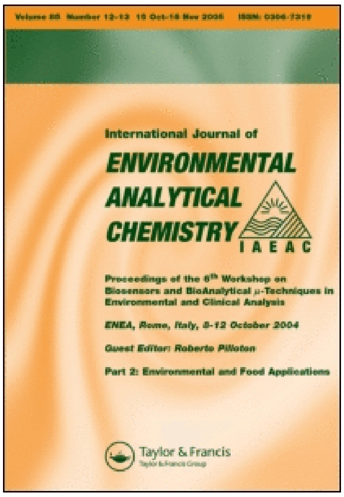

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A Procedure for the Fractionation of Aqueous Aluminum in Dilute Acidic Waters

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A Procedure for the Fractionation of Aqueous Aluminum in Dilute Acidic Waters

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A procedure was developed for the fractionation of aqueous aluminum. This procedure results in the determination of acid-soluble aluminum, non-labile monomeric aluminum and labile monomeric aluminum. Acid-soluble aluminum is thought to include colloidal aluminum and extremely non-labile organic complexes. Non-labile monomeric aluminum is thought to include monomeric alumino-organic complexes. Labile monomeric is comprised of aquo aluminum as well as inorganic complexes of aluminum. The inorganic speciation of aluminum may be calculated by using labile monomeric aluminum, pH, fluoride and sulfate data with a chemical equilibrium model.

This procedure was evaluated using synthetic and natural water solutions. In natural waters, levels of labile monomeric aluminum increased exponentially with decreases in solution pH, while non-labile monomeric aluminum was strongly correlated with organic carbon concentration. Non-labile monomeric aluminum was observed to be relatively insensitive to changes in solution pH. Results of the aluminum fractionation procedure were in relative agreement with an independent evaluation using the fluoride ion selective electrode.

KEY WORDS: Acidic deposition, aluminum, alumino-organic complexation, aluminum speciation.

INTRODUCTION

Aluminum is the third most abundant element within the earth's crust.[1] It occurs primarily in aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks and as clay minerals in well-weathered soils. In high elevation, northern temperate regions, the soils encountered are generally podzolic.[2] The process of podzolization involves the transport of aluminum from upper to lower soil horizons by organic acids leached from foliage as well as from decomposition in the forest floor.[3-6] Ugolini *et al.*[7] have observed that during podzolization there is little mobilization of aluminum from the adjacent watershed to surface waters. Concentrations of dissolved aluminum are low in most circumneutral waters due to the relatively low solubility of natural aluminum minerals. Stumm and Morgan[8] report a median aluminum value of $10\,\mu g\ Al \cdot l^{-1}$ for terrestrial waters, while Bowen[9] gives an average concentration of $240\,\mu g\ Al \cdot l^{-1}$ for freshwaters including bogs.

It has been hypothesized that mineral acids from acidic deposition have remobilized aluminum previously precipitated within the soil during podzolization or held on soil exchange sites.[10] Elevated levels of aluminum have been reported for acidic waters within regions that are receiving elevated inputs of acidic deposition.[10-16]

Elevated levels of aluminum in dilute (low ionic strength) acidic waters are of interest because: (1) aluminum is an important pH buffer,[13,17-19] (2) aluminum may influence the cycling of important elements like phosphorus[13,20] and organic carbon,[13,21] and (3) aluminum is potentially toxic to aquatic[22] and terrestrial organisms.[23] An understanding of the speciation of aluminum is essential for the evaluation of these processes.

Dissolved monomeric aluminum occurs as aquo aluminum, as well as hydroxide, fluoride, sulfate and organic complexes.[24,25] Past investigations of aluminum have often ignored non-hydroxide complexes of aluminum.[10,26,27] More recent studies of Driscoll *et al.*[28] and Johnson *et al.*[29] have demonstrated the significance of organic and fluoride complexes of aluminum in dilute acidic surface waters.

Baker and Schofield[22] observed that aluminum toxicity varies with pH and life history stage of white suckers (*Catostomus* *commersoni*) and brook trout (*Salvelinus fontinalis*). Aluminum solutions (>100 to $200\,\mu g\ Al \cdot l^{-1}$) resulted in reduction of survival of fish larvae. Aqueous hydroxy-aluminum forms were considered to be the most toxic to fish. pH, natural organic and inorganic (e.g. F^-) ligands significantly influence aluminum toxicity.[22,28] Elevated levels of soluble ligands restrict aluminum hydrolysis and mitigate aluminum toxicity to fish.

In terrestrial systems, Ulrich *et al.*[23] have hypothesized that acidic deposition has reduced forest productivity. Vegetation mortality is thought to occur from dissolution of aluminum mediated by mineral acids and subsequent uptake by fine roots. While considerably less well understood than aquatic toxicity, the work of Moore[30] suggests that aluminum toxicity to vegetation is also linked to aqueous speciation.

In view of the current interest in the effects of acidic deposition and the biogeochemistry of aluminum, it is desirable for researchers to be able to analytically differentiate between forms of aqueous aluminum. In this paper I will present an analytical procedure that can be used to fractionate aqueous aluminum and an evaluation of this procedure using synthetic and natural water samples. Potential errors associated with this technique will be discussed.

ANALYTICAL METHODS

In this methodology three measurements of aluminum were made:

Acid reactive aluminum (Alr):

Solutions were acidified to pH = 1 for 1 h and analyzed using the method of Barnes.[31]

Monomeric aluminum (Ala):

Solutions were rapidly extracted with 8-hydroxyquinoline in methyl isobutyl ketone as described by Barnes.[31]

Non-labile monomeric aluminum (Alo):

Non-labile monomeric and labile monomeric aluminum were separated by passing an aliquot of sample through a column of strongly acidic cation exchange resin (Amberlite 120). The cation exchange column used in this study was 1 cm in diameter and contained 9.5 ml of prepared resin. Batches of resin were prepared by displacing some of the exchangeable hydrogen ion with sodium, resulting in a resin that contained both hydrogen and sodium ions on exchange sites. The amount of sodium on the exchanger was adjusted such that when an eluant of comparable ionic strength to the solutions being analyzed was passed through the exchanger, the effluent pH was similar to the pH of the solutions being analyzed. In this way the pH change that samples experienced when processed through the exchange column was minimized.

This procedure was originally developed to evaluate aluminum chemistry in surface waters and soil solutions from the Adirondack region of New York and the Hubbard Brook Experimental Forest (HBEF), New Hampshire. An eluant ionic strength of 3×10^{-4}, which was comparable to the mean ionic strength of these waters was used.[29,32] In addition, two columns were used with prepared exchanger that resulted in effluent target pH values of 5 and 7. Target pH values of 5 and 7 were chosen because poorly buffered waters in New York[19] and in New Hampshire[29] often have pH values in this range. However, an exchange resin should be prepared so that the pH of processed samples will be comparable to the pH of the solutions being analyzed. If the ionic strength of a sample was less than the ionic strength of the eluant, then the pH of a sample after passage through the exchanger was greater than the target pH. Conversely, if the ionic strength of a sample was greater than the eluant, then the pH of the processed sample was generally less than the target pH of the exchanger.

An aliquot of water sample was placed in a sample reservoir and was passed through the cation exchange column with a peristaltic pump. After an initial volume of sample (50 ml to displace the eluant) was discarded, a volume of exchanger-processed sample, sufficient to perform the aluminum determination, was collected. After the sample was processed, eluant (3×10^{-4} mol $NaCl \cdot l^{-1}$) was passed through the column to rinse the exchanger bed prior to introduction of the next sample. Samples were extracted for analysis of aluminum immediately after processing through the cation exchange column using the method of Barnes.[31]

With these three measurements of aluminum, three aluminum

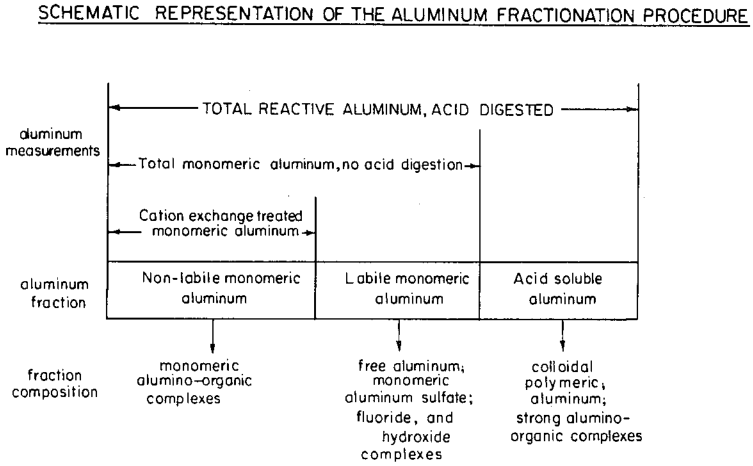

FIGURE 1. A schematic representation of the aluminum fractionation procedure.

fractions were determined (Figure 1).[32] Non-labile monomeric aluminum (Alo) was measured directly and is an estimate of monomeric aluminum that is organically complexed. Labile monomeric aluminum was determined by the difference between monomeric aluminum and non-labile monomeric aluminum (Ala–Alo). This fraction of aqueous aluminum would include aquo aluminum as well as hydroxide, sulfate and fluoride complexes of monomeric aluminum. Acid soluble aluminum, which is acid-reactive aluminum less total monomeric aluminum (Alr – Ala), represents an estimate of the aluminum that requires acid dissolution for the determination. This fraction would include colloidal aluminum, polymeric aluminum and very strongly bound alumino-organic forms.

The inorganic speciation of aluminum was calculated by using measured values of labile monomeric aluminum, pH, fluoride and sulfate with one of the chemical equilibrium models that are currently available.[33] Chemical equilibrium relationships for aqueous aluminum species used in this study are listed in Table I and these calculations are summarized by Driscoll[16] and Johnson *et al.*[29]

To independently evaluate the aluminum fractionation procedure I used the fluoride ion selective electrode. Free fluoride was

TABLE I

Equilibrium relationships used in this study.

Equation	Equilibrium constant	Reference
Hydroxide ligands		
$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$; KOH_1	$= 1.03 \times 10^{-5}$	34
$Al^{3+} + 2H_2O = Al(OH)_2{}^+ + 2H^+$; KOH_2	$= 7.36 \times 10^{-11}$	34
$Al^{3+} + 4H_2O = Al(OH)_4{}^- + 4H^+$; KOH_4	$= 6.93 \times 10^{-23}$	34
Fluoride ligands		
$Al^{3+} + F^- = AlF^{2+}$; KF_1	$= 1.05 \times 10^7$	35
$Al^{3+} + 2F^- = AlF_2{}^+$; KF_2	$= 5.77 \times 10^{12}$	35
$Al^{3+} + 3F^- = AlF_3$; KF_3	$= 1.07 \times 10^{17}$	35
$Al^{3+} + 4F^- = AlF_4{}^-$; KF_4	$= 5.37 \times 10^{19}$	35
$Al^{3+} + 5F^- = AlF_5{}^{2-}$; KF_5	$= 8.33 \times 10^{20}$	35
$Al^{3+} + 6F^- = AlF_6{}^{3-}$; KF_6	$= 7.49 \times 10^{20}$	35
Sulfate ligands		
$Al^{3+} + SO_4{}^= = AlSO_4{}^+$; KS_1	$= 1.63 \times 10^3$	36
$Al^{3+} + 2SO_4{}^= = Al(SO_4)_2{}^-$; KS_2	$= 1.29 \times 10^5$	36

determined by direct potentiometric determination using the fluoride ion selective electrode. Total fluoride was determined by electrode after addition of a total ionic strength adjustor and buffer (TISAB) solution. TISAB decomplexes fluoride, provides a constant solution ionic strength, adjusts solution pH so that hydrogen ion and hydroxyl interference is minimized. With values of free and total fluoride, aquo aluminum (Al^{3+}) activity was calculated with thermodynamic relationships (Table II). In turn, inorganic species of aluminum and organic aluminum were calculated (Table II). While it may be possible to use the fluoride ion selective electrode as an independent method to fractionate aluminum, I have chosen to use it just to evaluate the cation exchange separation procedure. Before the fluoride ion selective electrode can be used with confidence to fractionate aluminum, potential errors associated with application must be evaluated further.

For additional analytical details or description of the study sites from which the Adirondack New York or HBEF surface water

TABLE II

Calculation of aluminum speciation using the fluoride ion selective electrode.[a]

Aluminum bound fluoride

$$[\mathrm{FAl}] = [\mathrm{F_T}] - [\mathrm{F^-}] = [\mathrm{F_T}] - \{\mathrm{F^-}\}/\gamma_1$$

$$[\mathrm{F{-}Al}] = [\mathrm{AlF^{2+}}] + 2[\mathrm{AlF_2{}^+}] + [\mathrm{AlF_3}] + 4[\mathrm{AlF_4{}^-}] + 5[\mathrm{AlF_5{}^{2-}}] + 6[\mathrm{AlF_6{}^{3-}}]$$

$$[\mathrm{F{-}Al}] = \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}\mathrm{KF_1}/\gamma_2 + 2\{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^2\mathrm{KF_2}/\gamma_1 + 3\{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^3\mathrm{KF_3} + 4\{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^4\mathrm{KF_4}/\gamma_1 + 5\{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^5\mathrm{KF_5}/\gamma_2 + 6\{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^6\mathrm{KF_6}/\gamma_3$$

Aquo aluminum

$$\{\mathrm{Al^{3+}}\} = [\mathrm{F{-}Al}](\{\mathrm{F^-}\}\mathrm{KF_1}/\gamma_2 + 2\{\mathrm{F^-}\}^2\mathrm{KF_2}/\gamma_1 + 3\{\mathrm{F^-}\}^3\mathrm{KF_3} + 4\{\mathrm{F^-}\}^4\mathrm{KF_4}/\gamma_1 + 5\{\mathrm{F^-}\}^5\mathrm{KF_5}/\gamma_2 + 6\{\mathrm{F^-}\}^6\mathrm{KF_6}/\gamma_3)^{-1}$$

Hydroxide complexed aluminum

$$[\mathrm{Al{-}OH}] = \{\mathrm{Al^{3+}}\}\mathrm{KOH_1}/\{\mathrm{H^+}\}\gamma_2 + \{\mathrm{Al^{3+}}\}\mathrm{KOH_2}/\{\mathrm{H^+}\}^2\gamma_1 + \{\mathrm{Al^{3+}}\}\mathrm{KOH_4}/\{\mathrm{H^+}\}^4\gamma_1$$

Fluoride complexed aluminum

$$[\mathrm{Al{-}F}] = \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}\mathrm{KF_1}/\gamma_2 + \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^2\mathrm{KF_2}/\gamma_1 + \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^3\mathrm{KF_3} + \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^4\mathrm{KF_4}/\gamma_1 + \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^5\mathrm{KF_5}/\gamma_2 + \{\mathrm{Al^{3+}}\}\{\mathrm{F^-}\}^6\mathrm{KF_6}/\gamma_3$$

Sulfate complexed aluminum

$$[\mathrm{Al{-}SO_4}] = \{\mathrm{Al^{3+}}\}[\mathrm{SO_4{}^{2-}}]\gamma_2\mathrm{KS_1}/\gamma_1 + \{\mathrm{Al^{3+}}\}[\mathrm{SO_4}]\gamma_2\mathrm{KS_2}/\gamma_1$$

Inorganic monomeric aluminum

$$\mathrm{IMAl} = \{\mathrm{Al^{3+}}\}/\gamma_3 + [\mathrm{Al{-}OH}] + [\mathrm{Al{-}F}] + [\mathrm{Al{-}SO_4}]$$

Organic monomeric aluminum

$$\mathrm{OMAl} = \mathrm{Al_a} - \mathrm{IMAl}$$

[a] { }, species activity ($\mathrm{mol \cdot l^{-1}}$); [ ], species concentration ($\mathrm{mol \cdot l^{-1}}$).
[F—Al], aluminum-bound fluoride ($\mathrm{mol \cdot l^{-1}}$).
[Al—OH], hydroxide-complexed aluminum ($\mathrm{mol \cdot l^{-1}}$).
[Al—F], fluoride-complexed aluminum ($\mathrm{mol \cdot l^{-1}}$).
[Al—$\mathrm{SO_4}$], sulfate-complexed aluminum ($\mathrm{mol \cdot l^{-1}}$).
IMAl, inorganic monomeric aluminum ($\mathrm{mol \cdot l^{-1}}$).
OMAl, organic monomeric aluminum ($\mathrm{mol \cdot l^{-1}}$).
$\gamma_1, \gamma_2, \gamma_3$, mean activity coefficients for monovalent, divalent and trivalent species, respectively.
$\mathrm{KF_n}$, $\mathrm{KOH_n}$, $\mathrm{KS_n}$, thermodynamic stability constants for fluoride, hydroxide and sulfate complexes, respectively; see Table I for values.

samples were collected see Driscoll[16] or Johnson *et al.*,[29] respectively.

DISCUSSION OF THE PROCEDURE

Short-term transformations of aqueous aluminum are generally dependent on the concentration of monomeric aluminum (or more specifically the activity of aquo aluminum), rather than particulate aluminum. Because of the tendency for aluminum hydroxy cations to polymerize through double OH bridging when values of solution pH exceed 4.5 (Ref. 37), a considerable fraction of the "dissolved" aluminum reported in many analyses of natural water having neutral or slightly acidic pH values may consist of suspended microcrystals of aluminum hydroxide. Filtration of samples through 0.4 μm pore size membranes, a common practice in clarifying natural water prior to analysis, may fail to remove such material.[38] Therefore, it is desirable to use an analytical technique that is selective for monomeric aluminum, rather than assuming that filtration or centrifugation will remove all suspended material. While detection of aluminum by other analytical techniques may be used with this fractionation procedure, the technique of complexation by 8-hydroxyquinoline and rapid extraction has the advantage of selecting for monomeric aluminum. This technique has been evaluated and discussed by numerous researchers.[31, 37, 39–44]

The cation exchange resin has a strong affinity for aluminum. When solutions are passed through the cation exchange column, there is a competition between aqueous ligands and the exchanger for aluminum. Addition of synthetic aluminum solutions (18 μmol $\mathrm{Al \cdot l^{-1}}$ as $\mathrm{AlK(SO_4)_2}$ and $\mathrm{AlCl_3}$ at pH 5) to the cation exchange column resulted in complete removal ($<0.1\ \mu\mathrm{mol \cdot l^{-1}}$) at all application rates evaluated (up to 6.3 $\mathrm{ml \cdot min^{-1}}$ per ml of exchanger bed volume). Application of synthetic aluminum fluoride solutions (18 μmol $\mathrm{Al \cdot l^{-1}}$ with 1–10 μmol $\mathrm{F \cdot l^{-1}}$ at pH 5) to the cation exchange column revealed that the exchanger competes very effectively with fluoride for aluminum. Aluminum was completely removed from solution ($<0.1\ \mu\mathrm{mol \cdot l^{-1}}$) and effluent fluoride equalled influent levels. Treatment of synthetic and natural solutions by the cation exchange column resulted in the conversion of fluoride from predominantly aluminum bound fluoride to free fluoride.

It would appear that aquo aluminum was stripped from inorganic ligands by the polar cation exchange resin and therefore inorganic forms of aluminum (e.g., $\mathrm{Al^{3+}}$, $\mathrm{AlF^{2+}}$, $\mathrm{AlOH^{2+}}$) were readily removed from solution. Organic ligands, however, form strong complexes with aluminum and therefore more effectively compete with the cation exchange resin. Synthetic solutions of aluminum in the presence of a strong ligand, sodium citrate (18 μmol $\mathrm{Al \cdot l^{-1}}$, 1 mmol sodium citrate $\cdot l^{-1}$ at pH 5) were applied to the cation exchange column. The level of sodium citrate used was comparable to levels of dissolved organic carbon (DOC) observed in Adirondack[16] and HBEF[29] surface waters on an organic carbon basis. In this experiment, detection of aluminum in influent and effluent solutions was complicated because citrate effectively competes with 8-hydroxyquinoline for aluminum and therefore interfered with the analytical determination. As a result, in sodium citrate solutions aluminum had to be determined using the less sensitive and reproducible method of direct determination by atomic absorption spectrophotometry with a graphite furnace. Although this method of aluminum detection was less than satisfactory, the results of this experiment suggested that aluminum was effectively transported through the cation exchange column in the presence of relatively high levels of citrate.

Analog organic ligands with a strong affinity for aluminum (such as citrate) not only interfere with the 8-hydroxyquinoline determination of aluminum but are not entirely representative of organic ligands occurring in natural waters. Therefore, this fractionation procedure was evaluated further and in more detail using samples collected from acidic and non-acidic surface waters in the Adirondack region of New York[16,32] and at the HBEF, New Hampshire.[29,45]

The measurement of non-labile monomeric aluminum in natural water samples was somewhat dependent on the flow rate of solution through the column (Figure 2). My results indicate that at low application rates to the column, the amount of monomeric aluminum (non-labile) passing through the column was sensitive to flow. However, with higher application rates (above 2.7 ml $\cdot$ min^{-1} per ml of exchanger bed volume) the aluminum passing through the column became constant. These results indicate natural alumino-organic complexes exhibit a range of stability. Similar results have been demonstrated by Means *et al.*,[46] who observed labile metal complexes as well as very stable complexes in natural water samples.

The longer the sample retention time in the column, the greater the disruption of alumino-organic species by the resin. This disruption was minimized by operating the exchange column at a relatively high application rate (3.7–4.2 ml $\cdot$ min^{-1} per ml of resin bed volume). As mentioned previously, leakage of inorganic aluminum through the column was not observed at these application rates.

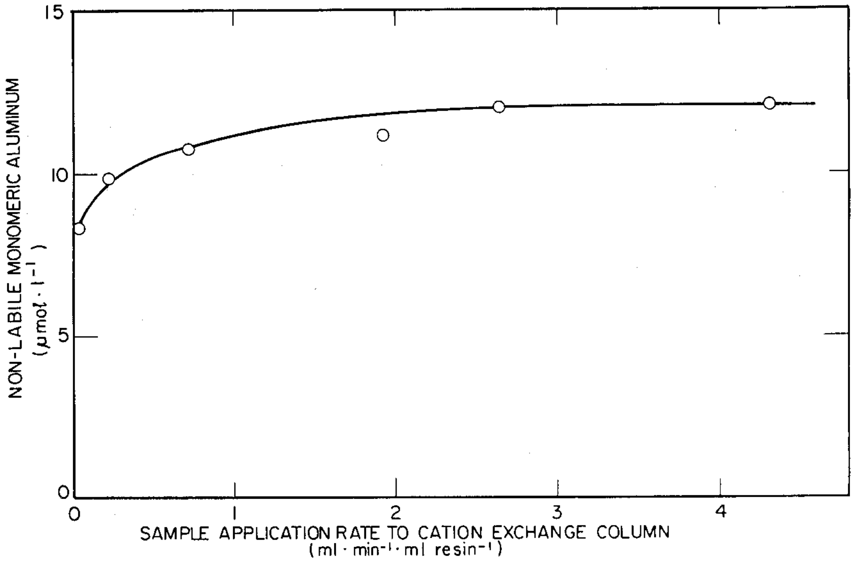

FIGURE 2. Concentration of monomeric aluminum from cation exchange column effluent (non-labile monomeric aluminum) as a function of the sample application rate to the column. This sample was collected from an unnamed stream in the Adirondack region of New York on 7/27/77 (pH = 4.32, TOC = 1.2 mmol $\cdot l^{-1}$).

In this analysis it was assumed that organic matter and alumino-organic complexes passed through the exchanger while aluminum associated with inorganic forms was retained on the exchanger. Therefore, an effective partitioning between inorganic and organic forms of monomeric aluminum was made. Several sources of evidence suggest that this assumption was reasonably valid. In samples from several Adirondack lakes and streams containing a wide range of total organic carbon concentration (0.17–12.0 mmol $C \cdot l^{-1}$) and pH values (4.0–7.2), the amount of TOC leaving the column ranged from 93–105% of that entering the column. Unfortunately, a mass balance on organic carbon is unsuitable to assess the extent to which dissolved organic carbon and organic forms of aluminum are retained within the column due to potential for organic carbon leaching from the organic resin.

Perhaps a better indicator of the limited extent to which organic carbon was retained within the resin was that there was little discernable difference in the UV spectral (200–400 nm) pattern between exchange column influent and effluent (Figure 3). It is evident that absorbance of column effluent exceeded influent absorbance at low wavelengths in some samples. The nature of this discrepancy was not apparent, although organic carbon leaching from the resin cannot be disregarded. UV absorbance patterns observed in this study were similar to those presented by Schnitzer and Khan[47] as being typical of naturally occurring organic carbon.

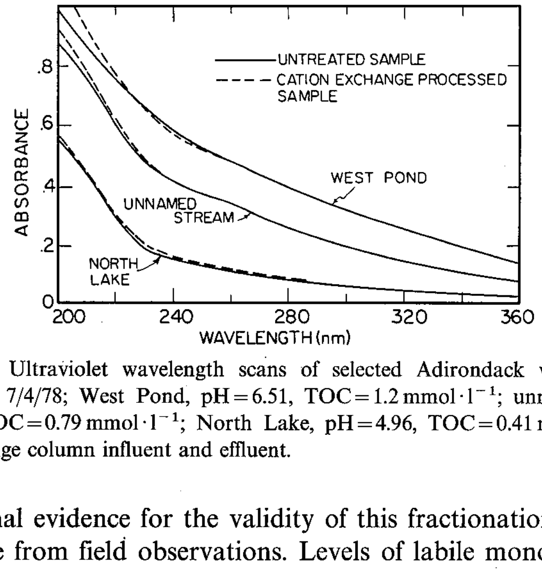

FIGURE 3. Ultraviolet wavelength scans of selected Adirondack water samples (collected on 7/4/78; West Pond, $pH = 6.51$, $TOC = 1.2\,mmol \cdot l^{-1}$; unnamed stream, $pH = 4.37$, $TOC = 0.79\,mmol \cdot l^{-1}$; North Lake, $pH = 4.96$, $TOC = 0.41\,mmol \cdot l^{-1}$) for cation exchange column influent and effluent.

Additional evidence for the validity of this fractionation technique is available from field observations. Levels of labile monomeric (and aquo) aluminum increased exponentially with decreases in pH in Adirondack[16, 32] ($pAl^{3+} = -6.55 + 2.55$ pH; $n = 321$, $r^2 = 0.93$, $p < 0.0001$) and HBEF[29] ($pAl^{3+} = -8.42 + 2.95$ pH; $n = 34$, $r^2 = 0.92$, $p < 0.0001$) surface waters. Non-labile monomeric aluminum was not correlated with pH, but was strongly correlated with organic carbon concentration in both Adirondack[16, 32] ($Alo = -3.26 \times 10^{-6} + 0.0204$ TOC, where Alo and TOC are in $mol \cdot l^{-1}$; $n = 322$, $r^2 = 0.76$, $p < 0.0001$) and HBEF (G. Lawrence, unpublished data, $Alo = -7.3 \times 10^{-7} + 0.0155$ DOC; $n = 69$, $r^2 = 0.85$, $p < 0.0001$) waters.

Driscoll *et al.*[32] observed pronounced temporal variations in aluminum fractions in Adirondack streams. During snowmelt and autumn rainfall events, pH values were low and levels of labile monomeric aluminum were high. During low flow, high pH ($pH > 5.5$) periods in the summer, monomeric aluminum levels were elevated ($> 10\,\mu mol \cdot l^{-1}$) but this aluminum was entirely attributed to non-labile monomeric aluminum. Driscoll *et al.*[32] and Johnson *et al.*[29] have reported that when aquo aluminum was calculated from the labile monomeric aluminum determination, values were compatible with aluminum trihydroxide solubility.

To evaluate the extent to which non-labile monomeric aluminum was sensitive to variations in pH, I spiked aliquots of Adirondack stream water with $1\,mmol \cdot l^{-1}$ Tris buffer and incrementally adjusted the pH over a range of values with 0.1 N HCl. These solutions were incubated for 1 week and analyzed for pH and non-labile monomeric aluminum. Variations in non-labile monomeric aluminum were relatively insensitive to variations in pH (Figure 4).

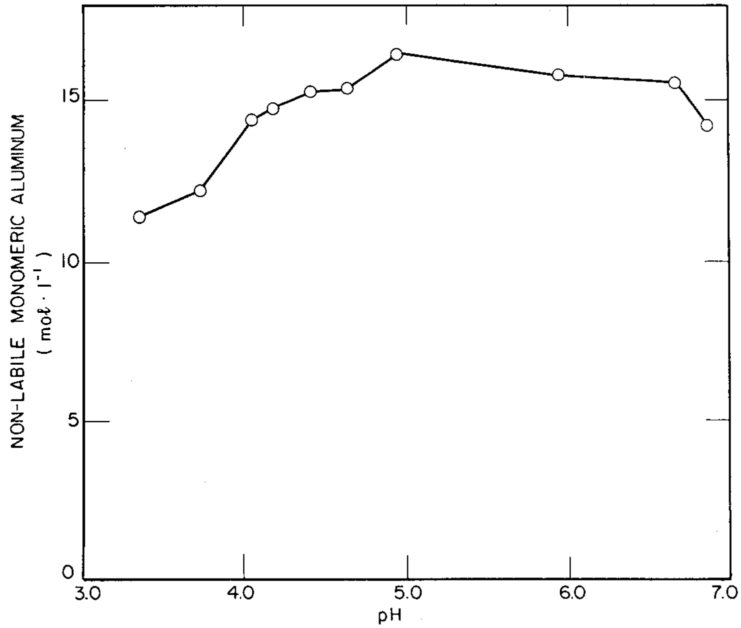

FIGURE 4. Non-labile monomeric aluminum concentration of aliquots of an unnamed stream sample (collected on 5/18/78; initially with $pH = 4.31$, $TOC = 0.70\,mmol \cdot l^{-1}$, $Alo = 15.4\,\mu mol \cdot l^{-1}$) which were buffered ($1\,mmol$ $Tris \cdot l^{-1}$) and pH-adjusted (0.1 N HCl).

The concentration of non-labile monomeric aluminum decreased 24% at pH 3.34 and 15% at pH 6.88 from a maximum value at pH 4.96. The reduction in the magnitude of the alumino-organic complex in the low pH range might be attributed to the disruption of the complex by hydrogen ion. The subtle reduction at higher (pH > 5) values may be due to aluminum hydrolysis and competition of hydroxide ligands with the organic ligands for the aluminum central metal cation.

These results, together with the observation that non-labile monomeric aluminum levels in natural water samples were not appreciably different when analyzed with pH-5 and pH-7 columns suggests that the pH change associated with cation exchange treatment affects the determination of non-labile monomeric aluminum only to a limited extent.

There are a number of potential sources of error associated with this fractionation procedure. 8-Hydroxyquinoline may desorb aluminum associated with particulate matter and therefore result in an overestimation of levels of monomeric aluminum. The exchanger may disrupt relatively labile organic complexes as suggested by Means *et al.*[46] Although this error is minimized by decreasing the sample retention time in the column, it undoubtedly still occurs to some extent. Alumino-organic complexes may exchange/adsorb on resin sites. If the pH within the exchanger bed is low, organic matter may complex hydrogen ion and thereby release aluminum to the resin and/or precipitate within the column. If the pH within the exchanger bed is higher than the sample pH, aluminum associated with organic ligands may hydrolyze and adsorb and/or precipitate within the column. It is noteworthy that all of these latter sources of error result in an underestimation of the organically complexed fraction of monomeric aluminum.

As previously mentioned, the fluoride ion selective electrode may be used to independently evaluate the cation exchange column procedure for the separation of inorganic and organic forms of monomeric aluminum. However, as with the exchange column procedure there are a number of potential sources of error associated with using the fluoride ion selective electrode to fractionate aluminum. These potential errors include hydroxide and non-aluminum cation interference in the determination of free fluoride, the measurement of fluoride associated with particulate matter in the determination of total fluoride, changes in the pH, aluminum and free fluoride levels after sampling and during the period of time the solution is being analyzed, and errors in and lack of thermochemical data used to make the calculations of ion distribution.

A comparison of the two methods was made on selected Adirondack surface water samples. To minimize problems associated with changes during sample storage, pH and free fluoride levels were measured and monomeric aluminum was extracted in the field shortly after sample collection. Organic monomeric aluminum determined by the fluoride ion selective electrode was compared with non-labile monomeric aluminum determined by the column fractionation procedure (Figure 5). In general, agreement was good between the two methods, but organic monomeric aluminum calculated from the fluoride ion selective electrode measurements was generally greater than non-labile monomeric aluminum determined

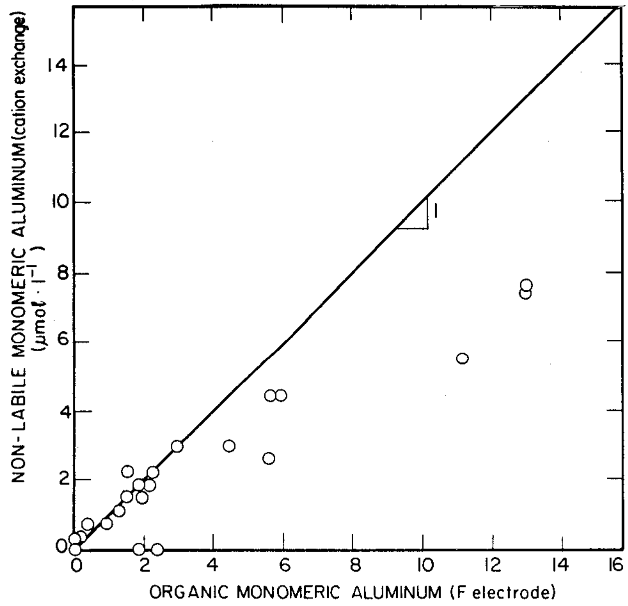

FIGURE 5. A comparison of non-labile monomeric aluminum levels determined using cation exchange column separation procedure with organic monomeric aluminum concentrations calculated using free and total fluoride determinations with thermochemical data (Tables I and II) for selected Adirondack surface water samples (collected on 1/20–1/22/83).

by the cation exchange column procedure. Further research is needed to quantify the errors associated with both fractionation techniques.

CONCLUSIONS

This procedure can be used to fractionate aqueous aluminum into acid-soluble aluminum, non-labile monomeric aluminum and labile monomeric aluminum. Acid-soluble aluminum is thought to include colloidal aluminum as well as very non-labile organic complexes. Non-labile monomeric aluminum is considered to approximate levels of organically complexed monomeric aluminum in solution. Labile monomeric aluminum would include aquo aluminum as well as inorganic complexes of aluminum. This procedure was applied with reasonable success to studies of dilute acidic waters from the Adirondack region of New York and the Hubbard Brook Experimental Forest in New Hampshire. This methodology is significant because it enables researchers to gain a better understanding of the biogeochemistry of aluminum.

Acknowledgements

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