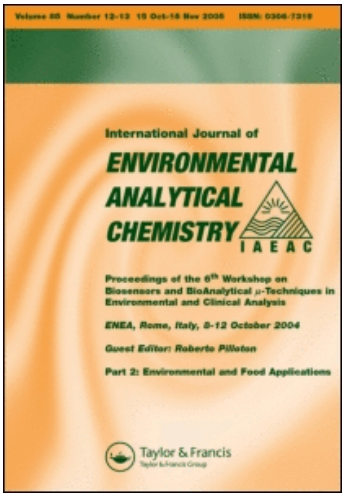

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P. Jones[a]
[a] Department of Environmental Sciences, Polytechnic South West, Plymouth, UK

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THE INVESTIGATION OF ALUMINIUM SPECIATION IN NATURAL AND POTABLE WATERS USING SHORT-COLUMN ION CHROMATOGRAPHY

P. JONES

Department of Environmental Sciences, Polytechnic South West, Plymouth, UK

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A highly sensitive and selective short-column ion chromatography method for the direct investigation of aluminium species in water samples is presented. Studies with pure aluminium standards indicated that aluminium species of general formula $Al(OH)_x^{(3-x)+}$, where x can have values from 1 to 4 depending on pH, gave a single peak, and the presence of fluoride or organic complexing acids gave additional peaks close to the solvent front. Once formed the aluminium fluoro species were stable enough to be chromatographed without significant decomposition.

Reservoir and drinking water samples were analyzed by this technique and showed a major change in aluminium speciation after passage through a potable water treatment plant involving the addition of aluminium sulphate. There was a major increase in the $Al(OH)_x^{(3-x)+}$ fraction, higher than $Al(OH)_3$ solubility models predict, suggesting significant supersaturation of inorganic aluminium in the drinking water.

KEY WORDS: Aluminium, speciation, water.

INTRODUCTION

The presence of aluminium in natural water systems is of major concern at present because of the potential threat to the health of a number of species including humans. The increase in soluble aluminium in areas with low-pH groundwater has been known for some time to be highly toxic to certain fish species (1), and is commonly linked to the 'acid rain' problem, particularly noticeable in Scandinavian countries. A recent and perhaps more controversial study by a medical group in the UK has shown a correlation between the level of aluminium in drinking water and the incidence of senile dementia.[2] Although much more work is needed before the full implication of the toxic effects of aluminium are known, it is generally agreed that a knowledge of the form or type of aluminium species in the water system is of vital importance. This was demonstrated by the work of Driscoll and co-workers who showed that the positively charged aluminium hydroxy species are much more toxic to fish than the organic complexes.[3] However, most of the published speciation studies have concentrated on ground, river and lake water with little mention of potable water, in spite of the widespread use of alum (aluminium sulphate) treatment. Thus, in the case of the medical survey mentioned above, there was no reference to the speciation of aluminium in the drinking waters, with only total values given.

The main methods presently used for aluminium speciation in fresh waters are based on the fractionation programme originally put forward by Driscoll *et al.*[3] There have been a number of modifications since then, some including the Barnes solvent extraction step.[4] A paper by Sullivan *et al.*[5] compares the different modifications with the conclusion that apart from some systematic differences they give similar results. The key step in all of these methods is the use of a cation-exchange column to separate the labile monomeric (inorganic) from the non-labile monomeric (organic) fractions. The labile monomeric concentration is obtained by subtracting the non-labile monomeric from the total monomeric figure. Finally, the most important inorganic fraction from the fish toxicity point of view, i.e., that containing the $Al^{3+}/Al(OH^{2+}/Al(OH)_2{}^{+}$ species, is then obtained after thermodynamic calculations have been used to estimate and subtract the aluminium fluoro species. Thus, a number of subtractions are used which could give rise to significant errors if the proportion of inorganic aluminium is small. Furthermore, there have been some indications that a proportion of the organic aluminium fraction may be sufficiently labile to dissociate on the cation-exchange column, and care is needed not to have too high a residence time on the column.[4] If this is the case it could result in an over-estimation of the inorganic aluminium fraction. Taking these factors into account, it would certainly seem more desirable to use direct determination techniques for the more important aluminium species.

One way of achieving direct determinations is to use high-performance ion-exchange chromatography with appropriate on-line detectors. The main concern with this approach would be the kinetic stability of the different aluminium species during the chromatography. In the last two years a number of studies have been published concerning the ion chromatography (IC) determination of inorganic aluminium using a variety of post-column reaction detectors.[6–8] In most cases the samples used contained the aluminium as the simple hydrated aluminium(III) cation. The method developed by Jones *et al.*[6] seemed particularly suited to speciation investigations as the detector, based on fluorescence, has a very high sensitivity and selectivity for aluminium, showing no response for iron, the main interferent in the colorimetric-based detectors. In the same paper it was shown that an aluminium peak was obtained for drinking water injected at its natural pH. Furthermore, small peaks were observed close to the solvent front. These were considered to contain aluminium, as the only other common metal to give a response is zinc, and this possibility was ruled out by way of standard additions. Further experiments involving the addition of fluoride to aluminium-containing solutions gave large early eluting peaks. This phenomenon was also observed by Bertsch and Anderson who recently published details of aluminium speciation studies[9] using IC in conjunction with their previously developed colorimetric post-column reaction detector.[8] Strong evidence for the chromatographic stability of fluoro and organic aluminium complexes was presented, supported by thermodynamic data, though speciation in natural water samples was not studied. Similar results were found in the author's work, particularly on fluoride aluminium species. This paper describes a preliminary study of aluminium speciation in aqueous media using short ion-exchange columns followed by application to reservoir and drinking water samples.

MATERIALS AND METHODS

Apparatus

The same set-up was used as for the earlier work on trace aluminium determination.[6] This consists of two Constametric III pumps (Laboratory Data Control, Riviera Beach, Fl, USA) used for eluent and post-column reagent delivery. Both were set at 1 ml min^{-1} for all work. The injector was a Rheodyne 7010 valve (Rheodyne, Cotati, CA, USA) fitted with a 100 μl sample loop. The cation-exchange column was a Dionex CG2 guard column kept at 50 °C by immersion in a water bath. The fluorescence detector was an LS4 spectrometer (Perkin Elmer, Beaconsfield, Bucks., UK) with the excitation wavelength set at 360 nm and the emission wavelength set at 512 nm.

Chromatographic conditions

The eluent was potassium sulphate, adjusted to pH 3.0 with dilute nitric acid. The concentration used was in the range 0.06 to 0.10 M depending on the elution speed required. The post-column reagent was prepared by adding 5 ml of 1 M sodium acetate to 500 ml of 0.002 M 8-hydroxyquinoline-5-sulphonate (8 HQS) and adjusting to pH 4.1 with glacial acetic acid. The final pH of the mixed eluent and post-column reagent streams should be close to 4.0. The post-column reagent coil was a 400 cm × 0.03 cm I.D. PTFE tubing kept at room temperature. With a combined flow rate of 2 ml min^{1} this gives a reaction time of approx. 10 sec.

Reagents and Standards

All reagents used were analytical-reagent grade unless otherwise stated. Distilled deionised water was obtained from a Milli Q system (Millipore, Bedford, MA, USA). Stock 1000 mg l^{-1} standards of aluminium, fluoride, and the organic acid were made up from potassium aluminium sulphate, sodium fluoride and citric acid, respectively. A humic acid sample was obtained from Fluka (Switzerland), M_r 600–1000, and a 100 mg l^{-1} standard was prepared containing a small amount of sodium hydroxide to prevent precipitation. Working standards were prepared daily and standard additions carried out at specified times before injection.

Water Samples

Reservoir water was collected in high-density polythene bottles and analysed the same day. Drinking water was analysed as required from a continuously running tap.

Determination of Aluminium Species by IC

Only the inorganic aluminium fraction, $Al(OH)_x^{(3-x)+}$ (i.e. the labile monomeric fraction excluding the aluminium fluoro species), was determined quantitatively. This was carried out by comparison with injections of pure aqueous aluminium standards (pH 3.0) (see text and figure legends for reference to this particular fraction).

RESULTS AND DISCUSSION

Studies in Synthetic Aluminium Solutions

pH

In previous work,[6] aluminium standards were adjusted to a pH less than 4 to ensure that all the aluminium was present as the simple Al^{3+} hydrated ion. Therefore, as expected, only one peak was observed. However, as explained in the Introduction, multiple peaks were observed when drinking water samples were injected. Since these samples had pH values much greater than 4, further studies were carried out on aluminium standards between pH 4 and pH 7. It was found that apart from the expected reduction in peak height due to the decreased solubility of aluminium, a single peak was obtained in all cases at the same retention time. It was concluded that if hydroxy species such as $Al(OH)^{2+}$ and $Al(OH)_2^{+}$ were present, they were rapidly converted to the simple hydrated Al^{3+} ion in the pH 3 eluent stream, thus giving only one peak. This is supported by the work of Bertsch and Anderson who also found single peaks in partially neturalised aluminium solutions when using their IC method.[9] It was also concluded that the presence of the much slower reacting polynuclear species, such as $Al_2(OH)_2^{4+}$ would be strongly retained because of the high positive charge, and if seen at all would give a very broad baseline disturbance.

Fluoride

During further studies of interfering ions for aluminium determinations by the IC method published previously,[6] fluoride was found to give a severe reduction in the aluminium peak height. At the same time multiple peaks were observed near the solvent front. Further investigations revealed a double peak not quite resolved. Bertsch and Anderson discovered a similar effect in their studies of soil pore waters[9] and comparison with thermodynamic calculations gave results consistent with the formation of AlF^{2+} and AlF_2^{+} species. Although for the work described here the two peaks near the solvent front were not quite resolved enough for accurate integration, the relationshiop between the relative peak height ratio and the pH for a fixed level of aluminium was also consistent with the formation of the above mentioned species. Thus, a high aluminium-to-fluoride ratio favoured the appearance of only one peak (AlF^{2+}), whereas the converse produced two strong peaks (AlF^{2+} and AlF_2^{+}). The pH was also important, a low pH favouring AlF^{2+}. From these results it was concluded that the aluminium fluoro species did not dissociate significantly during passage through the IC column. This is supported by the slow rate of formation as shown in Figure 1, where successive injections of an aluminium standard containing added fluoride showed that the reaction between aluminium and fluoride took approx. 30 min to reach equilibrium.

Organic Acids

If, as is generally accepted, aluminium forms complexes with organic acids such as humic/fulvic acids in natural waters, then the complexes are likely to be neutral or

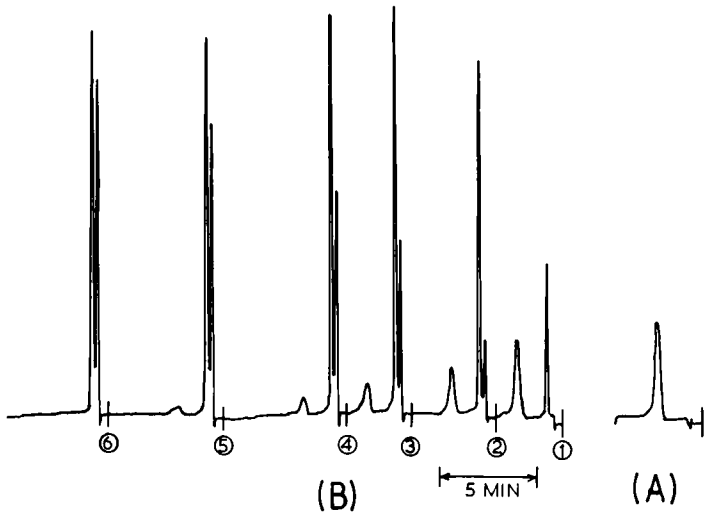

Figure 1 Effect of added fluoride on a standard aluminium solution. Chromatographic conditions: eluent, 0.09 M K_2SO_4 (pH 3.0); detection, same as post-column reaction conditions stated in the Materials and methods section. Sample: (A) 100 μl of a 0.1 mg l^{-1} aluminium standard, pH 3.0; (B) successive 100 μl injections (Nos. 1–6) of (A), started immediately after the addition of fluoride to produce a final concentration of 0.5 mg l^{-1}.

negatively charged. Therefore, assuming no dissociation during IC these organic complexes would come out unretained on the solvent front. To test this, 0.1 ppm aluminium standards were prepared containing, separately, citric acid and humic acid at the 10 ppm level and adjusted to pH 4. When analysed by the IC method, a large drop in the aluminium signal was observed in both cases, coupled with the appearance of a sharp peak on the solvent front. Interestingly, when humic acid was added to drinking water at a pH of 7.5, no apparent reaction occurred with the labile monomeric (inorganic) aluminium already present, even after two hours. However, when the drinking water sample was adjusted to pH 4, a significant reaction occurred (a large reduction in the inorganic aluminium peak height) after about 10 min (Figure 2). This indicates that the reaction between humic acids and inorganic aluminium is very slow or unfavourable unless the pH is relatively low. Bertsch and Anderson also observed peaks close to the solvent front when investigating mixtures of citric and oxalic acids with aluminium standards,[9] though there were indications that the citrate aluminium complex was quite labile, with some decomposition during chromatography.

Studies on Natural and Potable Waters

From the results described above it was apparent that the extra peaks obtained in the drinking water analysis shown in the previous paper[6] could be due to fluoride and/or organic complexes of aluminium. Further studies were carried out and Figure 3 shows a drinking water sample before and after the addition of fluoride and zinc. The eluent strength was reduced for this work to increase retention

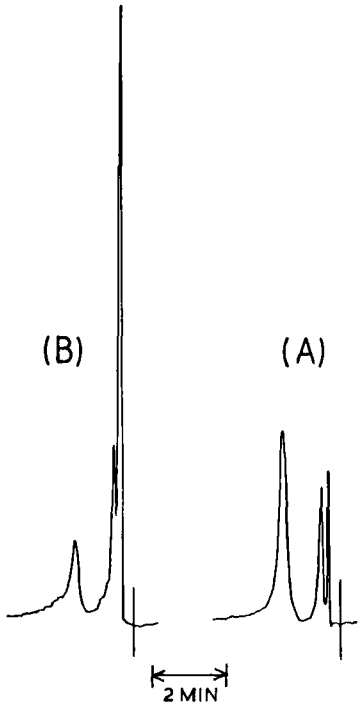

Figure 2 Effect of added humic acid on a drinking water sample. Chromatographic and detector conditions as in Figure 1. Sample: (A) 100 μl of a Plymouth drinking water sample after adjustment to pH 4.0; (B) 100 μl of (A) after the addition of humic acid to a concentration of 10 mg l^{-1} and allowed to stand for 10 min before injection.

times, thereby giving better differentiation between the peaks. Zinc was added as it is a possible interferent and if present in significant amounts may be mistaken for an aluminium species. From Figure 3 it can be seen that the conditions chosen were sufficient to differentiate the zinc from the two aluminium fluoro complexes, but there was a major overlap between one of the aluminium fluoro complexes (AlF_2^+) and the small peak at the solvent front which was presumed to be an aluminium/organic acid complex. Although peak overlap at the beginning of the chromatogram is likely to make quantitative estimation of the aluminium fluoro species difficult to calculate, it was considered that valuable speciation information could still be obtained by the short-column technique. In particular, the direct determination of the labile monomeric fraction (excluding the fluoro species) is possible. In addition, a semi-quantitative estimation of the aluminium fluoro species can be made if the fluoride content is small compared to the concentration of free aluminium. In this situation there will only be one aluminium fluoro peak, namely, the later eluting AlF^{2+}. This should not overlap too much with any peak on the solvent front resulting from the presence of aluminium organic species.

With these factors given due consideration, a preliminary study was carried out on fresh and potable waters in the Plymouth area (south-west England), to

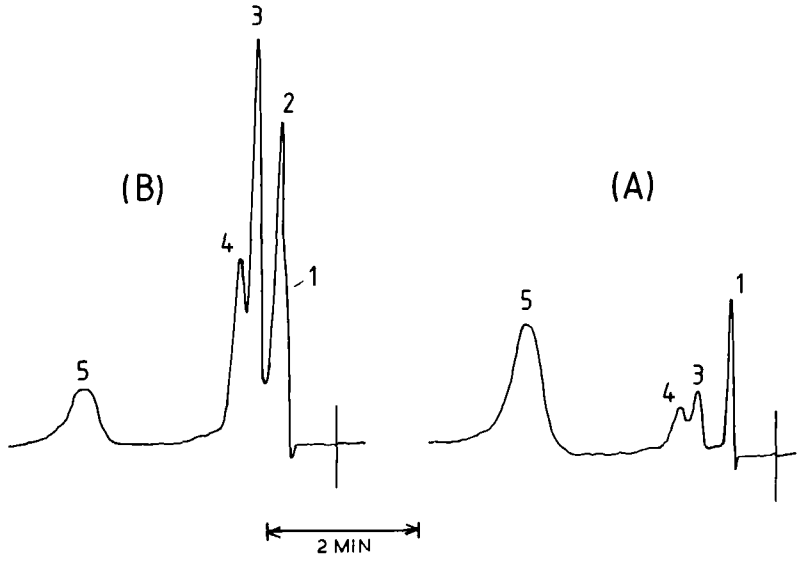

Figure 3 Effect of added fluoride and zinc on a drinking water sample. Chromatographic and detector conditions as in Figure 1 except eluent is 0.08 M K_2SO_4. Sample: (A) 100 μl of a Plymouth drinking water sample, pH 7.7; (B) 100 μl (A) after the addition of fluoride and zinc to a concentration of 0.5 mg l^{-1} and 0.1 mg l^{-1}, respectively (final pH 7.5). Peak interpretation: 1, non-labile monomeric aluminium; 2, AlF_2^+; 3, AlF^{2+}; 4, Zn(II); 5, $Al(OH)_x^{(3-x)+}$.

ascertain the change in aluminium speciation, if any, before and after passage through a potable water treatment plant. Most of the drinking water supplied to the city of Plymouth is derived from Burrator reservoir. This is situated on the south-western edge of Dartmoor, a region of bare moorland, average height approx. 350 m. The water drains into the reservoir from peaty soil which overlays a massive granite Batholith. Rainfall averages about 250 cm a year brought in mainly by a westerly airstream from the relatively pollution-free north Atlantic ocean. The water from Burrator reservoir, which is very soft, is piped to a local treatment plan plant where it undergoes alum treatment, filtering and pH adjustment before being delivered to the homes in the city. Comparison of the reservoir water and tap water revealed major changes in aluminium speciation brought about the alum treatment. Figure 4 shows typical ion chromatograms for the above mentioned waters during a period of normal rainfall, i.e. no storms or prolonged drought. The results from Figure 4 (i.e. peak 3, reflecting the concentration of the labile monomeric fraction excluding fluoro species) are shown in Table 1 compared with results from the Pyrocatechol Violet (PCV) method of Dougan and Wilson (10), and graphite furnace atomic absorption spectrophotometry (GFAAS). Considering the IC results, the most striking difference is the virtual disappearance of the organic aluminium peak (peak 1, the non-labile monomeric fraction) and the large increase in the inorganic aluminium peak (peak 3, labile monomeric, excluding the fluoro species). This is perhaps not too surprising as the alum treatment is used mainly to remove the coloured organic

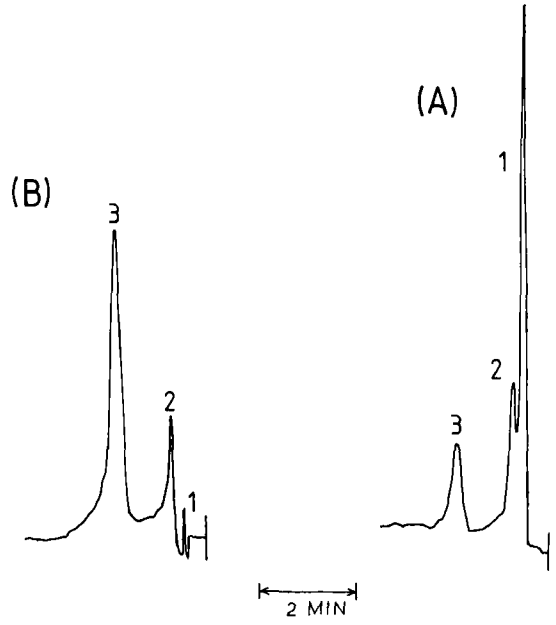

Figure 4 Comparison of aluminium speciation in reservoir and drinking water using ion chromatography. Chromatography and detector conditions as in Figure 1. Sample: (A), 100 μl of Burrator reservoir water (pH 5.9); (B), 100 μl of Plymouth tapwater (pH 7.9). Peak interpretation: 1, non-labile monomeric alouminium; 2, AlF^{2+}; 3, $Al(OH)_x^{(3-x)+}$. Concentrations for the inorganic aluminium species, peak 3, were obtained by comparison with pure aqueous aluminium standards (see Table 1).

Table 1 Results for aluminium species in reservoir and drinking water by three different methods[a]

Sample	*Technique*		
	GFAAS	*PCV*	*IC*[b]
Burrator reservoir	170(4)	53(10)	12(8)
Plymouth tapwater	93(10)	50(10)	44(3)
Remarks	total	total monomeric	labile monomeric

[a]The concentrations shown ($\mu g l^{-1}$) are means of three determinations with %RSD in parentheses. Same samples as in Figure 4.

[b]Peak 3, Figure 4.

matter in the water by co-precipitation. It is therefore quite likely to remove the organic aluminium complexes associated with humic/fulvic acids. The higher level of inorganic aluminium in the tap water can be attributed to the high pH. The results shown in the table is in fact higher than the solubility curve for aluminium hydroxide predicts ($27 \mu g l^{-1}$ at pH 8), but oversaturation so soon after fresh aluminium hydroxide precipitation at the treatment plant is not unexpected. The

Table 2 Concentrations of labile monomeric aluminium (excluding fluoro species) in reservoir and drinking water over a two-week period

	pH	*Concn. Al* ($\mu g\, l^{-1}$)[a]
Burrator reservoir		
1	6.1	6
2	5.9	12
3	5.8	9
Plymouth tapwater		
1	6.9	45
2	7.7	32
3	7.9	44
4	8.1	41
5	7.7	51

[a]Peak 3.

PCV method measures total monomeric aluminium and interestingly, this fraction shows little change from reservoir to drinking water. As expected the aluminium fluoro species (peak 2) overlapped with the organic aluminium peak. Even so, the chromatograms suggest that the fluoro complex is relatively unaffected by passage through the water treatment plant. Comparison with results from fluoride addition studies on aluminium standards, described in the previous section, suggests that the aluminium fluoro peak (peak 2) in the tapwater is between 5 and 10 $\mu g l^{-1}$ with respect to aluminium. The total aluminium concentration measured by GFAAS gives a little more speciation information, except perhaps a measure of the polymeric/colloidal fraction and serves mainly to show that the water conforms to the EEC recommended maximum aluminium concentration of 200 $\mu g l^{-1}$.

Further reservoir and potable water samples were taken over a two-week period and analysed solely the the IC method, using measurements of peak 3 to obtain the labile monomeric fraction, excluding fluoro species. The results are shown in Table 2 and indicate a relatively stable situation with regard to water treatment over this period. In all cases the concentration of labile monomeric aluminium in the drinking water was significantly higher than theoretical calculations of amorphous aluminium hydroxide solubility would suggest. This indicates either the solubility model is inaccurate or the water is not yet in equilibrium and is supersaturated.

CONCLUSION

The results from this study indicate that the short-column IC technique could be a useful alternative to the Driscoll fractionation approach. The particular advantage of the IC method is the direct determination of the most important fraction as far as fish toxicity is concerned, namely, $Al(OH)_x^{(3-x)+}$. The IC method also allows for the first time a direct study of aluminium fluoro species, without relying solely

on thermodynamic calculations. However, for more precise determinations of the fluorine-containing fraction, longer columns may be required to improve resolution. The organic aluminium fraction can certainly be differentiated and major changes in concentration easily monitored. Whether it will be possible to obtain reasonably quantitative estimations of this organic aluminium fraction is difficult to say at present. It has also been demonstrated that determinations of the inorganic aluminium fraction can be carried out in quite alkaline conditions (potable water in this case). The Driscoll method presumably would not be able to measure negatively charged inorganic aluminium species above pH 7, as these would pass straight through the cation-exchange column. Studies are now underway comparing the Driscoll fractionation method with the IC method for natural and drinking waters over a wide pH range.

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