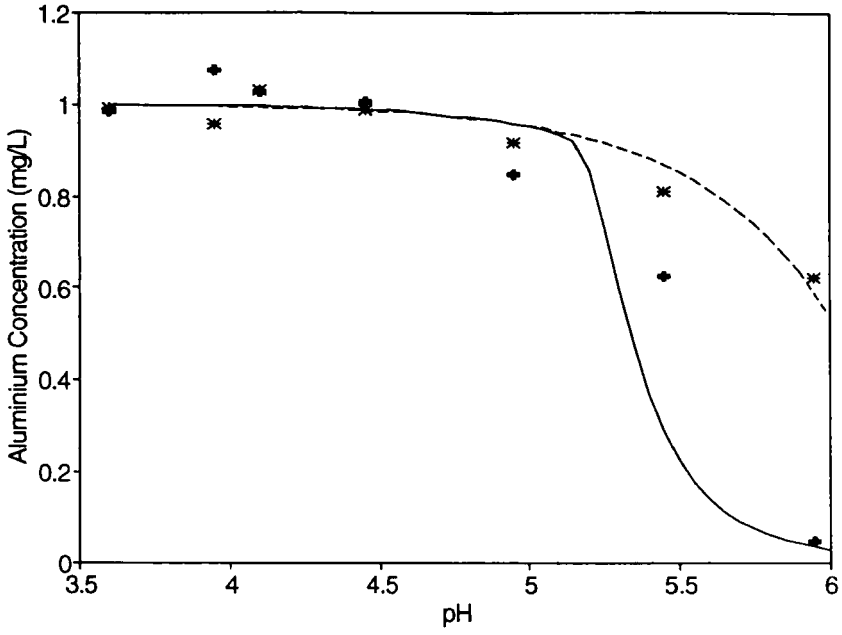

Figure 5 Comparison between measured (+) and predicted (—) values of quickly reacting aluminium in synthetic solutions at different pH values; $[Al]_{tot} = 37\ \mu M$. Total dissolved aluminium was measured (*) by ICP-OES and a curve fitted (– – –) to the measured values.

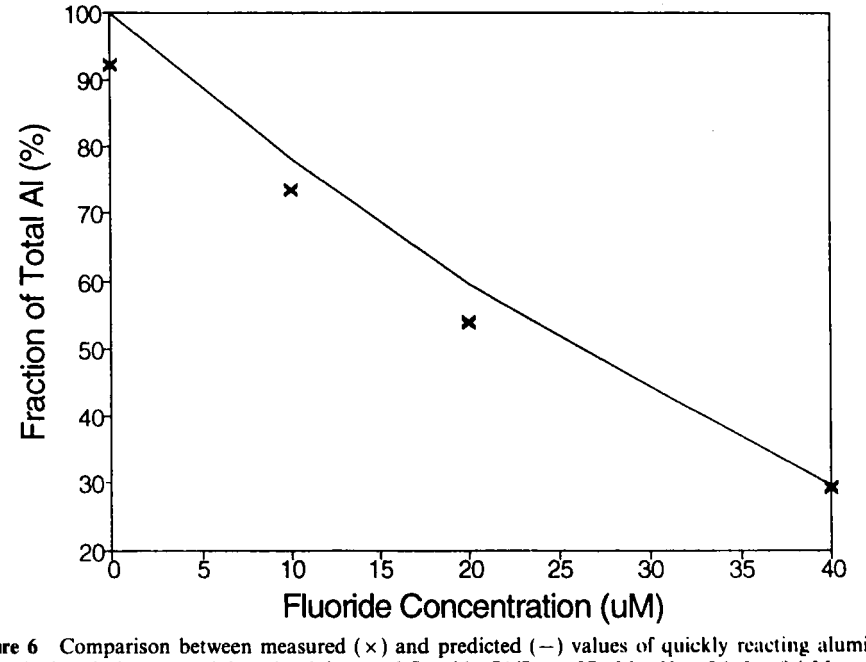

Figure 6 Comparison between measured (×) and predicted (–) values of quickly reacting aluminium in synthetic solutions containing aluminium and fluoride. $[Al]_{tot} = 37\ \mu M$, pH = 5.1, I = 0.1 M.

the concentrations of these appear to be insignificant at the aluminium concentrations used.

Aluminium glycinate and aluminium acetate appear to have reacted completely after 15 sec, but they react more slowly than the complexes mentioned above. After 2.3 sec, their reaction with oxine is incomplete relative to the hydroxo-complexes. However, the concentrations of acetate, glycine and similar compounds in natural waters are low,[114,115] so this is not likely to cause a problem. Even for the buffered solutions, with much higher concentrations (10 mM) of acetate or glycine than in natural waters, the effect of this kinetic difference is negligible.

Many aluminium complexes hardly begin to react within 14 sec. These include: $Al_{13}O_4(OH)_{24}^{7+}$, fluoro-complexes, mixed fluoro-hydroxo-complexes, citrato-complexes, and mixed citrato- hydroxo-complexes.

Figures 5–7 show some of these results. The predicted values have been calculated assuming a complete reaction of aluminium acetate and aluminium glycinate species relative to Al^{3+}. In general, there is good agreement between the measured and the predicted values. Some discrepancies may depend on uncertainties in the equilibrium constants, especially those which have been recalculated to match the ionic strength used. In some cases, discrepancies could depend on the presence of species that we haven't considered. This is especially likely at pH values around 5.3–6.0, where, for

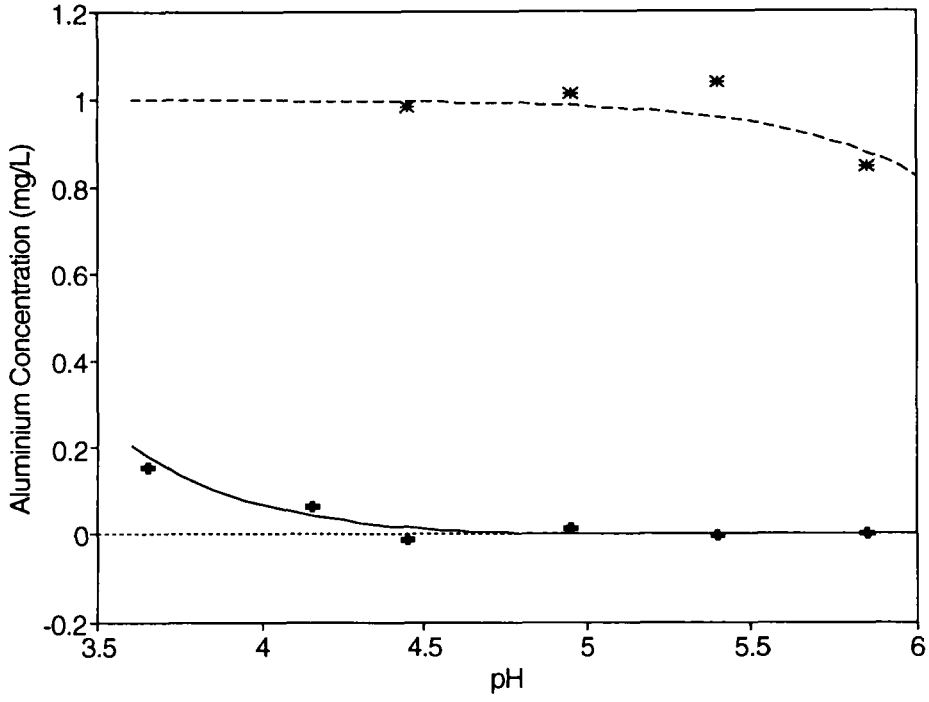

Figure 7 Comparison between measured (+) and predicted (—) values of quickly reacting aluminium in synthetic solutions containing aluminium and citrate. $[Al]_{tot}$ = 37 μM, $[Cit]_{tot}$ = 37 μM, I = 0.1 M. Total dissolved aluminium was measured (*) by ICP-OES and a curve fitted (– – –) to the measured values.

example, polynuclear hydroxo-complexes can occur in significant amounts. There is considerable doubt about which polymers actually exist.[3,103,109,116]

Around pH 5, discrepancies could depend on adsorption within the FIA system. This can be seen in Figure 5. Figure 6 shows that the results obtained for synthetic solutions containing aluminium fluoro-complexes at pH 5 were lower than expected, compared to standard solutions of pH 2.5. These results may also be affected by adsorption in the system.

We have also studied the complexes formed by aluminium with Nordic Reference Humic and Fulvic Acids. The concentrations of humic and fulvic acid used were comparable to those in the water from which they came (See Figures 8–9). The acids contain a small amount of aluminium, but this gave no signal. Neither did the acids themselves give a signal. In these cases, we could not compare our results with equilibrium calculations. However, Figures 8–9 show that the signal is much lower when fulvic or humic acids are present. These results were the same for a reaction time of 2.3–2.6 sec and for a rection time of 13.7–14.7 sec, so ligands of the acetato- or glycinato- type did not affect the result. However, maybe part of the aluminium-humic acid and aluminium-fulvic acid complexes react very quickly with oxine, at about the same rate as Al^{3+} does, whilst another part hardly begins to react in under 15 sec. The results of some other workers[34,36] suggest that this may be the case (see below).

Calculation of $[Al^{3+}]$

Neglecting the contribution to the signal from organic aluminium species that react partially with oxine, and assuming equilibrium, we can calculate $[Al^{3+}]$ using equilibrium calculations. Let $a = [Al^{3+}]$, $h = \{H^+\}$, $s = [SO_4^{2-}]$ and $A_{QR} = [Al]$ as determined by the present method, while β_{pqr} is the mixed equilibrium constant for the reaction:

$$pH^+ + qAl^{3+} + rSO_4^{2-} \Leftrightarrow H_pAl_q(SO_4)_r^{p+3q-2r} \tag{1}$$

Then, taking the following reactions into consideration,

$$Al^{3+} + H_2O \Leftrightarrow AlOH^{2+} + H^+ \qquad (\beta_{-110}) \tag{2}$$

$$Al^{3+} + 2H_2O \Leftrightarrow Al(OH)_2^+ + 2H^+ \qquad (\beta_{-210}) \tag{3}$$

$$Al^{3+} + SO_4^{2-} \Leftrightarrow AlSO_4^+ \qquad (\beta_{011}) \tag{4}$$

$$Al^{3+} + 2SO_4^{2-} \Leftrightarrow Al(SO_4)_2^- \qquad (\beta_{012}) \tag{5}$$

one obtains:

$$a = A_{QR}/(1 + h^{-1} \cdot \beta_{-110} + h^{-2} \cdot \beta_{-210} + s \cdot \beta_{011} + s^2 \cdot \beta_{012}) \tag{6}$$

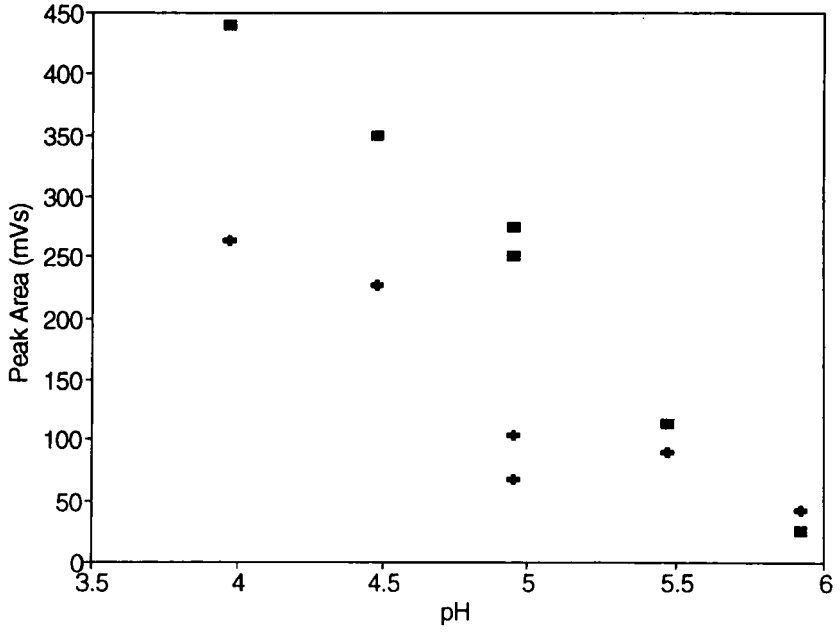

Figure 8 Measured values of quickly reacting aluminium at different pH values in synthetic solutions containing aluminium and Nordic Reference Humic Acid. $[Al]_{tot}$ = 7.4 μM (200 μg/l), I = 0.1 M; ■, No humic acid; +, 8.0 mg/l of humic acid.

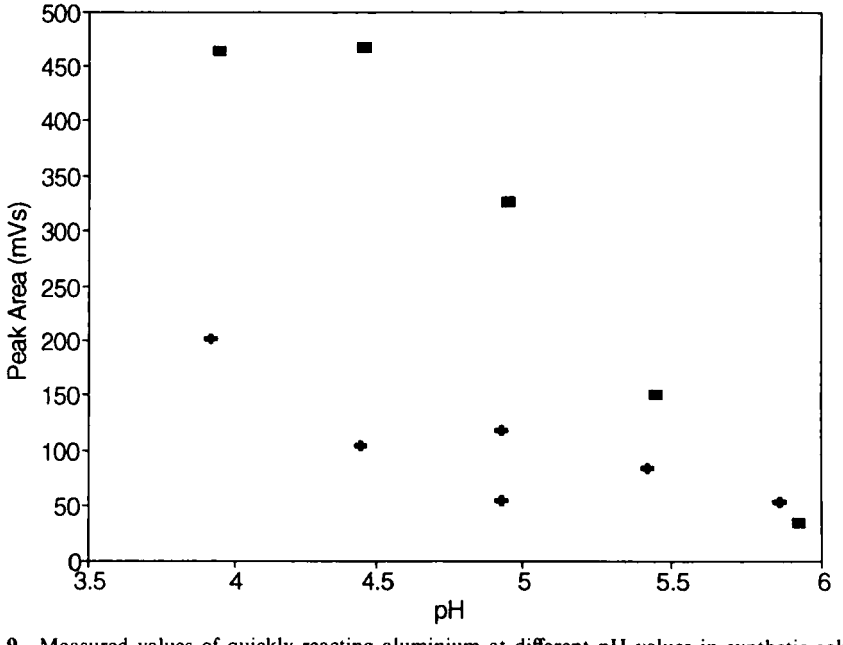

Figure 9 Measured values of quickly reacting aluminium at different pH values in synthetic solutions containing aluminium and Nordic Reference Fulvic Acid. $[Al]_{tot}$ = 7.4 μM (200 μg/l), I = 0.1 M; ■, No fulvic acid; +, 20.0 mg/l of fulvic acid.

The assumption that one can neglect organic aluminium species which react with oxine is questionable for natural waters with a high organic matter content. However, it is allowable to make this assumption for waters with a very low organic matter content.

Comparison with other methods

Gentry and Sherrington[43] found that large amounts of acetate or sulphate had no important effect on the determination of total aluminium with oxine, whereas fluoride reduced the amount of aluminium found. This reduction was larger at pH 5 than at pH 9.

Turner,[22] using a manual method for the complexation of aluminium with oxine followed by extraction, found that Al^{3+}, $AlOH^{2+}$, and $Al(OH)_4^-$ reacted with oxine within 10 sec. His results for the cationic complexes agree with ours. When determining labile forms of aluminium in acidified natural waters, the fate of $Al(OH)_4^-$ is, however, a minor problem, since it normally does not occur in measurable amounts in these waters.

Our quickly reacting aluminium is *not* the same as Driscoll's[28] labile monomeric aluminium, which included sulphato-, fluoro- and hydroxo-complexes, and possibly some organic complexes.[37] Nor is is the same as Barnes'[23] or LaZerte's[29] monomeric aluminium. We can separate the fluoro-complexes from the others. This is useful, as it eliminates one step in the calculation of the concentration of free aluminium ion, needed for toxicity evaluations.[117]

James *et al.*[26] used extraction after 15 sec reaction with oxine, so their results should be directly comparable to ours when we use a 3 m complexation coil. They found that Al^{3+} and $AlOH^{2+}$ reacted, but not $Al(OH)_2^+$. The fluoro- and citrato-complexes of aluminium appear to have reacted partly with the oxine.

Our results agree with those of Lalande's and Hundershot's[34] fast-oxine, pH-5 measurements for hydroxo- and fluoro-complexes. However, they found that they measured a small portion of the aluminium when it was present as citrato-complexes. When fulvic acid was present, they measured some of the aluminium which was bound to the fulvic acid. This may mean that some aluminium-fulvic acid complexes react very fast with oxine at pH 5.

Hodges[36] found that oxine can displace fulvic acid in under 15 sec when the level of Al^{3+} is low relative to the number of reactive ligands.

Bertsch and Anderson[31] found that they could not separate acetato- and sulphato-complexes of aluminium, $AlOH^{2+}$ or $Al(OH)_2^+$ from Al^{3+}. Citrato- and fluoro-complexes could, however, be separated from Al^{3+}. These results are clearly similar to ours. The authors concluded that when the ligand primarily formed outer-sphere complexes with Al, these complexes were totally dissociated in their system.

The detection limit and the frequency of injection

The lowest measurable aluminium concentration is about 25 μg/l (ca. 0.9 μM). The detection limit, defined as three times the standard deviation for 30 consecutive

injections of at sample[118] with a concentration of quickly reacting aluminium of approx. 10 μM, is at best between 5 and 10 μg/l (ca. 0.2–0.4 μM) for synthetic solutions and natural water samples with a low organic matter content. If the peak area is measured, the detection limit could be further improved by increasing the injection volume above the 250 μl normally used. An increase to 640 μl would improve the detection limit about 2.5 times. However, this would inevitably reduce the sample throughput. If peak heights are used, 345 μl seems to be the highest injection volume that gives any improvement of the signal worth mentioning. Still, the detection limit is only 10% better than the one obtained with the injection volume normally used.

The detection limit lies within the range of values for aluminium speciation methods reported in the literature; 0.2 – 50 μg/l (ca. 7 – 2000 nM).[25,32] If necessary the detection limit can also be improved by using another method of detection, e.g. fluorescence measurement[24] or flameless atomic absorption spectrophotometry.[29,40] In the latter case, the method would of course be hard to use for field work.

With the standard injection volume, we can inject 60 times per hour. The sample throughput is reduced to one-third of that if an injection volume of 640 μl is used.

Measurements made on natural waters

Our system has been tested on stream and groundwater. Figure 10 shows the total and quickly reacting dissolved aluminium concentrations found in water samples taken from Kolmården, Sweden in November 1989. Before measurement, the samples were filtered using Millipore 0.45 μm filters. Filtration is necessary as particles can clog the tubes. We measured total dissolved aluminium using ICP-OES.

Measurements made on natural water samples, especially from humus-rich waters, often show a larger standard deviation than those made on standard solutions. This may be due to the surface-active properties of some organic compounds, which could influence the segmentation.[119] As a consequence, the detection limit for natural water samples with a high organic matter content is considerably worse than the one mentioned above, viz, in the order of 40–180 μg/l (ca. 1.5-7 μM). Some results are shown in Table 3.

CONCLUSIONS

The present method gives an operationally defined measurement of *quickly reacting aluminium*, which may be both inorganic and organic. With a reaction time of about 2.3 sec, the following species are measured: Al^{3+}, $AlOH^{2+}$, probably $Al(OH)_2^+$, and sulphato-complexes. Compared to the above species the following species are measured only partly: glycinato-complexes and acetato-complexes. Species that hardly begin to react are: $Al_{13}O_4(OH)_{24}^{7+}$, fluoro- and mixed fluoro-hydroxo-complexes, and citrato- and mixed citrato-hydroxo-complexes.

Complexes with Nordic Reference Humic and Fulvic Acids *may* be measured partly. They are definitely not measured completely.

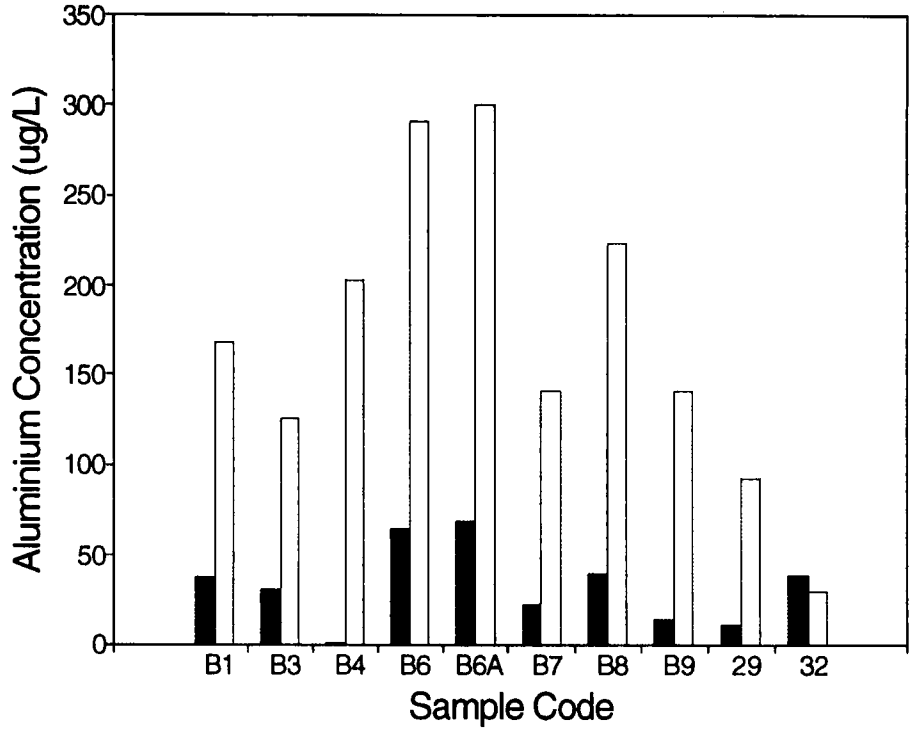

Figure 10 Comparison of quickly reacting aluminium determined by FIA (filled bars) and total dissolved aluminium determined by ICP-OES (empty bars) in natural water samples from Kolmården (Sweden), November 1989.

Table 3 Comparison of relative standard deviations of four consecutive injections obtained with 0.1–1.0 mg/l(3.7–37 μM) standard solutions and with natural water samples

Sample	*Colour*[a]	Mean signal (mVs)	RSD (%)
0.1 mg/l Al (3.7 μM)		220	3
0.2 mg/l Al (7.4 μM)		465	1
0.5 mg/l Al (18.5 μM)		1134	2
1.0 mg/l Al (37 μM)		2510	4
GI 10B	Brown	351	9
MBJ	Yellow	112	5
LL	Dark Brown	1014	18
GII	Brown	747	14
A4	Yellow	774	3
GI	Yellow	411	3

[a] The colour of the natural water samples gives an idea of the amount of organic matter they contain.

The measured values can be used to estimate the concentration of free aluminium ion, needed for toxicity evaluations.[117]

By using a flow injection system, one obtains fairly exact and reproducible control of the reaction time. The system is very rapid and easy to operate. It is also easy to control via automation using a computer. The method is suitable for use in field work, as the system is easy to transport, set up and operate. We can determine concentrations down to 25 μg/L (ca. 0.9 μM), and inject up to 60 times per hour. The detection limit is at best between 5 and 10 μg/l (ca. 0.2-0.4 μM) for synthetic solutions and natural water samples low in organic matter.

Other cations appear not to interfere when present at levels which are normal for natural waters. The potential interference from extractable substances present in natural waters that absorb at 390 nm, does not normally seem to be a serious problem. This means that with our method we measure the quickly reacting aluminium *directly, with just one measurement.* We do not measure the same aluminium species as does, for example, Driscoll. This means that our method could also be used as a complementary method, together with others, to obtain a more detailed speciation of aluminium.

Future Plans. At present we are working on a comparison of our method with a variation of Driscoll's[28] and LaZerte's[29] methods. We intend to study the reaction of the aluminium complexes of humic and fulvic acid further, so as to find out whether or not part of these complexes reacts with the oxine in our system. We also intend to study the behaviour of aluminium carbonato-, phosphato- and silicato-complexes in the FIA system. Organic ligands that will be studied include salicylate and oxalate. The removal of interferences from unknown, presumably organic, substances will also be studied.

Acknowledgements

We thank Anders Hanning and Peter Hedlund for early work with this method; Katarina Starberg for helping us with some of the experiments; Folke Ingman, Lage Nord, Anders Gustavsson, Vlastimil Kuban and Lars-Olof Öhman for helpful discussions; Rolf Jansson for technical help; Bo Lagerman for help with HALTAFALL; Lena Maxe, Staffan Ågren, Ann Catrine Norrström, Gunnar Jacks and Lars Lundin for providing natural water samples; the National Swedish Environmental Protection Board (SNV) for providing Nordic Reference Humic and Fulvic Acids and SNV, the Swedish Natural Science Research Council and The OK-Union Environmental Foundation for the financial support that made this work possible. The work was part of SNV's integrated project 'Effects of Acidification on Groundwater'.

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