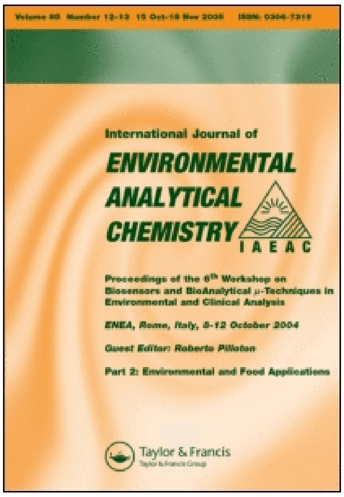

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

An Evaluation of the Use of Cation-Exchange Resin for the Determination of Organically-Complexed Al in Natural Acid Waters

C. A. Backes[a]; E. Tipping[a]
[a] Fresh water Biological Association, The Ferry House, Ambleside, Cumbria, U.K.

To cite this Article Backes, C. A. and Tipping, E.(1987) 'An Evaluation of the Use of Cation-Exchange Resin for the Determination of Organically-Complexed Al in Natural Acid Waters', International Journal of Environmental Analytical Chemistry, 30: 1, 135 — 143
To link to this Article: DOI: 10.1080/03067318708075461
URL: http://dx.doi.org/10.1080/03067318708075461

Intern. J. Environ. Anal. Chem., 1987, Vol. 30, pp. 135–143
Photocopying permitted by license only

Printed in Great Britain

An Evaluation of the Use of Cation-Exchange Resin for the Determination of Organically-Complexed Al in Natural Acid Waters

C. A. BACKES and E. TIPPING†
Freshwater Biological Association, The Ferry House, Ambleside, Cumbria LA22 0LP, U.K.

(*Received August 6, 1986; in final form January 12, 1987*)

The estimation of organically-complexed monomeric Al (Al_{org}) using the cation-exchange method developed by Driscoll was evaluated by comparison with equilibrium-dialysis measurements on solutions containing Al and isolated aquatic humic substances at pH 4–5.3. The cation-exchange method underestimates [Al_{org}] by up to 25%, the extent of the discrepancy increasing with ν (mol Al bound/g humic substances). An empirical equation that allows the correction of [Al_{org}] estimated by cation-exchange is given.

KEY WORDS: Aluminium, cation-exchange, acid waters, complexation, organics, humic substances.

INTRODUCTION

Soluble aluminium is commonly present in acid waters at concentrations of up to 1 mg/l.[1–3] The metal can be present in various chemical forms. Inorganic monomeric aluminium species consist of Al^{3+} and its complexes with hydroxide, fluoride and sulphate.

---

†To whom correspondence should be addressed.

Organic monomeric aluminium is that bound by organic ligands, the most important of which are likely to be humic substances. Colloidal and particulate forms of Al can also exist, ranging from polymerized hydrolyzed aluminium to aluminosilicate particles.

Probably the most widely-used (see e.g. refs. 3–5) method for determining monomeric organic Al—and thereby obtaining, by difference, estimates of monomeric inorganic Al—is the cation-exchange method of Driscoll.[6] Inorganic monomeric species in acid waters are cationic, and are assumed to be adsorbed by the resin, while organic monomeric species, which are anionic, are assumed not to be adsorbed. The method is convenient, reproducible and can be used in the field. However application of the method requires that organically complexed Al in the original solution remains complexed during passage through the resin column, and this is questionable, column residence times being in the range 10–50 seconds. It is therefore important to evaluate the cation-exchange technique by comparison with an equilibrium analytical method.

An attempt at such evaluation was made by Driscoll,[6] who compared, for field samples, Al speciation estimated using cation-exchange with that estimated via measurements with a fluoride-specific electrode. In the latter approach, free fluoride activity and total fluoride concentration were measured using the electrode, and the activity of Al^{3+} was calculated from established equilibrium constants for Al-F complexation, assuming that all the bound fluoride was bound by Al. From the Al^{3+} activity, concentrations of hydroxyl and sulphate complexes of Al were calculated, and finally organic monomeric Al was calculated by subtracting the computed total inorganic monomeric Al from the total monomeric Al. By this procedure it was found that at organic Al concentrations greater than ca. 100 μg/l the fluoride electrode method gave estimates of organic Al greater than those obtained by cation exchange, the values obtained differing by up to a factor of two. Because of the indirectness of the fluoride electrode method, and its inherent assumptions, we do not know whether it overestimated organic Al or the cation-exchange method underestimated organic Al. We therefore considered it necessary to evaluate the cation-exchange method by comparison with a more direct method.

In the work reported here we compared organic Al concentrations estimated by cation-exchange with those obtained by equilibrium dialysis. Experiments were carried out on synthetic solutions containing various amounts of Al, isolated aquatic humic substances (HS), and added base, having compositions similar to those encountered in natural acid waters. The HS chosen had been fractionated in order to remove molecules of lower molecular size that would have passed the dialysis membrane.

MATERIALS AND METHODS

Humic substances

Fulvic acid was extracted from the sediment of a small stream (Mosedale Beck, Cumbria, England) by the method described by Schnitzer and Khan[7] for soil fulvic acid. The isolate was dialysed exhaustively against 10^{-3} M HNO_3 in order to remove as much material of low molecular size as possible. The material used is referred to as MBFA.

Aquatic humic substances were isolated from a stream at Lochard Forest (Central Region, Scotland) by XAD-8 adsorption[8] and from Penwhirn Reservoir (Galloway, Scotland) by XAD-2 adsorption.[9] A large molecular size fraction was obtained from each of the resin-isolated humic preparations by gel chromatography on Sephadex G-75 eluted with 0.01 M NaOH under N_2. The fractions are referred to as LFHS and PRHS respectively.

Determination of Al

The procedure of Dougan and Wilson[10] as modified by Seip *et al.*[3] was followed, scaled down so that a 4 cm^3 sample could be used, and omitting the Fe reduction step, there being negligible Fe in the solutions used. It was found necessary to correct for interference by HS.

Fractionation of Al by cation-exchange

Two sizes of column were used to perform the fractionations. Most work was done with a resin volume of 2.1 cm^3, in a scaled-down version of the original method of Driscoll[6] (Freshwater Fisheries

Laboratory, Pitlochry, Scotland: unpublished). A larger column (volume 10 cm^3) was also employed, as in the original method. Samples and eluant were passed through the columns by gravity or by means of peristaltic pumps. In some experiments (nos. 1–22: see Table I) fractionations were performed with 10^{-3} M NaCl (pH 5.3) as eluant and also, on the same sample, with 2×10^{-3} M $NaNO_3$ adjusted to the pH of the experiment (4.0 or 4.5) with HNO_3. There were no systematic differences between the results with the different eluants. All the reported results refer to 10^{-3} M NaCl as eluant.

Equilibrium dialysis

Experiments with MBFA and LFHS were performed as follows. Solutions (800 or 1000 cm^3) of HS (20 mg/l), 2×10^{-3} M HNO_3 and, initially, 150 µg/l Al as $Al(NO_3)_3$, were adjusted to pH 4 or 4.5 with NaOH. A pair of bags made from thoroughly cleaned Visking dialysis tubing was added, each bag containing 5 or 8 cm^3 of 2×10^{-3} M HNO_3 adjusted to the appropriate pH with NaOH. After stirring overnight—a time previously established as adequate for inorganic monomeric Al to reach dialysis equilibrium—the pH was checked, and the two dialysis bags together with 100 cm^3 of outside-bag solution were removed for the determination of Al concentrations and for fractionation by cation-exchange (outside-bag solution only), all in duplicate. The experiment was continued by adding a small volume of $Al(NO_3)_3$ solution, readjusting the pH if necessary and adding two new dialysis bags. This was done until results for a range of total Al concentrations (150–850 µg/l) had been obtained.

Experiments with PRHS were performed similarly, except that only 250 cm^3 of outside-bag solution was employed, and a fresh solution was prepared for each experiment.

For the dialysis technique to work perfectly, no humic material should pass the membrane. However in the experiments described above it was found that after equilibration of Al small amounts of HS had passed the membrane to give inside-bag concentrations of up to 3 mg/l, although in most cases the concentration was $\leqq 1$ mg/l. Corrections for this effect were made as follows. At equilibrium the inorganic Al concentration is the same on both sides of the membrane. If A represents the outside-bag solution then, with square brackets denoting concentrations, we have, for monomeric Al

$$[\text{total Al}]_A = [\text{inorganic Al}]_A + [\text{organic Al}]_A \qquad (1)$$

$$= [\text{inorganic Al}]_A + \nu_A[\text{HS}]_A \qquad (2)$$

where ν_A = Al bound/unit weight of HS. Similarly for the inside-bag solution, represented by *B*;

$$[\text{total } Al]_B = [\text{inorganic Al}]_B + \nu_B[\text{HS}]_B. \qquad (3)$$

At equilibrium, the inorganic Al concentrations inside and outside the bag are equal, and if it is assumed that $\nu_A = \nu_B$ then

$$[\text{organic Al}]_A = \frac{[\text{total Al}]_A - [\text{total Al}]_B}{1 - [\text{HS}]_B/[\text{HS}]_A}. \qquad (4)$$

The ratio $[\text{HS}]_B/[\text{HS}]_A$ was in nearly all cases <0.1 (it would be zero for no leakage of HS).

RESULTS AND DISCUSSION

When minimal passage of humic substances through the dialysis membrane occurs, equilibrium dialysis is a suitable technique for determining organically bound and inorganic (dialysable) Al. With membranes of sufficiently small pore size, the method can be used on natural samples,[11] although there may be problems due to Donnan effects and adsorption of Al onto the dialysis membrane or container walls, especially at $\text{pH} > 5$.[12] In the present study Donnan effects were rendered negligible by working at an ionic strength of 2×10^{-3} M: calculations, based on a study[12] of Al complexation by an aquatic humic fraction, showed that in our experiments the difference in Al concentrations across the membrane due to the charge on the HS would have been less than 1%. Loss of Al due to adsorption would not have affected our results, since it was the Al speciation at equilibrium (i.e. after any adsorption had taken place) that was determined.

The optimal flow rate for the large (10 cm^3) cation-exchange columns was 4 cm^3/min/cm^3 resin, in agreement with Driscoll.[6] For the small (2.1 cm^3) column, an optimum rate of 1.5 cm^3/min/cm^3 resin was found. These flow rates were determined for solutions in which the Al/HS ratio was relatively low (see below).

The complete set of experimental results is presented in Table I. In nearly all cases the cation-exchange method gave lower values of [Al$_{\text{org}}$] than did equilibrium-dialysis. The discrepancy between the results from the two methods depends on the value of ν (mol Al bound/gHS), as shown in Figure 1. The discrepancy worsens as ν increases. From Table I (experiments 23–35) it can be seen that the smaller column gives somewhat lower estimates of [Al$_{\text{org}}$] than does the larger. The results from equilibrium-dialysis and cation-exchange can be related by the empirical expression

$$\nu_{\text{ED}} = \nu_{\text{CE}} + k\nu_{\text{CE}}^2. \qquad (5)$$

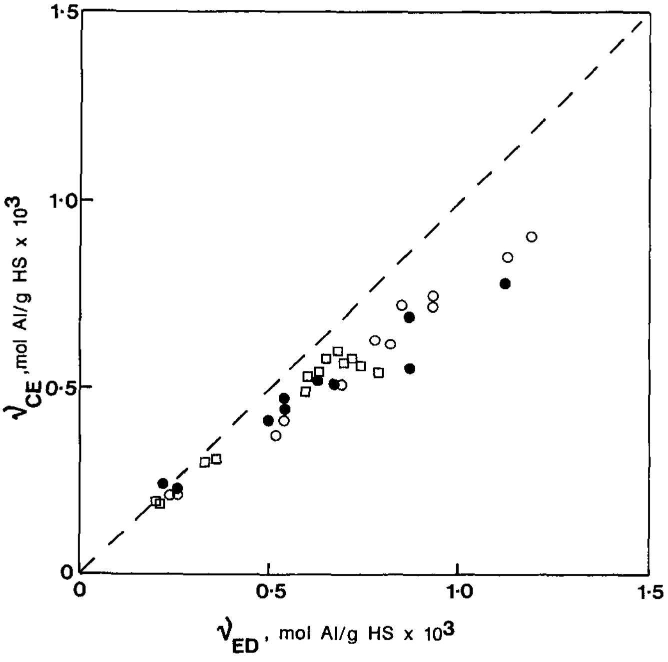

Figure 1 Comparison of values of ν (mol Al bound/gHS) estimated by equilibrium-dialysis and by cation-exchange (small column). Key: ○, MBFA; ●, LFHS; □, PRHS.

Table I Organic Al determined by equilibrium-dialysis (ED) and by cation-exchange (CE). The subscripts *m* and *org* refer to total monomeric and organically-complexed Al. Note that a humic concentration of 1 mg/l corresponds approximately to 0.5 mg/l dissolved organic carbon

Expt.	Type of HS	[HS], mg/l	pH	$[Al_m]$, μM	$[Al_{org}]$, μM		
					ED	CE(small)	CE(large)
1	LFHS	20	4.0	5.6	5.2	4.5	—
2	LFHS	20	4.0	11.9	10.0	8.1	—
3	LFHS	20	4.0	16.7	10.7	8.7	—
4	LFHS	20	4.0	22.6	13.3	10.1	—
5	LFHS	20	4.0	31.5	17.4	10.9	—
6	LFHS	20	4.5	5.6	4.4	4.7	—
7	LFHS	20	4.5	11.9	10.7	9.4	—
8	LFHS	20	4.5	16.3	12.6	10.4	—
9	LFHS	20	4.5	21.5	17.4	13.7	—
10	LFHS	20	4.5	28.9	22.2	15.6	—
11	MBFA	20	4.0	5.6	5.1	4.2	—
12	MBFA	20	4.0	11.5	10.3	7.4	—
13	MBFA	20	4.0	17.8	13.7	10.1	—
14	MBFA	20	4.0	21.9	15.5	12.5	—
15	MBFA	20	4.0	27.0	17.0	14.3	—
16	MBFA	20	4.0	30.4	18.5	14.9	—
17	MBFA	20	4.5	5.6	4.8	4.1	—
18	MBFA	20	4.5	11.5	10.8	8.2	—
19	MBFA	20	4.5	17.8	16.4	12.3	—
20	MBFA	20	4.5	21.1	18.6	14.3	—
21	MBFA	20	4.5	27.4	22.5	17.0	—
22	MBFA	20	4.5	29.6	23.7	18.1	—
23	PRHS	10	4.5	14.0	7.0	5.7	5.7
24	PRHS	10	4.6	7.3	6.0	5.3	5.3
25	PRHS	10	4.6	14.3	7.9	5.4	6.2
26	PRHS	10	4.6	15.0	6.3	5.4	6.2
27	PRHS	10	4.7	12.6	7.4	5.6	5.3
28	PRHS	10	5.3	6.2	5.9	4.9	5.1
29	PRHS	20	4.1	35.2	13.6	12.0	13.4
30	PRHS	20	4.2	34.0	14.3	11.6	13.0
31	PRHS	20	4.5	26.2	13.0	11.6	12.8
32	PRHS	20	4.7	7.4	7.2	6.1	6.4
33	PRHS	20	5.1	6.7	6.6	6.0	6.0
34	PRHS	30	4.5	6.4	6.2	5.7	5.8
35	PRHS	30	5.1	6.3	5.9	5.6	5.8

For the large column $k = 2.2 \times 10^5$ gHS/mol Al (13 points, $r = 0.93$), for the small column $k = 4.0 \times 10^5$ gHS/mol Al (35 points, $r = 0.98$). If values of $[Al_{org}]$ obtained by equilibrium-dialysis are assumed to be the true ones, then Eq. (5) can be used to correct values obtained by cation-exchange, given an estimate of [HS].

A probable explanation for the discrepancies described above is provided by the results shown in Figure 2. These refer to experiments with the cation-exchange columns in which the effect of flow rate was examined as a function of *v*. It is seen that although satisfactory performances are given by both large and small columns at low *v*, at higher values of *v* it becomes impossible to obtain a plateau region in the plot of $[Al_{org}]$ against flow rate. The difficulty cannot be overcome simply by increasing the flow rate because of the "breakthrough" of inorganic Al at flow rates $> 6\,cm^3/min/cm^3$

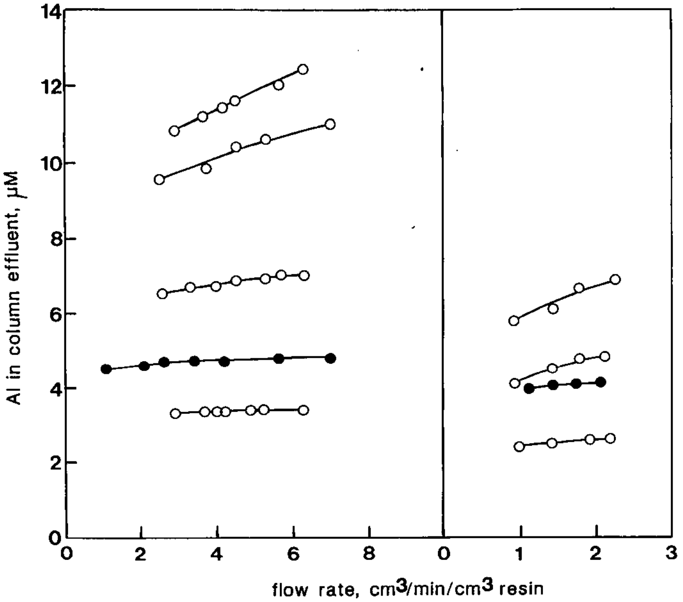

Figure 2 Effect of column flow rate on the estimation of $[Al_{org}]$ at different values of *v*. The results are for 10 mg/l (○) or 20 mg/l (●) PRHS, at pH ~ 4.5. The left-hand plots refer to a $10\,cm^3$ volume of resin, with values of v_{CE} (bottom-to-top) as follows: 0.34, 0.24, 0.67, 1.00, 1.13. The right-hand plots refer to a $2.1\,cm^3$ volume of resin with values of v_{CE} of 0.25, 0.21, 0.47, 0.65.

(large column) or 2.2 $cm^3/min/cm^3$ (small column). The behaviour at high ν most likely reflects Al binding to weaker humic complexing sites, not occupied at lower values of ν. Published data[4] on $[Al_{org}]$ and dissolved organic carbon concentrations indicate that in natural waters, ν can be as high as 10^{-3} mol Al/gHS; therefore poor column performance at high ν can certainly be of practical significance.

In conclusion we can state that the cation-exchange method is a useful indicator of $[Al_{org}]$, but that at high values of ν appreciable underestimation of $[Al_{org}]$ may occur. This however, can be corrected for with Eq. (5). If enough sample is available, a large cation-exchange column is preferable to a smaller one.

Acknowledgements

We thank R. Harriman, (Freshwater Fisheries Laboratory, Pitlochry) for help with preliminary experiments, discussions and comments on the manuscript. T. J. Sullivan (Northrop Services, Corvallis, Oregon) also made useful comments on the manuscript. We are grateful to J. Hawksford for typing the manuscript. This work was carried out under EEC contract ENV.865.UK. Additional support came from the Royal Society Surface Waters Acidification Project and the Natural Environment Research Council.

References

1. C. T. Driscoll, J. P. Baker, J. J. Bisogni and C. L. Schofield, *Nature* **284**, 161 (1980).
2. C. L. Schofield, *Acid Rain/Fisheries* (R. E. Johnson, ed.) (Amer. Fish. Soc., Bethesda, Maryland, 1982), pp 57–67.
3. H. M. Seip, L. Müller and A. Naas, *Water Air Soil Poll.* **23**, 81 (1984).
4. N. M. Johnson, C. T. Driscoll, J. S. Eaton, G. E. Likens and W. H. McDowell, *Geochim. Cosmochim. Acta* **45**, 1421 (1981).
5. R. F. Wright and O. K. Skogheim, *Vatten* **39**, 301 (1983).
6. C. T. Driscoll, *Intern. J. Environ. Anal. Chem.* **16**, 267 (1984).
7. M. Schnitzer and S. U. Khan, *Humic Substances in the Environment* (Marcel Dekker, New York, 1972).
8. E. M. Thurman and R. L. Malcolm, *Environ. Sci. Technol.* **15**, 464 (1981).
9. R. F. C. Mantoura and J. P. Riley, *Anal. Chim. Acta* **76**, 97 (1975).
10. W. K. Dougan and A. L. Wilson, *Analyst* **99**, 413 (1974).
11. B. D. LaZerte, *Can. J. Fish. Aquat. Sci.* **41**, 766 (1984).
12. C. A. Backes and E. Tipping, *Water Res.* **21**, 211 (1987).