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EVALUATION OF ALUMINUM SPECIATION USING SYNTHETIC AND NATURAL SAMPLES:

FINAL REPORT

by

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INTRODUCTION

Aluminum is the third most abundant element present in the earth's crust and is ubiquitous in both soils and aquatic sediments. When mobilized in lake and stream waters, aluminum has been shown to be toxic to various fish species (Schofield and Trojnar, 1980). The potential for aluminum toxicity, however, is directly related to the chemical form of aluminum present in freshwater systems. The chemical speciation of aluminum is a complex problem that is dependent on a wide variety of chemical and physical conditions that exist within a natural water system. Sample pH, temperature, colloidal material, fluoride and sulfate concentrations, and total organic carbon (TOC) content all influence the chemical speciation and subsequent bioavailability of aluminum.

A major problem in assessing aluminum toxicity has been a failure to adequately identify and quantify the various forms of aluminum present. Many analytical techniques used for aluminum determinations require an acid digestion of the raw water sample prior to chemical analysis. These procedures, while generally adequate for measuring "total" aluminum, do not provide the information necessary for the fraction of aluminum that is actually toxic or potentially toxic to aquatic organisms. Similarly, sample collection and handling protocols can alter aluminum equilibrium relationships so that natural speciation conditions are no longer in effect.

The USEPA-sponsored National Surface Water Survey (NSWS) was initiated in 1984 to document the chemical and biological status of lakes and streams in the U.S. that were identified as potentially sensitive to acid deposition inputs (NAPAP Project Reference No. El-23). One of the goals of this program is to quantify the chemistry of lakes and streams throughout the United States with a focus on areas of low alkalinity waters. Many of the chemical parameters that were selected for inclusion in this survey were chosen to elucidate the factors that affect the availability of aluminum to aquatic systems.

A Workshop on Analytical Methodology and Quality Assurance Protocols for the NSWS was held in Denver, Colorado, in January 1984 to review the proposed procedures for use in the survey. The participants in the workshop included prominent scientists involved with aluminum speciation studies in freshwater systems. The consensus of the participants was that several analytical methodologies have been, or are being used, for aluminum speciation studies and that not enough data exist to reliably compare the various procedures. As a result, the speciation data obtained from freshwater systems may be very different depending on the analytical procedures that have been used. Because of the uncertainty associated with these procedures, the workshop summary recommended that a rigorous methods intercomparison be conducted using at least six different techniques and a large number of natural samples from varied sampling locations. The attendees also recommended the use of synthetic and natural samples with and without the presence of complexing ligands to aid in the interpretation of the methods intercomparison. The results of this study would be invaluable when analyzing historical data sets, interpreting data collected from the NSWS, and conducting future aluminum speciation studies.

The research plan that was developed for this project and the research that has been completed to date address the needs of the scientific community as described in the workshop proceedings.

References

Schofield, C. and J. R. Trojnar. "Aluminum Toxicity to Brook Trout (Salvelinus fontinalis) in Acidified Waters," in T. Y. Toribara, M. W. Miller, and P. E. Morrow (eds.), Polluted Rain, Plenum Press, N.Y. , 1980, pp. 341-363.

RESEARCH PLAN

Background

The analytical procedures that have been used for aluminum speciation studies include colorimetric, fluorimetric, electrometric, and spectroscopic techniques. These procedures have generally been selected based on their sensitivity and/or selectivity for a specific species or class of aluminum compounds. Depending on which method is employed, a range of aluminum species from monomeric labile Al^{3+} to "total" Al is operationally defined as being detected. Intermediate classes of Al compounds, such as inorganically complexed and organically complexed Al, are also classified on the basis of the sample collection, processing, and analysis protocols that are used.

The workshop participants identified six methods of aluminum speciation that have been or are now being used to quantify the various aluminum fractions. They recommended that a rigorous methods intercomparison be conducted in order to correlate the results obtained from different procedures and to help determine which method or methods are most appropriate for aluminum speciation studies. The analytical procedures that were identified include the following:

1. Oxine extraction (May et al., 1979)
2. Oxine extraction with preliminary dialysis (LaZerte, 1984)
3. Lumogallion fluorescence (Hydes and Liss, 1976; Kramer, 1983; Playle et al., 1982)
4. Chelex resin batch ion-exchange (Campbell et al., 1983)
5. Pyrocatechol violet colorimetry (Heliwell et al., 1983)
6. Bound/free fluoride method (LaZerte, 1984)

These procedures involve differing separation and detection techniques being used to provide information on the chemical forms of aluminum present in freshwater systems. The focus of our research plan was to understand the variables that affect aluminum speciation and to conduct extensive laboratory investigations to evaluate the methods listed.

Selection of Methods

A literature search for aluminum chemistry data was carried out prior to the final design of the laboratory intercomparison study. Over 450 literature citations were obtained and reviewed prior to developing a list of candidate methodologies. In addition to the methods that have been identified by the workshop participants, other test procedures were reviewed. Examples of these methods are the American Society for Testing and Materials (ASTM) procedure for Aluminum in Water (D 857-79), a modified oxine extraction procedure used during Phase I of the NSWS, and a semi-automated pyrocatechol method developed for Phase II of the NSWS. A preliminary evaluation of each methodology was conducted at the onset of this study to eliminate any procedures that were not appropriate for speciation studies. The final list of methods that was selected for the intensive intercomparison experiments was submitted to the USEPA Project Officer for approval. These methods, which are listed below, are identical to the ones identified by the workshop participants. Some of the references, however, have been updated to reflect improvements in methodology that have been realized since 1984.

1. Oxine extraction (Campbell et al., 1986)
2. Oxine extraction with preliminary dialysis (LaZerte, 1984)
3. Lumogallion fluorescence (Kramer, 1983)
4. Chelex resin batch ion-exchange (Campbell et al., 1983)
5. Pyrocatechol violet colorimetry (Kerfoot et al., 1986)
6. Bound/free fluoride method (David, 1984)

Study Design

The natural samples used for the methods intercomparison were originally intended to be collected in separate sample containers in conjunction with Phase II of the NSWS. NSWS sampling protocols were to be used for collection. The funding cycle for the comparison work did not, unfortunately, coincide with the Phase II sampling schedule. Efforts to obtain aliquots of the NSWS samples after collection were further complicated by the small sample volume that remained after the routine survey analyses were completed. Our approach in obtaining natural samples, therefore, was to collect new samples with sufficient volume to allow us to thoroughly evaluate each speciation procedure. In selecting the lakes for our study, we attempted to obtain samples from lakes that had previously been sampled in the NSWS. Twelve of the lakes from which we were able to obtain samples had been used in the NSWS. The additional lakes from which we were able to acquire samples had been used in either the Adirondack Lakes Survey conducted in 1984 or the U.S. Fish and Wildlife Survey conducted in 1980.

Samples from Rhode Island, Connecticut, and New York were collected in 13-L high density polyethylene pails and shipped to our laboratory where they were maintained at 4°C prior to analyses. The sampling dates and locations are listed in the water chemistry data section. Samples from Michigan were collected in 500-mL high density bottles and shipped to our laboratory by express delivery in refrigerated mailers. Upon receipt in the laboratory, these samples were also stored at 4°C prior to analysis. The sample collection containers were cleaned with deionized water prior to shipment to the field sites.

Methods Comparison

The lake samples used for this portion of the work were chemically characterized to aid in the interpretation of the aluminum concentration data obtained. Major anion and cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, H^{+}, $NH4^{+}$, $SO4^{2-}$ NO_3^{-}, $C1^{-}$, and PO_4^{3-})analyses were performed as well as dissolved organic carbon (DOC), color, turbidity, acid neutralizing capacity (ANC), fluoride, iron, and conductivity. These data, combined with the water chemistry data from previous sampling periods, were used to relate the observed speciation results to the physical and chemical characteristics of the water. A complete summary of the water chemistry measurements made at our laboratory and those measured during previous surveys are tabulated in the Water Chemistry Data section. Included in this section is a summary of the methods used by our laboratory.

Standard Reference Materials

One of the inherent problems in comparing different analytical procedures that have been used for the determination of aluminum speciation has been a lack of a suitable reference material that simulates the various forms of aluminum found in natural waters. The use of a reference solution that contains aluminum in only a monomeric labile form without any complexing matrix components will not provide a true estimate of the bias and precision of a method when used for natural samples. The presence of organic matter, fluoride, sulfate, phosphate, and iron have all been shown to affect the measured aluminum concentration depending on the analytical methodology being used. The large variance in results reported from the Canadian laboratory intercomparison study entitled Long Range Transport of Atmospheric Pollutants (LRTAP) No. 13 emphasizes this point for not only speciated aluminum but total aluminum as well. The pH of the sample being measured also has a pronounced effect on the aluminum species that will be detected.

In order to provide meaningful data on the comparability of different methodologies, a reference material was needed that contains the matrix components common to natural waters. We have formulated a set of synthetic solutions that contain these matrix components at levels characteristic of freshwater samples. Target concentrations for these solutions were selected from median concentration data from New England and upper Midwestern lakes sampled during the NSWS. Organic complexing ligands have been added to some of these samples to simulate high organic carbon waters that are known to bind free aluminum. The formulation of these samples and preliminary stability data are presented in the Experimental Methods and Results Section.

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ALUMINUM SPECIATION THEORY

The Chemistry of Aluminum in Natural Waters

Aluminum is a Group III element having an atomic weight of 26.98 and atomic number of 13. The ground state electronic configuration is $1S^1 2S^2 2P^6 3S^2 3P^1$ giving it a stable valence of +3 in the oxidized form. The chemistry of aluminum in natural waters is mostly based on the +3 valency state.

Aluminum is the third most abundant element in the earth's crust. With an atomic radius of 0.1432 nm and electronegativity of 1.5, it is too reactive to occur free in nature and therefore occurs in various mineral forms (e.g., gibbsite, feldspars, micas, hornblendes). Aluminum in natural waters is the result of mobilization and dissolution of these minerals due to weathering processes and precipitation reactions. Concentrations of aluminum in natural waters are, however, low ranging from less than 5 μg Al/L to over 200 μg Al/L (Burrows, 1977).

Due to the amphoteric nature of aluminum, its chemistry in the pH range 3-6 is essentially the chemistry of aluminum hydroxides (Hayden and Rubin, 1974). Most natural waters have appreciable concentration levels of ligands such as fluoride, sulfate, silicates, phosphates, and organic acids (e.g., fulvic and humic) that form complexes with aluminum. The concentrations of these complexes are pH dependent (Rubin, 1985). Aluminum solutions in the acidic pH range of 3-6 have also been shown to polymerize (Turner, 1976; Hsu, 1966). Although the types of these polymers in natural waters have not been well characterized, such polymers do occur in acidic natural waters (Laxen and Harrison, 1981).

Aluminum Speciation

Speciation of an element, as defined by Florence (1982), is "the determination of the individual physicochemical forms of that element which together make up its total concentration in a sample." The physicochemical forms of aluminum which have been found to occur in natural waters can be defined under the following categories:

1. Total dissolved aluminum
2. Particulate aluminum
3. Inorganic mononuclear aluminum
4. Polynuclear aluminum
5. Organic mononuclear aluminum

Total Dissolved Aluminum

Total dissolved aluminum is operationally defined as the fraction of aluminum that passes through a membrane filter with 0.45 μm pore size. This fraction is predominantly inorganic mononuclear aluminum and organic mononuclear aluminum. Polynuclear aluminum and colloidal aluminum (Al(OH)3) also pass through this pore size. Wagemann and Brunskill (1975) have studied the effect of filter pore size on concentrations of aluminum in filtrates from natural waters. They found that the concentration of aluminum in the filtrate depends on the pore size of the membrane and the type of membrane used. Kennedy and Zellwager (1974) have also reported that fine-grained particulate material can also pass through a 0.45 μm membrane filter and cause errors up to an order of magnitude or more in the determination of dissolved aluminum in natural waters. Noller et al. (1985) have proposed an analytical scheme for speciation of aluminum in natural waters based on filter pore size and pH levels.

Based on these findings, it is apparent that the operationally defined

Total Dissolved Aluminum fraction based on filtration through a 0.45 μm membrane is meaningful only if it is linked with the type of membrane used and the pH of the sample solution. This also indicates that the measurement of total aluminum in an unfiltered acid-digested sample may provide a more meaningful estimate of the total aluminum reservoir in natural waters.

Particulate Aluminum

Particulate aluminum, as currently defined, is the fraction of aluminum which does not pass through the 0.45 μm pore size membrane filter. This is primarily aluminum adsorbed onto the surfaces of solid particles. The nature of these solid particles has not been well characterized; however, it can be speculated that they include the debris from algae, planktonic organisms, microorganisms such as bacteria, and suspended sediments. The adsorbed aluminum may also include colloidal aluminum and organic aluminum of high molecular weight. The nature of the adsorption has not been studied. It can be assumed that the process of adsorption of aluminum molecules to solid particles may involve chemisorption. Like Total Dissolved Aluminum, the operational definition of particulate aluminum is meaningful only when the type of membrane, the pH of the sample solution, and the filter pore size are known. This is particularly important since some particulate aluminum may still be detected on a 0.2 μm filter membrane after a solution has passed through a 0.45 μm membrane (Kennedy and Zellweger, 1974).

Inorganic Mononuclear Aluminum

Inorganic mononuclear aluminum species include all the simple inorganic complexes as well as the hydrolysis products and the complexes of fluoride, sulfate, phosphate, and silicates (e.g., Al^{3+}, $A1F_X$, $Al(0H)_x$ and $A1(S0_4)_X$). In an acidic (pH 3-6) sample solution, Al^{3+} undergoes a hydrolysis reaction as described by Hem and Roberson (1967). The reactions and their equilibria are depicted below;

1. $Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+$

$$K_1 = \frac{[AlOH^{2+}][H^+]}{[Al^{3+}]}$$

therefore; $p[Al^{3+}] = p[AlOH^{2+}] + pH - pk_1$

where: p is defined as the negative log of the concentration

2. $Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2{}^+ + 2H^+$

$$k_2 = \frac{[AlOH_2{}^+][H^+]^2}{[Al^{3+}]}$$

therefore; $p[Al^{3+}] = p[Al(OH)_2{}^+] + 2\ pH - pk_2$

In a basic sample solution, the following reaction takes place:

3. $Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4{}^- + 4H^+$

$$k_3 = \frac{[Al(OH)_4{}^-][H^+]^4}{[Al^{3+}]}$$

therefore; $p[Al^{3+}] = p[Al(0H)_4{}^-] + 4pH - pk_3$

Similar equilibrium reactions can be described for fluoride and sulfate complexes. These are depicted below;

Fluoride Complexes

4. $Al^{3+} + F^- \rightleftharpoons AlF^{2+}$

$$k_4 = \frac{[AlF^{2+}]}{[Al^{3+}][F^-]}$$

therefore; $p[Al^{3+}] = p[AlF^{2+}] - p[F^-] - pk_4$

5. $Al^{3+} + 2F^- \rightleftharpoons AlF_2^+$

$$k_5 = \frac{[AlF_2^+]}{[Al^{3+}][F^-]^2}$$

therefore; $p[Al^{3+}] = p[AlF_2^+] - 2p[F^-] - \mathbf{pk_5}$

6. $Al^{3+} + 3F^- \rightleftharpoons AlF3$

$$\frac{[AlF_3]}{[Al^{3+}][F^-]^3}$$

therefore; $p[Al^{3+}] = p[AlF_3] - 3p[F^-] - pk_6$

7. $Al^{3+} + 4F^- \rightleftharpoons AlF_4^-$

$$k_7 = \frac{[AlF_4^-]}{[Al^{3+}][F^-]^4}$$

therefore; $p[Al^{3+}] = p[AlF_4^-] - 4p[F^-] - pk_7$

8. $Al^{3+} + 5F^- \rightleftharpoons AlF_5^{2-}$

$$k_8 = \frac{[AlF_5^{2-}]}{[Al^{3+}][F^-]^5}$$

therefore; $p[Al^{3+}] = p[AlF_5^{2-}] - 5p[F^-] - pk_8$

9. $Al^{3+} + 6F^- \rightleftharpoons AlF_6^{3-}$

$$k_9 = \frac{[AlF_6^{3-}]}{[Al^{3+}][F^-]^6}$$

therefore; $p[Al^{3+}] = p[AlF_6^{3-}] - 6p[F^-] - pk_9$

Sulfate Complexes

10. $Al^{3+} + SO_4^{2-} \rightleftharpoons AlSO_4^+$

$$k_{10} = \frac{[AlSO_4^+]}{[Al^{3+}][SO_4^{2-}]}$$

therefore; $p[Al^{3+}] = p[AlSO_4^+] - p[SO4^{2-}] - pk_{10}$

11. $Al^{3+} + 2SO_4^{2-} \rightleftharpoons Al(SO_4)_2^-$

$$K_{11} = \frac{[Al(SO_4)_2^-]}{[Al^{3+}][SO_4^{2-}]^2}$$

therefore; $p[Al^{3+}] = p[Al(SO_4)_2^-] - 2p[SO_4^{2-}] - pk_{11}$

The equilibria for aluminum silicates and phosphates have not been included in this discussion since their concentration levels are low in natural water.

The values for the equilibrium constants, K_n, have been determined independently by several investigators. These values have been compiled in Table 1. The equilibrium constants are important in aluminum speciation studies especially in the Bound/Free Fluoride method for speciating inorganic aluminum species in natural waters.

The hydrolytic reactions in aqueous media have been studied extensively by Rubin (1985). He has recently disproven the existence of $Al(OH)_2^+$ and has proposed a new scheme to illustrate the hydrolysis of aluminum (see Figure 1). These hydrolysis reactions are pH dependent and such pH dependency is illustrated in Figure 2. Manaham (1975) has also indicated that below pH 4.0, $Al(H_2O)_6^+$ predominates; between pH 4.5 and pH 6.5, the species present include $A1(OH)^{2+}$, $Al(OH)_3(s)$, and fluoride and sulfate complexes of aluminum. For pH values greater than 7.0, $Al(OH)4^-$ is the major ionic form of aluminum present.

From Table 1 it is apparent that the equilibrium constants for the sulfate complexes are generally smaller than those for fluorides. Since sulfate is often related to acid rain, however, its influence in aluminum complexation cannot be disregarded. The relationships between free and complexed aluminum for both fluoride and sulfate as a function of pH and different ionic strengths are reported in Roberson and Hem (1969).

Table 1. Equilibrium Relationships for the Important Inorganic Aluminum Complexes

(from Driscoll, 1984)

Equation	Equilibrium Constant	Reference
A. Hydroxide ligands		
$Al^{3+} + H_2O - Al(OH)^{2+} + H^+$	- 1.03×10^{-5}	May et al., 1979
$Al^{3+} + 2H_2O - A1(OH)_2^+ + 2H^+$	- 7.36×10^{-11}	May et al., 1979
$Al^{3+} + 4H_2O = A1(OH)_A'' + 4H^+$	- $6.93 \times 10\text{-}^{23}$	May et al., 1979
B. Fluoride Ligands		
$Al^{3+} + F^- - A1F^{2+}$	- 1.05×10^{7}	Hem, 1968
$Al^{3+} + 2F^- = A1F_2^+$	- 5.77×10^{12}	Hem, 1968
$Al^{3+} + 3F^- = A1F_3$	- 1.07×10^{17}	Hem, 1968
$Al^{3+} + 4F^- = A1F_4^-$	- 5.37×10^{19}	Hem, 1968
$Al^{3+} + 5F^- = A1F_5^{2-}$	- 8.33×10^{20}	Hem, 1968
$Al^{3+} + 6F^- - A1F_6^{3-}$	- 7.49×10^{20}	Hem, 1968
C. Sulfate Ligands		
$Al^{3+} + SO_4^= = A1SO_4^+$	- 1.63×10^{3}	Behr and Wendt, 1962
$Al^{3+} + 2SO_4^= = A1(S0_A)_2^-$	- 1.29×10^{5}	Behr and Wendt, 1962

HYDROLYSIS OF ALUMINUM (III)

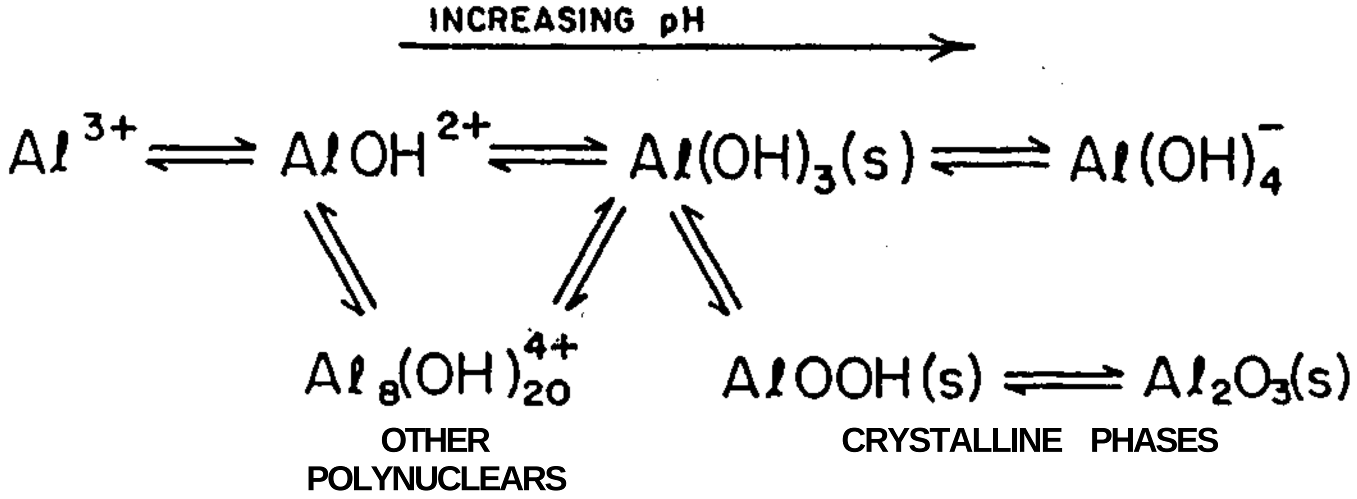

Figure 1. Aluminum III Hydrolysis Mechanisms (from Rubin, 1985)

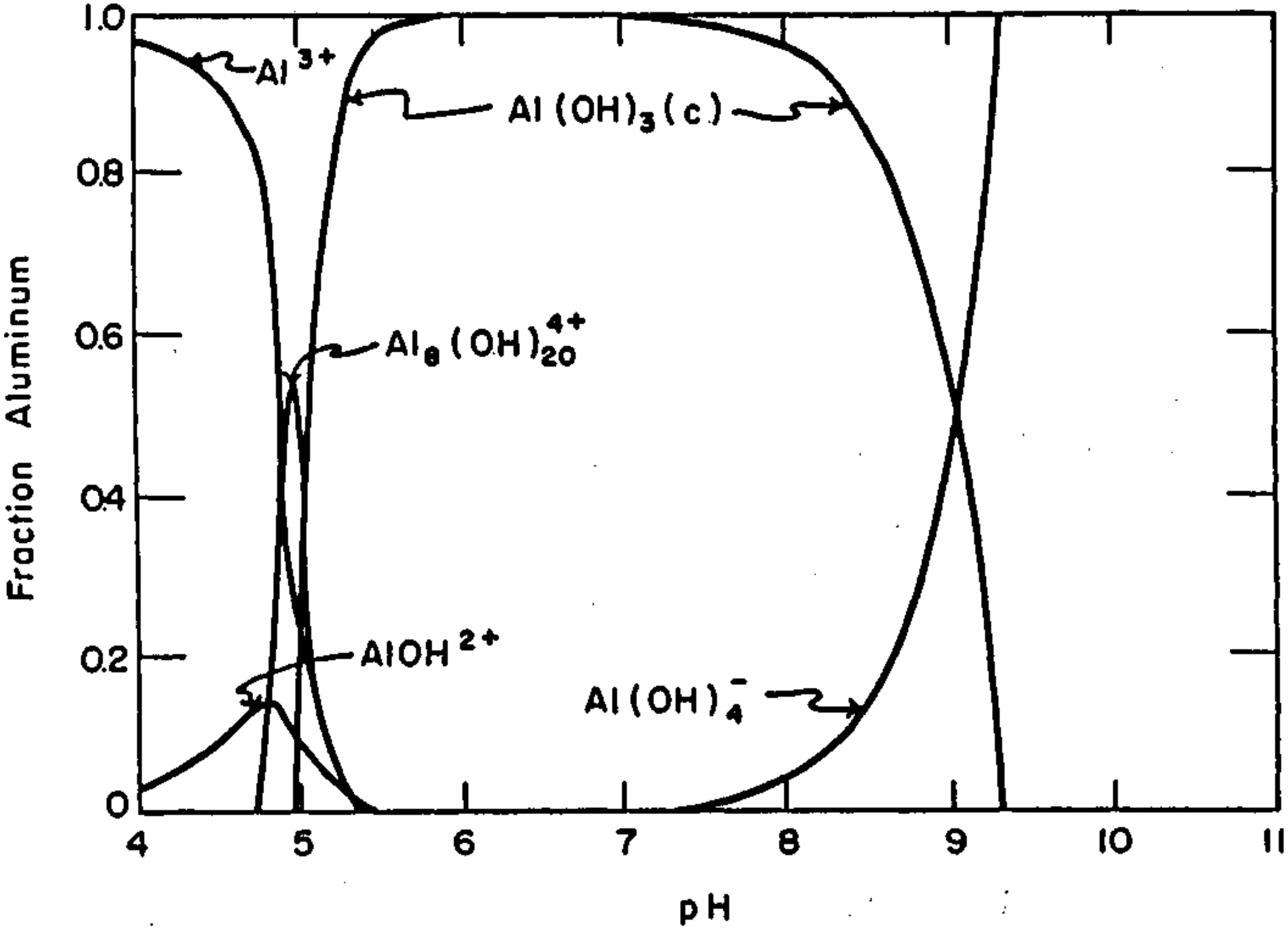

Figure 2. Distribution of Hydrolyzed Aluminum (III) as a function of pH (from Rubin, 1985)

Polynuclear Aluminum

There is no agreement as to the forms and structures of the polynuclear aluminum species which are present in aqueous solutions. There appears to be substantial evidence for the formation of the polymeric species $Al_2(OH)_2^{4+}$ in acidic solutions. Using a computer program based on least squares analysis, Aveston (1965) has indicated that both a dimer and a polycation, $Al_{13}(OH)32^{7+}$, are formed. In their paper, "Detection of Metal Ion Hydrolysis by Coagulation", Matijevic et al. (1961) have suggested the octamer $Al_8(OH)20^{4+}$ as the principal hydrolyzed species. Recently, Rubin (1985) has also provided substantial evidence for the formation of this octamer. The hydrolysis equation which leads to the formation of this polymer has been postulated by Rubin (1985) and is depicted in Figure 1. Polynuclear aluminum species in natural waters have not been well characterized. Data on their concentration levels in natural waters are difficult to find in the literature, presumably due to their low levels.

Organic Aluminum

The types of organic compounds commonly found in natural waters have not been fully characterized. There is evidence, however, for the occurrence of low molecular weight organics such as citric acid, oxalic acid, and lactic acid. The higher molecular weight organics include polyphenols, carboxylic phenols, aromatic polycarboxylates, unsaturated cyclic-hydroxyketones, fulvic, and humic acids. Of all of these organic compounds in natural waters, fulvic, and humic acids are the most important in terms of aluminum chemistry. In most studies, organo-aluminum complexes are assumed to be those of fulvic and humic acids, for which equilibrium and stability constants data are not well known.

The larger organic molecules, including humic matter and polyphenols, which complex with aluminum have a tendency to aggregate, flocculate, and settle to the bottom of lakes, streams, and rivers. Dissolved organic aluminum concentrations, therefore, are dependent on the conditions present during sample collections. Under disturbed conditions, for example, the fraction of organic aluminum can be expected to be higher in concentration because of resuspended bed materials.

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WATER CHEMISTRY DATA

Tables 1-9 present the chemistry data from the 17 lakes that were used for the aluminum speciation comparison studies. Each table contains the Illinois State Water Survey (ISWS) measured concentration data as well as the data from earlier sampling periods. The methods used by the ISWS are described in Table 10. Dissolved inorganic carbon (DIC) and pH values are for air-equilibrated samples. Cation and anion sums omit those ions whose concentrations are below the method detection limit. Values for HCO_3^- are used instead of the NSWS acid neutralizing capacity (ANC) data to derive the sum of anion values. We also do this except in cases where no HCO_3^- values exist, then ANC is used unless ANC <0. Values for SO_4^{2-} are derived from ion chromatography (IC) results and ISWS total aluminum concentrations represent "total dissolved aluminum" determined by inductively coupled plasma spectrometry.

ISWS cation to anion ratios for the 15 lakes with complete chemistry analyses ranged from 0.91-1.71 with a mean ion balance ratio of 1.13 and a standard deviation 0.20. Ion balance ratios tabulated from the NSWS, U.S. Fish and Wildlife, and Adirondack Lakes data ranged from 0.81-1.55 with a mean and standard deviation of 1.13 and 0.18, respectively. In general, there is good agreement between the data collected in earlier studies and our results, despite the differences in sampling dates and variations in sample handling protocols. The similarities in the various data sets allow us to more reliably interpret our speciation results in terms of their applicability to existing NSWS aluminum concentration values.

Table 1. Adirondack Lakes Survey (ALS)

	Little Cherry Patch Pond (ALS #020240) (Collection Period)		Brandy Pond (ALS #020115) (Collection Period)	
Parameter	7/23/84[a]	7/31/87[b]	7/19/84[a]	7/31/87[b]
pH (air-equil.)	7.37	6.50	4.89	5.08
Ca^{2+} (µeq/L)	448.1	413.3	190.1	198.5
Mg^{2+} "	219.6	205.7	54.3	63.9
K^{+} "	12.3	46.0	7.7	43.5
Na^{+} "	934.8	1340.6	602.6	812.9
NH_4^{+} "	<0.9	4.4	<0.9	3.3
H^{+} "	0.0	0.6	12.8	8.3
Σ Cations (µeq/L)	1614.8	2010.6	867.5	1130.4
SO_4^{2-} (µeq/L)	134.6	94.4	92.1	89.4
Cl^{-} "	1069.0	1755.8	595.2	1064.8
NO_3^{-} "	<0.08	0.8	<0.08	0.5
F^{-} "	3.1	3.5	3.7	3.2
ANC "	236.8	164	-2.3	-3.8
HCO_3^{-} "	---	---	---	---
Σ Anions (µeq/L)	1443.5	2018.5	691.0	1157.9
Cond. (µS/cm)	187.5	229	105.9	136.8
Color (PCU)	100	---	240	---
P (µg/l)	36	<40	30	<40
Mn "	55	43	55	49
Fe "	460	312	54	451
Al (tot.) "	77	75	183	69
Al (ext.) "	---	---	---	---
DIC (mg/l)	5.67	---	3.03	---
DOC "	12.2	14.9	19.2	8.39
SiO_2 "	3.4	0.52	5.7	0.39

a. Adirondack Lakes
b. Illinois State Water Survey Data

Table 2. Adirondack Lakes Survey (ALS)

	Follensby Clear Pond (ALS #020116) (Collection Period)		Sochia Pond (ALS #020197) (Collection Period)	
Parameter	**7/19/84**[a]	**7/31/87**[b]	**7/26/84**[a]	**7/31/87**[b]
pH (air-equil.)	7.40	7.17	4.58	4.52
Ca^{2+} (µeq/L)	228.5	227.3	18.0	18.8
Mg^{2+} "	101.2	100.2	7.4	7.2
K^{+} "	10.5	43.5	3.6	46.0
Na^{+} "	72.6	79.8	1.7	3.1
NH_4^{+} "	<0.9	1.7	<0.9	3.9
H^{+} "	0	1.0	23.6	30.1
Σ Cations (µeq/L)	412.8	452.6	57.0	109.1
SO_4^{2-} (µeq/L)	95.8	104.6	53.5	55.4
Cl^{-} "	43.4	58.7	3.7	5.9
NO_3^{-} "	<0.08	0.6	<0.08	0.8
F^{-} "	3.4	2.7	1.2	1.5
ANC "	249.5	223	-23.2	-25.3
HCO_3^{-} "	---	---	---	---
Σ Anions (µeq/L)	392.1	389.6	58.4	63.6
Cond. (µS/cm)	42.7	43.8	14.6	17.3
Color (PCU)	5	---	10	---
P (µg/l)	13	<40	13	<40
Mn "	<6	<3	18	31
Fe "	9	4	89	17
Al (tot.) "	<4	<11	5	<11
Al (ext.) "	---	---	---	---
DIC (mg/l)	2.99	---	0.48	---
DOC "	2.1	2.29	2.1	1.76
SiO_2 "	5.7	0.8	0.1	0.04

a. Adirondack Lakes

b. Illinois State Water Survey Data

Table 3. NSWS - Michigan Lakes
Richardson Lake (NSWS #2B2-075)

	Sample Collection Period	
Parameter	**11/5/84[a]**	**6/26/87[b]**
pH (air-equil.)	6.54	6.14
Ca^{2+} (µeq/L)	37.9	33.1
Mg^{2+} "	26.3	26.6
K^{+} "	13.8	<41
Na^{+} "	9.6	10.2
NH_4^{+} "	0.0	1.7
H^{+} "	0.2	0.7
Σ Cations (µeq/L)	87.8	72.3
SO_4^{2-} (µeq/L)	47.9	41.0
Cl^{-} "	6.8	7.1
NO_3^{-} "	0.0	0.8
F^{-} "	1.1	2.5
ANC "	25.4	12.8
HCO_3- "	18.9	---
Σ Anions (µeq/L)	74.7	64.2
Cond. (µS/cm)	9.3	14.7
Color (PCU)	21	---
P (µg/l)	17.0	<40
Mn "	10.0	3
Fe "	20.0	7
Al (tot.) "	12.0	<11
Al (ext.) "	6.0	---
DIC (mg/l)	0.32	---
DOC "	5.50	4.90
SiO_2 "	0.00	<0.01

a. National Surface Water Survey Data
b. Illinois State Water Survey Data

Table 4. NSWS Lakes - Michigan Lakes

	Casey Lake (NSWS #2B3-027) Sample Collection Period		Lake Annie (NSWS #2B3-058) Sample Collection Period	
Parameter	10/16/84[a]	6/30/87[b]	10/18/84[a]	7/8/87[b]
pH (air-equil.)	8.69	8.75	6.77	5.78
Cl^{2+} (μeq/L)	859.8	907.7	36.4	31.2
Mg^{2+} "	765.8	775.1	27.1	27.2
K^+ "	21.2	<41	11.0	<41
Na^+ "	32.6	35.5	17.0	18.2
NH_4^+ "	0.0	1.7	0.0	1.1
H^+ "	0.0	0.0	0.2	1.6
Σ Cations (μeq/L)	1679.3	1720.0	91.7	79.3
SO_4^{2-} (μeq/L)	74.5	81.7	43.7	57.9
Cl^- "	15.2	16.6	7.9	10.4
NO_3^- "	1.1	4.2	1.5	0.5
F^- "	2.2	2.4	0.9	1.6
AN "	1713.0	1420	32.0	8.8
HCO_3^- "	1500.1	---	24.2	---
Σ Anions (μeq/L)	1593.1	1525.0	78.2	79.2
Cond. (uS/cm)	157.2	158.2	11.4	16.5
Color (PCU)	15	---	11.4	---
P (μg/L)	5.0	<40	13	<40
Mn "	0.0	1	0.0	4
Fe "	30.0	18	10	8
Al tot "	29.0	<11	93	17
Al ext "	1.0	---	12	---
DIC (mg/L)	18.6	---	0.38	---
DOC "	4.00	4.91	3.40	4.16
SiO_2 "	2.53	0.42	0/00	<0.01

a. National Surface Water Survey Data
b. Illinois State Water Survey Data

Table 5. NSWS Lakes - Michigan Lakes

	Ostrander Lake (NSWS #2B3-071) Collection Period		Catract Basin (NSWS #2B3-028) Collection Period	
Parameter	**10/25/84[a]**	**6/15/87[b]**	**10/16/84[a]**	**6/8/87[b]**
pH (air-equil.)	7.59	7.06	8.37	7.37
Ca^{2+} (μeq/L)	207.1	188.0	525.9	480.2
Mg^{2+} "	42.8	40.5	315.1	263.1
K^+ "	9.7	<41	18.7	<41
Na^+ "	10.0	9.3	171.4	210.2
$NH_4{}^+$ "	1.1	---	0.0	2.8
H^+ "	0.0	0.1	0.0	0.0
Σ Cations (μeq/L)	270.7	237.9	1031.1	956.3
$SO_4{}^{2-}$ (μeq/L)	77.4	76.3	104.8	85.8
Cl^- "	9.9	10.2	75.7	65.4
$NO_3{}^-$ "	0.0	2.0	5.5	5.6
F^- "	0.9	1.8	3.8	3.6
ANC "	163.2	123.0	866.5	603
$HCO_3{}^-$ "	140.9	---	777.4	---
Σ Anions (μeq/L)	229.1	213.3	967.2	762.4
Cond. (μS/cm)	22.2	28.8	101.7	90.0
Color (PCU)	15	---	83	---
P (μg/L)	11.0	<40	11.0	<40
Mn "	0.0	1	90.0	7
Fe "	10.0	6	850.0	812
Al (tot.) "	16.0	<11	64.5	39
Al (ext.) "	0.0	---	4.0	---
DIC (mg/L)	1.76	---	9.38	---
DOC "	4.80	5.76	7.15	14.3
SiO_2 "	0.09	<0.01	8.48	0.66

a. National Surface Water Survey Data
b. Illinois State Water Survey Data

Table 6. NSWS Lakes - Michigan Lakes

	Delene Lake (NSWS #2B2-098) Sample Collection Period		Grand Sable (NSWS #2B3-009) Sample Collection Period	
Parameter	10/17/84[a]	7/6/87[b]	10/20/84[a]	8/3/87[b]
pH (air-equil.)	7.24	6.83	8.32	8.11
Ca^{2+} (μeq/L)	125.7	127.7	711.3	687.9
Mg^{2+} "	49.4	48.9	399.8	393.8
K^{+} "	8.7	<41	20.7	43.5
Na^{+} "	14.4	16.3	37.4	36.5
NH_4^{+} "	0.0	1.7	0.5	3.9
H^{+} "	0.1	0.1	0.0	0.0
Σ Cations (μeq/L)	198.3	194.7	1169.7	1165.6
SO_4^{2-} (μeq/L)	28.5	38.1	104.7	116.7
Cl^{-} "	5.4	5.9	9.0	10.4
NO_3^{-} "	0.3	0.5	2.5	1.5
F^{-} "	1.2	2.1	2.2	3.9
ANC "	129.0	102	982.9	---
HCO_3^{-} "	92.3	---	925.9	---
Σ Anions (μeq/L)	127.7	148.1	1044.3	---
Cond. (μS/cm)	19.6	27.2	102.7	111.0
Color (PCU)	45	---	---	---
P (μg/L)	11.0	<40	14.0	<40
Mn "	30.0	1	0.0	<3
Fe "	190.0	17	40.0	8
Al (tot.) "	25.0	<11	9.0	<11
Al (ext.) "	2.0	---	5.5	---
DIC (mg/L)	1.29	---	10.64	---
DOC "	10.30	6.88	11.90	5.37
SiO_2 "	0.80	0.41	5.49	0.60

a. National Surface Water Survey Data
b. Illinois State Water Survey Data

Table 7. NSWS Lakes - Michigan Lakes

	Cranberry Lake (NSWS #2B2-049) Sample Collection Period		Johnson Lake (NSWS #2B1-047) Sample Collection Period	
Parameter	10/20/84[a]	7/30/87[b]	10/22/84[a]	8/13/87[b]
pH (air-equil.)	5.17	4.97	4.58	4.81
Ca^{2+} (μeq/L)	33.4	33.4	57.4	62.4
Mg^{2+} "	18.1	18.9	30.4	28.8
K^+ "	9.7	<41	8.7	<41
Na^+ "	4.3	6.4	6.1	7.7
NH_4^+ "	1.1	1.7	1.7	2.2
H^+ "	6.7	10.7	26.3	15.4
Σ Cations (μeq/L)	73.3	71.1	130.6	116.5
SO_4^{2-} (μeq/L)	46.2	57.1	133.0	117.9
Cl^- "	6.2	6.2	10.2	7.1
NO_3^- "	0.1	1.6	4.7	1.0
F^- "	0.7	1.5	0.7	1.6
ANC "	0.4	---	-37.2	---
HCO_3^- "	2.0	---	0.3	---
Σ Anions (μeq/L)	55.2	---	148.9	127.6
Cond. (μS/cm)	10.6	14.1	27.9	28.0
Color (PCU)	25	---	5	---
P (μg/L)	39.0	<40	2.0	<40
Mn "	40	32	100.0	32
Fe "	50	14	0.0	34
Al (tot.) "	16	<11	61.0	11
Al (ext.) "	10	---	45.0	---
DIC (mg/L)	0.35	---	0.19	---
DOC "	5.90	4.46	0.50	1.28
SiO_2 "	0.18	0.17	0.00	0.17

a. National Surface Water Survey Data
b. Illinois State Water Survey Data

Table 8. New England Lakes - NSWS and U.S. Fish and Wildlife Survey (USFWS)

	Killingly Pond (NSWS #1D3-029) Sample Collection Period		Wilbur Pond (USFWS #1146) Sample Collection Period	
Parameter	**11/4/84**[a]	**3/20/87**[b]	**12/12/84**[c]	**3/20/87**[b]
pH (air-equil.)	4.97	5.10	3.98	4.44
Ca^{2+} (μeq/L)	33.9	63.6	64.9	47.9
Mg^{2+} "	23.0	29.7	29.6	21.0
K^{+} "	5.9	<41	11.8	<41
Na^{+} "	125.5	162.5	100.0	81.3
NH_4^{+} "	1.6	---	---	---
H^{+} "	10.8	7.9	104.7	36.3
Σ Cations (μeq/L)	200.6	263.7	311.0	186.5
SO_4^{2-} (μeq/L)	127.7	139.6	138.5	122.9
Cl^{-} "	111.5	146.7	95.9	50.8
NO_3^{-} "	2.3	3.2	---	<0.5
F^{-} "	6.6	2.4	---	2.1
ANC "	-2.6	-2.3	-90.0	-2.82
HCO_3^{-} "	0.9	---	---	---
Σ Anions (μeq/L)	249.0	291.9	234.4	175.8
Cond. (μS/cm)	33.6	41.5	64	33.5
Color (PCU)	5	5	150	50
P (μg/L)	2.4	<40	---	<40
Mn "	112.0	120.9	41	18.3
Fe "	28.0	31.6	---	125.8
Al (tot.) "	172.9	236.0	357	164
Al (ext.) "	79.0	---	---	---
DIC (mg/L)	0.18	0.79	---	1.13
DOC "	0.67	1.57	10.5	5.53
SiO_2 "	1.01	0.33	---	0.78

a. National Surface Water Survey Data
b. Illinois State Water Survey Data
c. U.S. Fish and Wildlife Survey

Table 9. New England Lakes - NSWS

	Bailey Pond (NSWS #1D1-020) Sample Collection Period		Long Pond (NSWS #1D3-025) Sample Collection Period	
Parameter	11/4/84[a]	3/20/87[b]	11/8/84[a]	3/20/87[b]
pH (air-equil.)	6.78	6.37	7.63	6.50
Ca^{2+} (μeq/L)	101.0	145.8	160.2	202.0
Mg^{2+} "	64.8	85.2	47.7	50.2
K^{+} "	25.1	44.6	12.5	<41
Na^{+} "	136.2	172.7	88.7	103.1
NH_4^{+} "	1.1	---	0.0	---
H^{+} "	0.1	0.1	0.0	0.3
Σ Cations (μeq/L)	329.2	448.4	309.1	366.4
SO_4^{2-} (μeq/L)	127.5	152.1	91.4	110.4
Cl^{-} "	114.4	169.2	52.8	56.4
NO_3^{-} "	0.0	<0.5	0.0	<0.5
F^{-} "	3.9	3.2	7.0	3.1
ANC "	63.3	70.3	149.3	163
HCO_3^{-} "	44.1	---	142.2	---
Σ Anions (μeq/L)	289.9	394.8	293.4	332.9
Cond. (μS/cm)	38.4	61.2	34.6	42.5
Color (PCU)	80	40	40	45
P (μg/L)	33.7	<40	11.0	<40
Mn "	15.0	7.6	0.0	67.2
Fe "	309.0	55.5	310.0	387.4
Al (tot.) "	133.1	93.1	17.0	34.8
Al (ext.) "	13.5	---	2.8	---
DIC (mg/L)	0.49	1.19	1.71	3.21
DOC "	8.38	4.93	3.90	4.13
SiO_2 "	3.99	0.52	4.03	0.78

a. National Surface Water Survey Data
b. Illinois State Water Survey Data

Table 10. Analytes and Methods Used for Lake Chemistry Characterizations

Parameter	Method	References 1983 USEPA	 1986 USEPA	 Other	Method Detection Limit[a]
pH (H^+)	Electrometric		150.6		0.01 pH units
Conductivity	Electrometric		120.6		0.1 uS/cm
SO_4	Ion Chromatography		300.6		0.03 mg/L
NO_3	Ion Chromatography		300.6		0.03 mg/L
NH_4	Automated Colorimetry		350.7		0.02 mg/L
Cl	Ion Chromatography		300.6		0.03 mg/L
F	Electrometric		340.6		0.003 mg/L
P	ICP Spectrometry			Jarrell-Ash, 1982	0.04 mg/L
Fe	ICP Spectrometry	200.7			0.005 mg/L
Ca	ICP Spectrometry	200.7			0.002 mg/L
Mg	ICP Spectrometry	200.7			0.003 mg/L
Na	ICP Spectrometry	200.7			0.014 mg/L
K	ICP Spectrometry	200.7			1.6 mg/L
Mn	ICP Spectrometry	200.7			0.001 mg/L
Si (SiO_2)	ICP Spectrometry	200.7			0.01 mg/L
Al (total dissolved)	ICP Spectrometry	200.7			0.011 mg/L
	GFAA Spectroscopy	202.2			0.004 mg/L
ANC[b]	Titrimetric			NSWS[c]	5 ueq/L
DOC[d]	Oxidation-IR	415.1			0.05 mg/L
Color	Colorimetric (PCU)	110.2			0 PCUs

a. **Method** detection limits calculated according to Glaser et al., 1981.
b. Acid neutralizing capacity
c. National Surface Water Survey Methods Manual (Hillman, et al., 1986)
d. Dissolved organic carbon

References

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SEPARATION OF MONOMERIC INORGANIC AND ORGANIC ALUMINUM BY EQUILIBRIUM DIALYSIS

Background

Dialysis, as defined by Sawyer (1978), is a process which employs a membrane of a particular permeability. The membrane is wetted by the solvent, allowing ions to pass through the membrane while large molecules of organic substances or colloidal particles are unable to pass.

There are three main types of dialysis: Donnan dialysis, equilibrium dialysis and electrodialysis. Donnan dialysis is a process by which ions are transported across an ion exchange membrane as a result of an ionic strength gradient. The volume of the receiver solution (dialysate) is smaller and of higher ionic strength than that of the sample solution (retentate). Equilibrium dialysis is a process by which ions are transported across a cellulose membrane until the concentrations of the ion of interest on the opposite sides of the membrane are equal at equilibrium. The volume of the receiver solution is smaller and of lower ionic strength (deionized water is commonly used) than the sample solution. The driving force is the concentration gradient. Electrodialysis uses electrical energy to cause the flow of ions against a concentration gradient.

Type of Dialysis Membranes

The type of dialysis depends in part on the type of membrane used. There are basically four types of dialysis membranes. These are 1) Ion-exchange membranes, 2) Gradocol membranes, 3) Cellophane membranes, and 4) Spectra/Por membranes.

Ion-Exchange Membranes

There are two types of ion exchange membranes: cation exchange membranes and anion exchange membranes. These membranes are used exclusively in Donnan dialysis. The cation types are used for the enrichment of cations and the anion types are used for the enrichment of the anions. Examples of these membranes are:

Cation type - P - 1010 (RAI Research Corp., Hauppauge, NY)
- Nafion 125 or 811 (Dupont, Wilmington, DE)
Anion type - R - 1035 (RAI Research Corp., Hauppauge, NY)

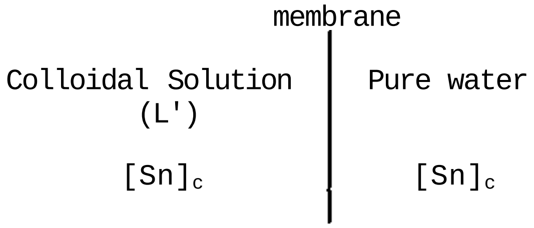
Gradocol membranes are collodion membranes and are made from nitrocellulose polymers. Their use in dialysis is limited. They are frequently used in ultrafiltration experiments. The cellophane membranes are sometimes called Visking membranes or cuprophane. They are used very often in equilibrium dialysis and electrodialysis. The composition of cellophane membranes is given below (Tuwiner, 1962):

Cellulose %	
Alpha	89.1
Beta	6.5
Gamma	4.5
10% KOH Solubility, %	15.2
Ash, %	0.06
Calcium, %	0.036
Iron, %	0.0005
Copper, %	0.0005
Manganese, %	0.0001
Ether extract, %	0.23

The Spectra/Por membranes are made from natural cellulose. They contain nominal quantities of contaminants. The evaluation of the equilibrium dialysis procedure contained in this report uses Spectra/Por 6 with 1,000 molecular weight cut-off (MWCO), 11.5 mm diameter dialysis membrane tubing as reported by LaZerte (1984).

Principles of Equilibrium Dialysis (from Elford, 1937)

Consider a colloidal solution L'separated from pure water by a membrane as shown below,



The rate of removal of a diffusible ion [Sn] from (L') is partly determined by the distribution ratio $r_n = [Sn]_{c'}/[Sn]_{c''}$

$$\text{Therefore,}\quad d\,[Sn]_{c'}/dt = [Sn]_{c'}\,\frac{1}{r_n}\,Kn$$

where t = time
Kn = coefficient directly proportional to the area of the membrane and the diffusion coefficient of [Sn] in the membrane.

Kn is also inversely proportional to the volume of solution (L') and the thickness of the membrane. Assuming Kn is a constant, then the reciprocal of the distribution ratio is a measure of the rate of dialysis. The distribution ratio (r_n) is also directly proportional to the volume of dialysate which would contain the same quantity of the substance [Sn] as is contained in one volume of the solution (L').

The rate of diffusion of a solute through a membrane depends on many factors (Craig and Konigsberg, 1961). These factors are 1) nature of the membrane, 2) nature of the solvent, 3) nature of the solute, 4) temperature, 5) effective area of the membrane with respect to the volume of the solution of higher concentration, and 6) the effective concentration gradient.

Literature Review

Published literature on the use of equilibrium dialysis for the separation of inorganic and organic aluminum species in natural water is not prevalent. LaZerte (1984) was one of the first researchers to apply this method to aluminum speciation studies. His method is based on a 24 hour dialysis at room temperature. The method has recently been evaluated by Backes and Tipping (1987a). They used 0.002 molar HNO_3 as the dialysate instead of deionized water. The results they obtained using this method were comparable to those using a method based on ion exchange.

The equilibrium dialysis method and acid-base titration have been used to investigate the interactions between Al and a fraction of aquatic humic substances in the pH range 3-5 by Backes and Tipping (1987b). In their investigation they reported that the recovery of Al in the equilibrium dialysis experiment was pH dependent. At pH 3-3.5 more than 90% was recovered, but only about 50% was recovered at pH 4.5. The poor recovery at pH 4.5 was attributed to adsorption of Al onto the dialysis apparatus.

Recently, LaZerte et al. (1988) have modified the equilibrium dialysis method by conducting the experiment at 4°C with the hope of eliminating precipitation of aluminum at room temperature. In their paper, they report comparable results with ion exchange techniques.

The limited use of the equilibrium dialysis method for the separation of inorganic and organic aluminum species is probably due to the potential problems with the experiments. These problems have been discussed by Weber (1983) and are listed below.

1. Permeation of organic matter through the dialysis membrane.
2. Adsorption of organic matter on the membranes.

3. Adsorption of low concentration metal ions on the membranes.

4. Inorganic aluminum in equilibrium with organic complexed aluminum.

These problem areas were the focus of our evaluation studies.

Experimental Conditions

The equilibrium dialysis membrane used was the Spectra/Por 6 type with MWCO of 1000, 11.5 mm diameter. The tube was cut into 10 cm pieces. These were pretreated by washing with 1% nitric acid (Ultrex) and several times with deionized water. They were kept in water and refrigerated when not in use.

A Turner Model 112 digital fluorometer which has a double beam optical balance was used to determine aluminum concentrations in the dialysate and retentate solutions. An excitation wavelength of 465 nm and an emission wavelength of 555 nm were used in all measurements. All pH measurements were made on an Amber Science Solution analyzer, Model 4503.

Equilibrium dialysis was performed following the procedures described by LaZerte (1984). In all experiments, 100 mL samples were in contact with the receiver dialysis tube containing 5 mL of deionized water, except for the pH studies where the receiver solution was 5 mL of nitric acid plus 0.001 M ammonium nitrate solution adjusted to the appropriate pH with ammonium hydroxide. The time of dialysis was set at 24 hours which was predetermined to be the time for equilibrium to be established in a separate experiment.

At the end of dialysis, the 5 mL receiver solution (dialysate) was made up to 20 mL, and 20 mL of the outside solution (retentate) were taken for analysis by the fluorometric method according to Hydes and Liss (1976). With samples having more than 5 mg/L organic matter, analysis was done by graphite furnace atomic absorption spectrophotometry (GFAA).

Dialysis Studies

The following studies were conducted using the above method.

1. Investigation of time taken for equilibrium to be established in the dialysis of 25 µg Al/L.

2. Effect of pH on Al dialysis.

3. pH changes during the dialysis of 100 µg Al/L.

4. Precision

    a. Effect of pH on precision.
    b. Effect of Al concentration on precision.
    c. Precision in natural water samples.

5. Effect of ionic strength on Al dialysis.

6. Influences of fluoride and sulfate on Al dialysis.

7. Losses of Al to dialysis tube and container.

8. Stirred vs. unstirred dialysis of 1) 50 µg Al/L and 2) Synthetic Reference Material containing 100 µg Al/L.

9. Diffusion of humic substances across the membrane.

10. Application of equilibrium dialysis to the separation of inorganic and organic aluminum in natural water samples.

Results and Discussion

Time of Dialysis

Reports in the literature by LaZerte (1984) and Backes and Tipping (1987b) indicate that 24 hours is the nominal time for equilibrium to be established in aluminum dialysis. Experiments were conducted to find out whether an extended dialysis time will affect the distribution of aluminum species in both the dialysate and the retentate. The results of the experiments are shown in Table 11. The results indicate that there are not significant changes in the distribution of aluminum in both the dialysate and in the retentate with a longer period of time and equilibrium is established at the end of 24 hours. All subsequent experiments were based, therefore, on 24 hour dialysis times.

Table 11. Equilibrium Dialysis Time for 25 μg A1/L Standard Solution

Time (Hours)	24	48	168
Dialysate (μg/L)[a] (Inorganic Al)	20.4	22.8	20.8
Retentate (μg/L)[b] (Dialyzable + Non-dialyzable Inorganic Al)	19.5	19.1	22.5

a. Concentration of aluminum in 5 mL dialysate.
b. Concentration of aluminum in 100 mL retentate.

Table 12. pH Changes During the Dialysis of 100 μg Al/L Standard Solution

Dialysate pH[a]	1.96	2.97	4.34	4.95	5.03	6.11	7.20	8.62
Initial retentate pH[b]	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Retentate pH after 24 hours	3.40	4.10	4.30	4.20	5.00	4.10	4.10	4.20

a. Dialysate solutions were made up from 0.001 molar ammonium nitrate solution. The solutions were adjusted to the appropriate pH with either nitric acid or ammonium hydroxide.
b. Retentate solutions were 100 mL of 100 μg Al/L prepared in dilute nitric acid.

Effect of pH on Dialysis

One of the factors which affect the rate of dialysis is the pH of the dialysate or the retentate. In order to investigate the effect of dialysate pH on Al dialysis, the pH of the retentate was fixed at 4.00. Aluminum recoveries in the dialysate were then monitored at different pH levels. The results are shown in Figure 3. The highest aluminum recoveries were obtained at acidic pH values of 1.96 and 2.97. A pH of 1.96 seems to be the ideal pH of dialysate to be used. Table 12, however, shows that at this dialysate pH, retentate pH dropped from 4.00 to 3.40 after 24 hours of dialysis. The drop is significant and may alter the equilibria of aluminum species in the sample solution. A dialysate pH of 2.97 seems to be the appropriate pH to be used since retentate pH does not alter significantly at the end of 24 hours of dialysis. It must be noted from Figure 3 that retentate aluminum at the end of dialysis follows a trend similar to the dialysate aluminum. This indicates that the pH tends to be the determining factor in the aluminum distribution between the dialysate and the retentate. The effect of retentate pH on Al dialysis was also studied. The pH of the dialysate was fixed at 5.00. The results are shown in Figure 4. The highest dialysate aluminum recoveries were obtained at a retentate pH of 3.10. This is expected since at this acidic pH most of the aluminum is in the dialyzable state (i.e., $A1(H20)^{3+}$, $A10H^{2+}$). Figure 4 also indicates that between the pH of 5.02 and 7.17 most of the aluminum is in the non-dialyzable state (i.e., $Al_{13}0_4(OH)_{24}^{7+}$, $Al(0H)_3$) and, more importantly, conditions are favorable for the adsorption of aluminum to the walls of the dialysis membrane. These results are in agreement with those reported by Morgan (1967).

Precision

The reliability of experimental results is partly determined by how precise

Figure 3. Effect of Dialysate pH on Al Dialysis
(pH of Retentate was Fixed at 4.0)

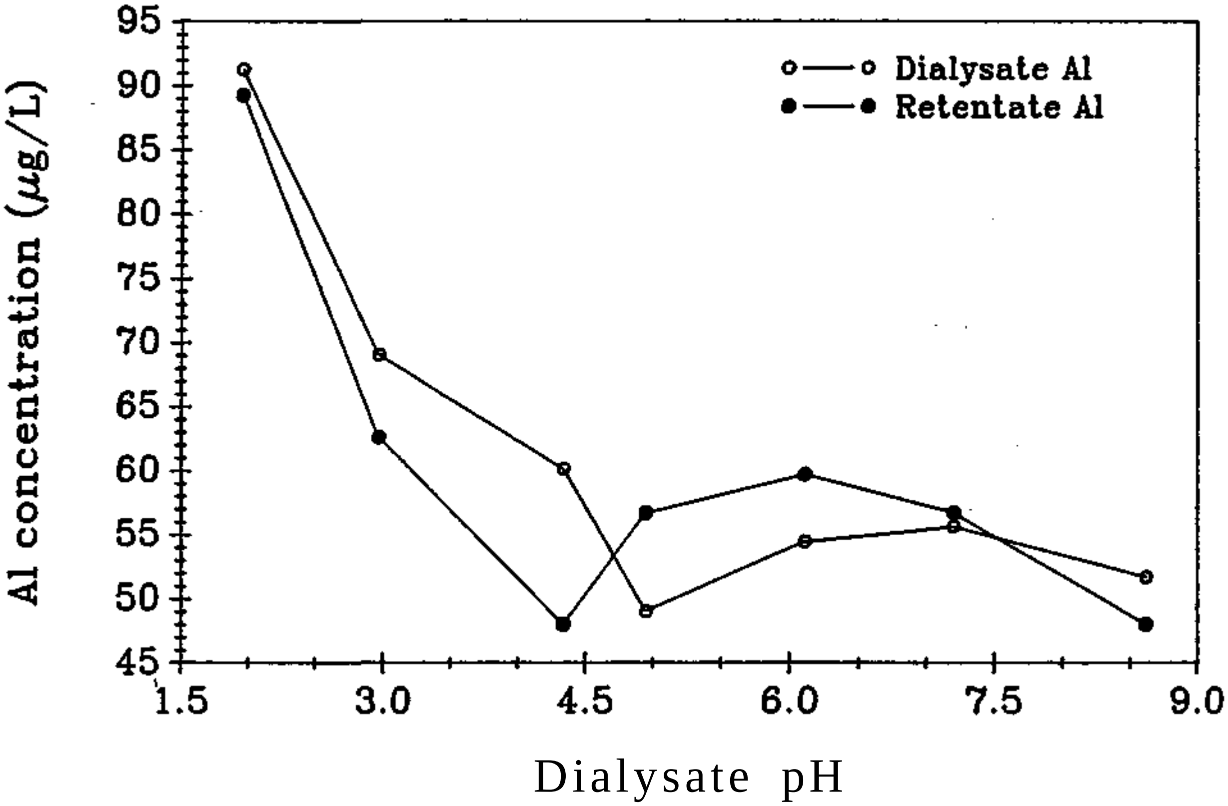
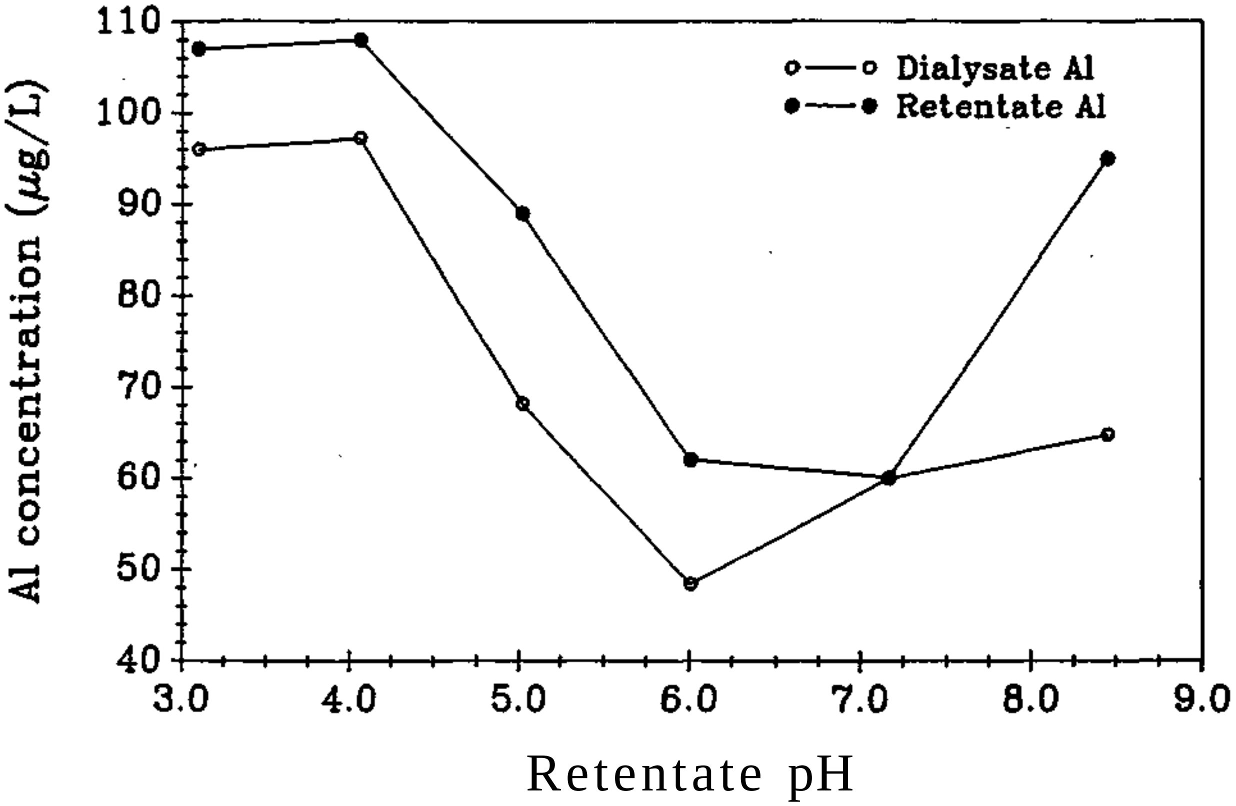


Figure 4. Effect of Retentate pH on A1 Dialysis
(pH of Dialysate was Fixed at 5.0)



the results are. In view of this, the precision of aluminum dialysis was studied at different aluminum concentration levels using deionized water as the dialysate. The retentate pH was fixed at 4.0 and the dialysis was allowed to proceed for 24 hours at 25°C. The results are represented graphically in Figure 5. The precision for the dialysate aluminum at low concentrations (10 μg/L - 20 μg/L) is rather poor. At 70 μg Al/L and above, the precision ranged from 5.9% RSD at 70 μg/L to 19.2% RSD at 200 μg/L. In all cases, the precision of the retentate aluminum was low. The poor precision at low aluminum concentration levels is mainly due to losses of Al to the dialysis tube and the container since these losses vary from one tube to another.

Precision studies using a natural water sample (Killingly Pond) were also carried out using the same experimental conditions previously described. The results are shown in Table 13. Precision in dialysate aluminum was high (24.3% RSD) whereas the precision in retentate aluminum was low. The low precision in retentate aluminum is probably due to the fact that the rate of migration of dialyzable aluminum to the tube walls is nearly constant. The diffusion rate of dialyzable aluminum through the membrane is probably variable due to the adsorption problem discussed above and this will result in different dialysate aluminum concentration levels.

The Influences of Fluoride and Sulfate on AL Dialysis

Studies were conducted to examine the effect of fluoride and sulfate on Al dialysis. The results are shown in Table 14. From the results obtained, fluoride appears to enhance the amount of dialyzable aluminum whereas sulfate decreased the amount of dialyzable aluminum. This is likely due to the slow equilibration of sulfate as suggested by Lazerte (1984). Sulfate may also enhance the adsorption of aluminum to the wall of the membrane.

Figure 5. Effect of Aluminum Concentration on Dialysis Precision

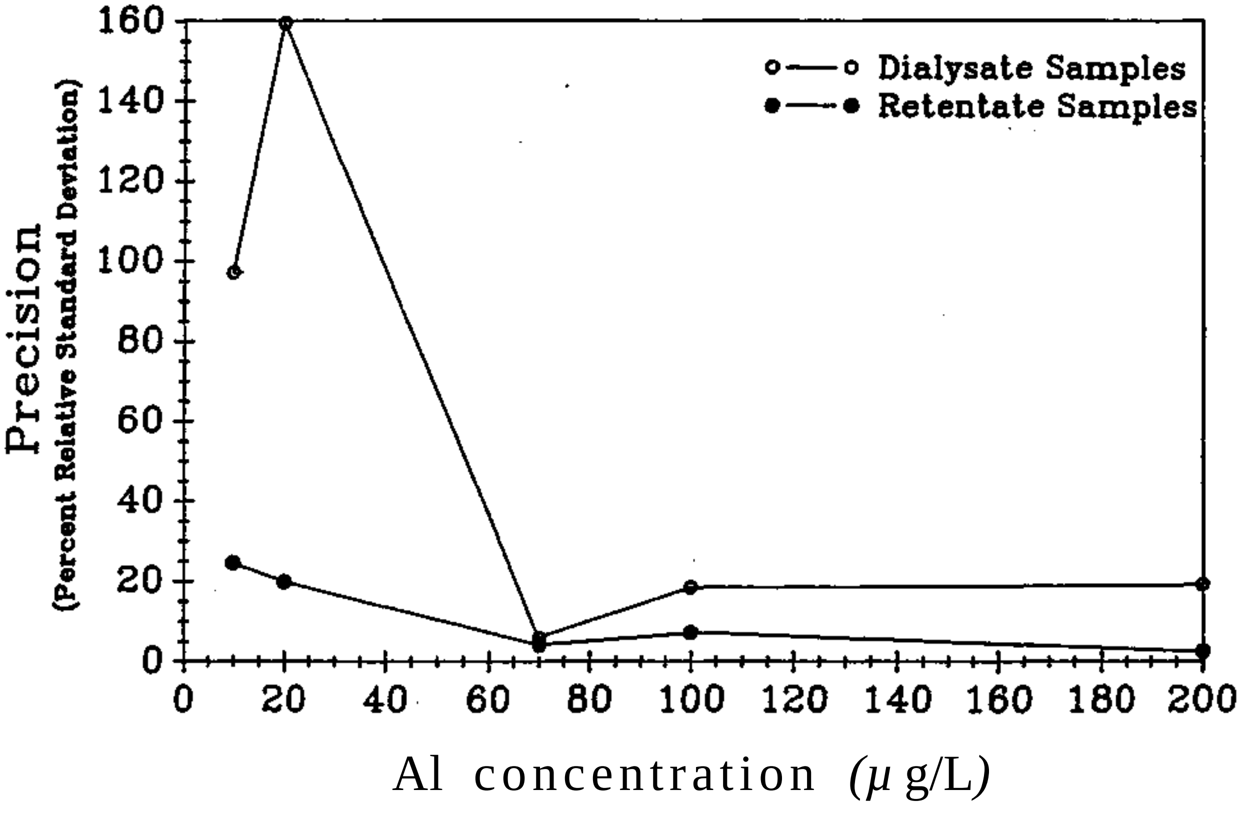


Table 13. Dialysis Precision in Natural Samples - Killingly Pond

Experiment No.	Total Dissolved AL (µg/A)	Dialysis Concentrations (µg/L) Dialysate (Inorganic Al)	Retentate (Org. + Inorg. Al)
1	232	**51.8**	80.5
2	232	48.4	95.6
3	232	85.0	95.8
4	232	58.4	96.0
5	232	55.6	100.2
Summary Statistics: Mean (x)		59.85	93.62
Standard Deviation (s)		14.55	7.58
Relative Standard Deviation (RSD)		0.243	0.081
% RSD		24.3	8.1

Table 14. The Influences of Fluoride and Sulfate on Al Dialysis[a]

Concentration of Fluoride or Sulfate Added to 50 µg Al/L	Fluoride and Sulfate Absent	50 µg F^-/L	100 µg F^-/L	50 µg SO_4^{2-}/L	100 µg SO_4^{2-}/L
Dialysate (Inorganic Al)	19.60	37.52	33.64	8.96	15.64
Retentate (Dialyzable + Non-dialyzable Inorg. Al)	23.42	39.06	45.3	20.14	18.76
Amount of Al Lost	25.21	15.60	17.13	27.00	33.00

a. 24 hr. dialysis in a 150 mL polypropylene beaker
Dialysate (DI water) - 5 mL
Retentate (Samples) - 100 mL

Losses of Aluminum to Dialysis Membrane and Container

Losses of aluminum to the' membrane tube and container is a potential problem in dialysis. This problem was investigated at room temperature and at 4°C as suggested by Lazerte (1984). The results are shown in Tables 15 and 16, respectively. The results indicate that a substantial amount of aluminum is adsorbed onto the membrane tube walls during both 24 hour dialysis at room temperature and 6 day dialysis at 4°C. Losses of aluminum to the walls of the beaker are, however, minimal. The membrane used in the dialysis is Spectra/Por 6 which is made from cellulose. The hydroxyl groups characteristic of cellulose make the membrane a good substrate for dialyzable aluminum species to be adsorbed. The mechanism of adsorption, however, is not well understood.

Dialysis Membrane Blank

Each dialysis membrane tube was soaked in 1% nitric acid (Ultrex^R) overnight followed by washing it several times with deionized water before use in the dialysis experiment. Despite this treatment, blank values of 13.6-22.3 µg Al/L were found. The source of this high blank value is not known. The composition of the cellulose membrane does not indicate the presence of aluminum. The contamination might be from the plasticizer and the glycol used to preserve the tube. Further investigation into the sources of the blank contamination is still needed.

Stirred Versus Unstirred Dialysis

Lazerte's (1984) method of dialysis avoids stirring. Elford (1937), however, has reported that the rate of dialysis is affected by stirring. An experiment was conducted to examine the effect of stirring on dialysis. The results are shown in Table 17. From the results shown, it is apparent that stirring does have an effect on the aluminum distribution in the dialysate and

Table 17. Stirred vs. Unstrlrred Dialysis of
(1) 50 μg Al/L and (2) Synthetic
Reference Material (100 μg Al/L)

	Stirred		Unstirred	
	(1)	(2)	(1)	(2)
Dialysate (μg/L) (Inorganic Al)	7.9	45.9	5.8	30.9
Retentate (μg/L) (Dialyzable + Non-dialyzable Inorg. Al)	8.0	62.1	24.5	76.7

Table 18. Diffusion of Humic Substances Across
the Dialysis Membrane

Sample	Original DOC (mg/L)	Dialysate DOC (mg/L)	Retentate DOC (mg/L)	Adsorbed to Tube Wall (mg/L)	$[HS]_D/[HS]_R$
Humic Substances without Al	2.97	0.05	2.55	0.37	0.02
Humic Substances + 100 μg Al/L equilibrated for two weeks	4.19	0.54	3.18	0.47	0.17

HS - Humic Substance
D - Dialysate
R - Retentate

Table 15. Losses of Al to Dialysis Tube and Container During Al Dialysis at Room Temperature for 24 Hours

	Sample Type							
	Blank	DI Synthetic	DI Synthetic	DI Synthetic	DI Synthetic	Synthetic Ref. Material	Biscuit Brook[a]	Killingly Pond[a]
Concentration (μg Al/L)	———	10	20	50	100	100	193.0	224.7
pH of Retentate	———	5.00	4.69	4.22	3.91	4.69	5.28	5.22
Dialysate (Inorganic Al)	———	2.4	3.8	3.6	37.6	30.9	23.42	93.08
Retentate (Dialyzable + Non-dialyzable Inorg. Al)	———	3.4	8.8	23.6	62.8	76.7	64.8	144.9
Al Adsorbed onto Tube Walls[b]	13.6	37.6	72.8	172.8	225.1	115.1	164.4	229.2
Fresh Samples	———	9.2	21.7		101.1	103.4	193.0	224.7
Samples from Dialysis Beakers Left for 24 hrs.	———	9.3	20.2	50.4	109.9	96.8	84.9	191.8

Dialysate (DI water) - 5 mL
Retentate (Samples) - 100 mL

[a] Natural samples

[b] Dialysed tubes were soaked in 15 mL 1% HNO_3 (Ultrex) overnight. 5 mL ammonium acetate - acetic acid buffer (pH - 7.06) were added to bring the pH to 5.0-5.1 before fluorometric analysis with lumogallion.

Table 16. Losses of Al to Dialysis Tube During Al Dialysis at 4°C for Six Days

	Sample Type							
	Blank	DI Synthetic	DI Synthetic	DI Synthetic	DI Synthetic	Synthetic Ref. Material	Biscuit[a] Brook	Killingly[a] Pond
Concentration (μg Al/L)		10	20	50	100	100	193.0	224.7
pH of Retentate		5.00	4.69	4.22	3.91	4.69	5.28	5.22
Dialysate (Inorganic Al)		0	0	12.1	52.3	46.5	44.3	162.4
Retentate (Dlalyzable + Non-dialyzable Inorg. Al)		1.4	2.8	12.81	71.1	89.4	71.4	169.4
Al Adsorbed onto Tube Walls[b]	22.3	34.8	70.3	154.5	163.0	69.6	123.1	223.2
Fresh Samples		9.2	21.7		101.1	103.4	193.0	224.7
Samples from Dialysis Beakers Left for 24 hrs.		9.25	20.2	50.4	109.9	96.8	84.9	191.8

Dialysate (DI water) - 5 mL
Retentate (Samples) - 100 mL

[a] Natural samples

[b] Dialysed tubes were soaked in 15 mL 1% HNO_3 (Ultrex) overnight. 5 mL ammonium acetate - acetic acid buffer (pH - 7.06) were added to bring the pH to 5.0-5.1 before fluorometric analysis with lumogallion

the retentate. The effect is, however, on the negative side. The results indicate that unstirred 24 hour dialysis is appropriate for the separation of inorganic aluminum. Stirring probably disturbs the diffusion of the inorganic aluminum, and that can affect the diffusion rate.

Diffusion of Humic Substances Across the Membrane

The diffusion of charged organic matter through the dialysis membrane affects the recovery of aluminum in the dialysate. Using a 1000 MWCO membrane, and considering the variable molecular weight nature of humic substances, the loss of humic substances to the dialysate was investigated. The results are shown in Table 18. In the absence of aluminum, less organic matter enters the dialysate. This is indicated by the $[HS]_D/[HS]_R$ ratio of 0.02. The presence of aluminum tends to enhance the diffusion of organic matter to the dialysate.

As suggested by Backes and Tipping (1987b), it is necessary to correct for the error created by the dialysate organic matter. This can be corrected by their formula, which is given below:

$$[\text{Organic Al}]_R - [\text{Total Al}]_R - (\text{Total Al}]_D$$

$$1 - [HS]_D/[HS]_R$$

where R - Retentate
D - Dialysate

Equilibrium Dialysis of Natural Samples

The equilibrium dialysis method was applied to the separation of inorganic and organic aluminum in natural lake water samples. The results are shown in Table 19. The data obtained from the total dissolved aluminum determinations by graphite furnace atomic absorption spectrophotometry are also tabulated in Table 19 for comparison.

Table 19. Inorganic and Organic Al in Lake Samples Determined by Equilibrium Dialysis (Al Species were Analyzed by GFAA)

Lake Sample	DOC (mg/L)	pH	Dialysis Results Inorganic Monomeric Al (µg/L)	Organic Al (µg/L)[a]	Total Dissolved Al (µg/L)[b]
Wilbur	5.53	4.44	107	57	164
Follensby Clear	2.3	7.17	9	---	<11
Killingly	1.57	7.71	202	34	236
Bailey	4.93	6.37	12	81	93
Little Cherry	14.9	6.50	12	63	75
Long	4.13	6.50	5	30	35
Sochia	1.76	4.52	12	---	<11
Brandy	8.4	5.08	53	16	69

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a. Calculated from Total Dissolved Al - Dialysed Inorganic Monomeric Al
b. From Tables 1-9

Conclusions

Evaluation studies have been conducted on the 24 hour dialysis. The results indicated that:

1. 24 hour dialysis at room temperature can be used to separate inorganic and organic aluminum.
2. The precision in % RSD of the experimental results is poor at low aluminum concentration levels and may be acceptable at higher aluminum concentration levels (≥ 70 µg/L aluminum).
3. The problem of adsorption could not be minimized by acid washing as suggested by Weber (1983).

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OXINE EXTRACTION

Background

Oxine extraction has been used in combination with other methods, such as dialysis and ion exchange, to study aluminum speciation in natural waters. Campbell et al. (1986) employed this combination of methods to determine the species of aluminum present in certain acidic freshwaters of Canada. The oxine extraction procedure was also used during Phase I of the National Surface Water Survey (Hillman et al., 1986). A flowchart for the procedures used in their study is shown in Figure 6. All three of these procedures were studied during the course of the ISWS study. A discussion of the evaluation of the oxine method follows. Descriptions and evaluations of both dialysis and ion-exchange procedures are provided elsewhere in this report.

Reaction Description

Aluminum reacts with 8-hydroxyquinoline (Oxine) to form a chelate which is extractable into an organic solvent such as chloroform, toluene or methyl isobutyl ketone (MIBK). The reaction between aluminum and oxine is known to be pH dependent. Brzezinska and Trzosinska (1983) determined experimentally that the optimal pH range for the formation of the desired aluminum-oxine chelate was pH 3 to pH 5. The extraction phase of the procedure is also known to be pH dependent with the ideal conditions for extraction occurring between pH 5 and pH 9 (Wright and Skogheim, 1983). As a result of these and other studies (Barnes, 1976; Campbell et al., 1983; and Lazerte, 1984) the protocol for this method consists of the chelation reaction at pH 3-4 then addition of buffer to raise the pH to pH 8.3 followed by extraction into an organic solvent.

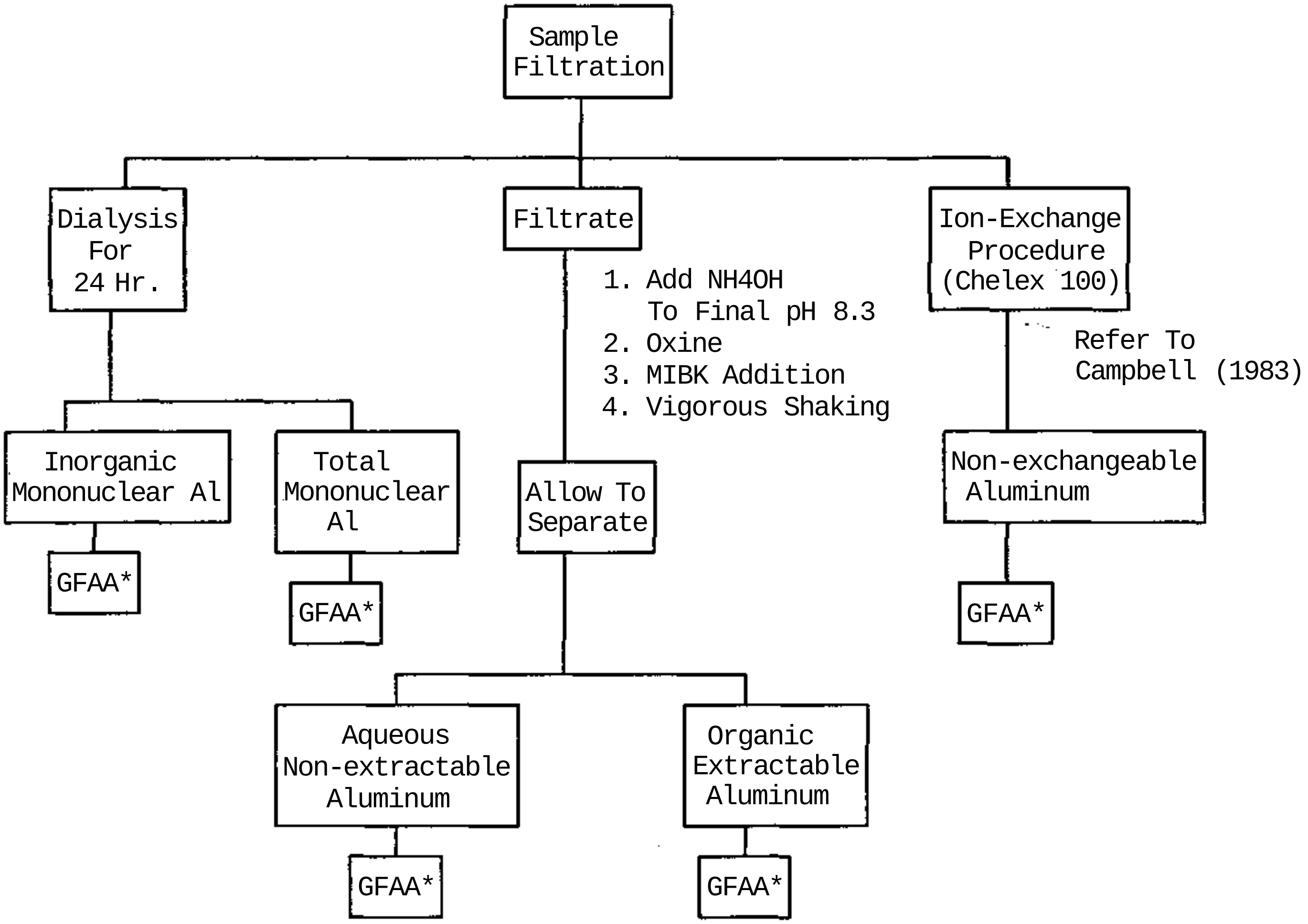

Figure 6. Oxine Extraction Flowchart for Aluminum Speciation (from Campbell et al., 1986)

*GFAA = Graphite Furnace Atomic Absorption

Interferences

The importance of maintaining the prescribed pH at each phase of the procedure needs emphasis. Should the chelation reaction occur in the range of pH 4-6, the oxine will also react with negatively charged species such as AlF_4^- and AlF_5^{2-}, the result being a positive error in the extractable aluminum concentration found. This error may not be considered significant, however, because of the normally low concentrations of these negatively charged aluminum complexes in natural waters.

Another problem may exist due to the slow reaction of positively charged species, such as $AlOH^{2+}$ and $Al(OH)_2^+$ with oxine in the pH range 3.0-5.0. If the extraction is performed at a pH of 5.0, not all of the extractable aluminum will be recovered (Bruce et al., 1983). This will result in a negative error in the extractable aluminum concentration found in the sample.

Interferences that result from improper pH are not the only ones to consider. Once the solution pH is raised to 8.3 just prior to the extraction, the remaining aluminum in the sample is present as $Al(OH)_4^-$. This species may react with the oxine that remains in solution, may be extracted into the organic fraction, and will then be determined as extractable aluminum. It is evident from the preceding discussion that this method is not specific to only one species of aluminum. It is in fact impossible to determine which species of aluminum is extracted and analyzed by using only data obtained by this method. Only when oxine extraction data are combined with those produced by other speciation methods does it become possible to suggest the aluminum species that have been determined by using oxine extraction.

Finally, it is suspected that other components of natural waters such as other metals and organic compounds will interfere with this method, particularly the extraction procedure. Support for this as a potential problem can be found in the data reported from experiments in which humic and fulvic acids were added to the test solutions. These data can be found in Table 20.

Literature Review

The first use of oxine extraction for the determination of aluminum was reported in 1933 by Alten et al. Their colorimetric method for Al was based on conversion of an acid quinolate solution to an azo dye. The direct determination of aluminum as a measure of the color intensity of the yellow solution obtained by the extraction of the aluminum quinolate with chloroform was reported by Alexander (1941). Alexander's method has been adapted and modified by a number of researchers. Goto et al. (1958) and, later, Okura et al. (1962) used chloroform to extract the aluminum oxinate followed by a spectrophotometric determination of Al to differentiate among the forms of Al in aqueous solutions. Turner (1969) described 8-Quinolinolate extraction methods for the determination of Al^{3+} , mononuclear hydroxyaluminum ions, polynuclear hydroxyaluminum ions, and the initial solid phase aluminum complex that results from the addition of a base to $AICI_3$ solutions.

Later, Fishman (1972) reported a procedure in which the determination of aluminum in natural waters was based on oxine extraction. A comprehensive work on the determination of specific forms of aluminum in natural waters based on oxine extraction has been reported by Barnes (1976). The determination of mononuclear dissolved aluminum in near-neutral waters has been reported by May et al. (1979). In their method, concentrations of mononuclear dissolved Al are determined in samples of natural waters and in solutions prepared by solvent extractions from suspensions of clay minerals. Quantitation of the aluminum 8-hydroxyquinoline complex was by spectrophotometric analysis. The method has been adapted and modified for the determination of both labile and total aluminum in soil extracts by Bruce et al. (1983). The most recent method involving 8-hydroxyquinoline is a fast extraction (10-15 seconds) of the aluminum-oxine complex into methyl-isobutyl ketone (MIBK) followed by graphite furnace atomic absorption determination of the aluminum present in the extract. This method has recently been used in aluminum speciation projects by Lazerte (1984) and Campbell et al. (1986). In addition, this procedure was used for Phase I of the NSWS sampling program. The method of oxine extraction followed for our evaluation was adapted from Campbell et al. (1986).

Experimental Conditions

The procedure for the determination of the fast oxine extractable aluminum (Campbell et al., 1986) begins with the addition of the following reagents to the filtered natural water sample: 8-hydroxyquinoline solution (5%), NH_4OH, pH 8.3 buffer and methyl isobutyl ketone (MIBK). The reaction vessel is a separatory funnel which is shaken for 10-15 seconds after the addition of the MIBK. After a brief period to allow the separation of the organic layer, the MIBK layer is removed and analyzed for aluminum by graphite furnace atomic absorption (GFAA) spectrophotometry. Standards in the range of 5-100 μg Al/L were used to generate a calibration curve each time the test samples were analyzed.

The aluminum concentration determined by the GFAA analysis represents the oxine-extractable aluminum portion of the sample.

Results and Discussion

The possible errors that may result from this method were discussed previously in the background portion of this method evaluation. Despite the uncertainty associated with the amount of aluminum determined by this method, data from the determination of the oxine-extractable aluminum in both natural and synthetic samples were used to estimate the precision of the procedure. The data obtained from the analysis of the synthetic reference samples were also used to provide an estimate of the method bias.

Precision

The precision of the oxine extraction procedure was derived from the data that resulted from the analysis of synthetic samples with and without the addition of fulvic and humic complexing ligands. Table 20 shows the results obtained from these analyses. The matrix of the synthetic samples was formulated to approximate the median ion concentrations measured during Phase I of the NSWS. Both the target and the measured oxine-extractable aluminum values are listed in Table 20.

The data in Table 20 indicate good precision (5% RSD) at high concentrations of aluminum and moderate precision (20% RSD) when the concentration of aluminum is low. These differences are not inconsistent with the uncertainties inherent in analysis of aluminum by GFAA. Of far greater interest is the disparity between the target and found concentrations of the samples to which fulvic and humic acids were added. Not only was the measured oxine extractable aluminum only 56% of the target value, the precision of 20% was much greater than the 5% seen at a similar concentration level but without the organic constituents. The reason for this may be due to ligand competition between the oxine and the fulvic or humic acids.

The results for the samples with the added organic ligands also indicate that the fast oxine extraction method does not measure all of the monomeric aluminum in the sample. It appears that at least some of the aluminum associated with humic and fulvic acids is not detected by the oxine extraction method.

Table 20. Estimates of Precision from Oxine Extraction of Synthetic Samples

Sample	n[a]	Target Value (µg Al/L)	Mean Concentration Found (µg Al/L)[b]	Standard Deviation (µg Al/L)	Precision RSD (%)
Synthetic I	4	20	19.0	3.7	19.5
Synthetic II	4	100	98.5	5.1	5.2
Synthetic III[c]	4	80	44.5	8.9	20.0

a. Number of determinations.
b. Fast oxine-extractable aluminum.
c. Synthetic II with humic (1 mg/L) and fulvic (1 mg/L) acids added.

Bias

It is difficult to determine the bias of the method for there are no certified reference materials for oxine-extractable aluminum. There are, however, certified reference materials for total aluminum measurements. Analysis of these samples for aluminum concentration after oxine extraction does provide useful information regarding the accuracy of the method.

Two reference samples were used for this portion of the evaluation. These were a highly characterized natural water sample, Riverine Material SLRS-1, and an EPA reference sample, WP386 diluted 1/10, provided by the USEPA Environmental Monitoring Systems Laboratory, Cincinnati, Ohio. The data from these extractions and analyses are found in Table 21.

These data indicate that although the amount of oxine-extractable aluminum is unknown, the difference between the known total aluminum and the aluminum extracted is somewhat larger than the imprecision inherent in the method (Table 20). Whether this difference resulted from a bias in the method or because only a portion of the total aluminum was in oxine-extractable form cannot be determined from this information.

Analysis of Lake Samples

To obtain more information for the evaluation, four New England lake samples and six Michigan lake samples were analyzed using the fast oxine extraction method. The results from the analysis of the extractions are shown in Table 22 and Table 23. A comparison of the total dissolved aluminum found in the New England samples to that found in the Michigan samples indicates the New England lakes contain much higher levels of aluminum. Again, because the concentration of the extractable portion of aluminum in these samples is unknown it is impossible to say for certain whether the method is or is not reliable based on these determinations alone. The New England lake data do follow similar patterns to the synthetic samples containing fulvic and humic acids (Table 20). This supports the contention stated earlier that organic components in natural waters interfere with the oxine extraction method. The levels of aluminum in the Michigan lakes are sufficiently low that the differences between total and extractable aluminum are not significantly different, given the uncertainty associated with the measurements.

Conclusions

While the precision achieved in the extraction and analysis of synthetic samples prepared by the ISWS indicate that the method can produce reproducible results, the validity of these results is still questionable. Interferences are known that can result in both overestimates and underestimates of the extractable aluminum. The most disturbing of these interferences are organic components normally found in natural waters. This study has shown that when such compounds are present the result is only partial extraction of the available aluminum.

The method is very quick and simple to follow. Because the extraction procedure is carried out at a pH of 8.3, fluoride interferences are eliminated. However, the method is not specific to a single form of aluminum. The data it produces are influenced by both the pH at which each stage of the procedure is performed and the time allowed for separation of the organic layer. These problems, coupled with those already mentioned, place the usefulness of this procedure as a method for aluminum speciation in question.

Table 21. Oxine Extraction Experiments

Sample	**True Value (µg Al/L)**	**Measured Value (µg Al/L)**	**Difference (µg Al/L)**
Riverine Material SLRS-1 (Natural)	23.5	**30.8**	**7.3**
EPA WP386 (1/10 Dilution)	**50.0**	**41.5**	**8.5**

Table 22. Fast Oxine Extractable Aluminum in Four New England Lakes

Lake Sample	pH of Sample	Total Dissolved Al (µg/L)[a]	Oxine Extractable Al (Mg/L)[b]
Bailey	6.19	**93**	**42**
Killingly	4.19	236	**144**
Long	6.13	**35**	**14**
Wilbur	4.47	**164**	**91**

a. From Tables 1- 9.
b. Fast reactive, inorganic aluminum.

Table 23. Fast Oxine Extractable Aluminum in Six Michigan Lakes

Lake Sample	pH of Sample	Total Dissolved Al (µg/L)[a]	Oxine Extractable Al (µg/L)[b]
Delene	**6.83**	**<11**	12
Ostrander	7.06	**<11**	20
Catract	7.37	**39**	19
Casey	8.75	**<11**	13
Annie	5.78	**17**	**18**
Richardson	**6.14**	**<11**	7

a. From Tables 1-9.
b. Fast reactive, inorganic aluminum.

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BOUND/FREE FLUORIDE COMPUTATIONAL METHOD

Background

One procedure used to speciate inorganic aluminum in natural waters is the bound/free fluoride computational method. The fluoride electrode technique involves the measurements of free fluoride (fluoride activity) and total fluoride in a sample. Stability constants are then used in conjunction with pH values, SO_4^{2-} , and total aluminum concentrations to obtain the speciation of inorganic aluminum. The assumption in the use of the bound/free fluoride procedure is that inorganic monomeric aluminum (Al^{3+}) will be preferentially bound by fluoride in solution and that this complex will not be measured in the free fluoride measurement. The differences between the total (decomplexed) and free fluoride determinations are a measure of the inorganic aluminum in solution.

Several papers have been published on this subject. Driscoll (1984) and Johnson et al. (1981) determined the inorganic speciation of aluminum by using the bound/free fluoride technique. In their methods, free fluoride was determined by direct measurement using the fluoride electrode. David (1984) adopted the free fluoride procedure in his aluminum speciation studies of soil and river water samples. The method has also been evaluated by Lazerte (1984) and more recently by Hodges (1987). Despite the fact that the method is widely used in the speciation of inorganic aluminum, its applicability to very acidic and alkaline water samples is limited by problems associated with the free fluoride measurements. These problems have been highlighted by Schafran (1984) and are summarized below.

1. Natural water samples have pH values ranging from 3.5 to as high as 8.5. Direct measurements of free fluoride using the fluoride electrode in samples with pH greater than 7.5 are unreliable due to

hydroxide ion interference.

2. In the acidic region of pH 3.5 to 4.5, the equilibrium involving HF and possibly HF makes the electrode response very unstable and significantly increases the time of analysis.
3. Because of the low ionic strength of natural waters resulting in low conductivity, the rate of response of the electrode to fluoride activity is very slow.

These limitations of the fluoride procedure were examined in our laboratory using both synthetic and natural water samples. A proposed modification for free fluoride measurements in natural waters by adding a low-level total ionic strength adjustment buffer (TISAB) before analysis has also been developed.

Experimental Conditions

An Orion combination fluoride ion-selective electrode (Model No. 96-09-00) was used in with an Amber Science solution analyzer (Model 4603) with EMF (mV) expansion capability. Temperature was corrected to 25°C using a temperature probe. Orion TISAB III concentrate with CDTA was used to determine total fluoride. An internally formulated solution, TISAB II with CDTA, was also used for the total fluoride measurements. There was no difference between the results obtained using TISAB III and the internally prepared TISAB II. Both TISAB II and III are added to a solution to provide a constant background ionic strength, decomplex fluoride, and adjust solution pH. A low level TISAB solution, designed to be used in solutions that do not contain any complexing ligands, was prepared following the procedure recommended method by Orion, Inc. This solution was prepared by adding 57 mL glacial acetic acid to 500 mL deionized water, followed by 58g NaCl. The pH of the solution was adjusted to 5.37 using 5 molar NaOH. The final solution volume was 1 L.

The calibration and analysis procedures followed the method provided in the Orion Inc. Fluoride Ion-selective Electrode Manual. Time of analysis ranged from 20 to 45 min. for each sample.

Results and Discussion

Table 24 indicates the fluoride measurement results obtained from the analysis of a USEPA Fluoride Quality Control sample with and without the addition of a buffer solution. The high value obtained without the addition of the buffer is due to the hydroxyl ion interference described previously. The pH of this USEPA quality control sample is 7.58 which is high enough to produce sufficient hydroxyl ions to interfere with the fluoride measurement. The experiment illustrates that addition of a low-level TISAB provides comparable results to those obtained with TISAB III for synthetic samples that do not contain complexing ligands. The improved accuracy is the result of pH adjustment and increased ionic strength. Table 25 shows the analysis response times obtained on quality control solutions with and without the addition of low-level TISAB. As expected, direct measurements of fluoride in aqueous media which have a low conductivity take a longer time to reach a stable response value than the same solution to which a buffer is added to raise its ionic strength.

In order to test the reliability of the modified free fluoride measurement method, the following experiment was conducted. Aluminum concentrations ranging from 40 µg/L to 150 µg/L were added to a solution with a fixed fluoride concentration of 57.6 µg/L at a pH of 4.0. Free fluoride (low-level TISAB added) and total fluoride (TISAB II added) were then measured. The results are shown in Table 26.

pF (free measured) was then plotted against pF (free calculated) to test their correlation. The plot is shown in Figure 7. The plot shows that the two

Table 24. Fluoride Measurements in Quality Control Solutions

Sample Type	Fluoride Measured (mg/L)	True Value (USEPA Mean) (mg/L)
Quality Control Sample	**1.89**	1.00
Quality Control Sample + Low-level TISAB	1.09	1.00
Quality Control Sample + TISAB III	1.11	1.00

Table 25. Time of Analysis

Sample Type	Conductivity	Time to Reach A Stable Response, (min.)
Quality Control Check Solution	2.74 µS/cm	**45**
Quality Control Check Solution + Low-level TISAB	70.8 mS/cm	**20**

Table 26. Measured and Calculated Fluoride Concentrations

Al Added (µg/L)	[F] Total (mg/L) TISAB III	[F] Free (mg/L) Low-level TISAB	[F] Calculated Free (mg/L)^]
40	0.05	0.04	0.039
60	0.04	**0.03**	0.029
90	0.04	**0.03**	0.029
120	0.04	**0.03**	0.029
150	0.04	**0.02**	0.019

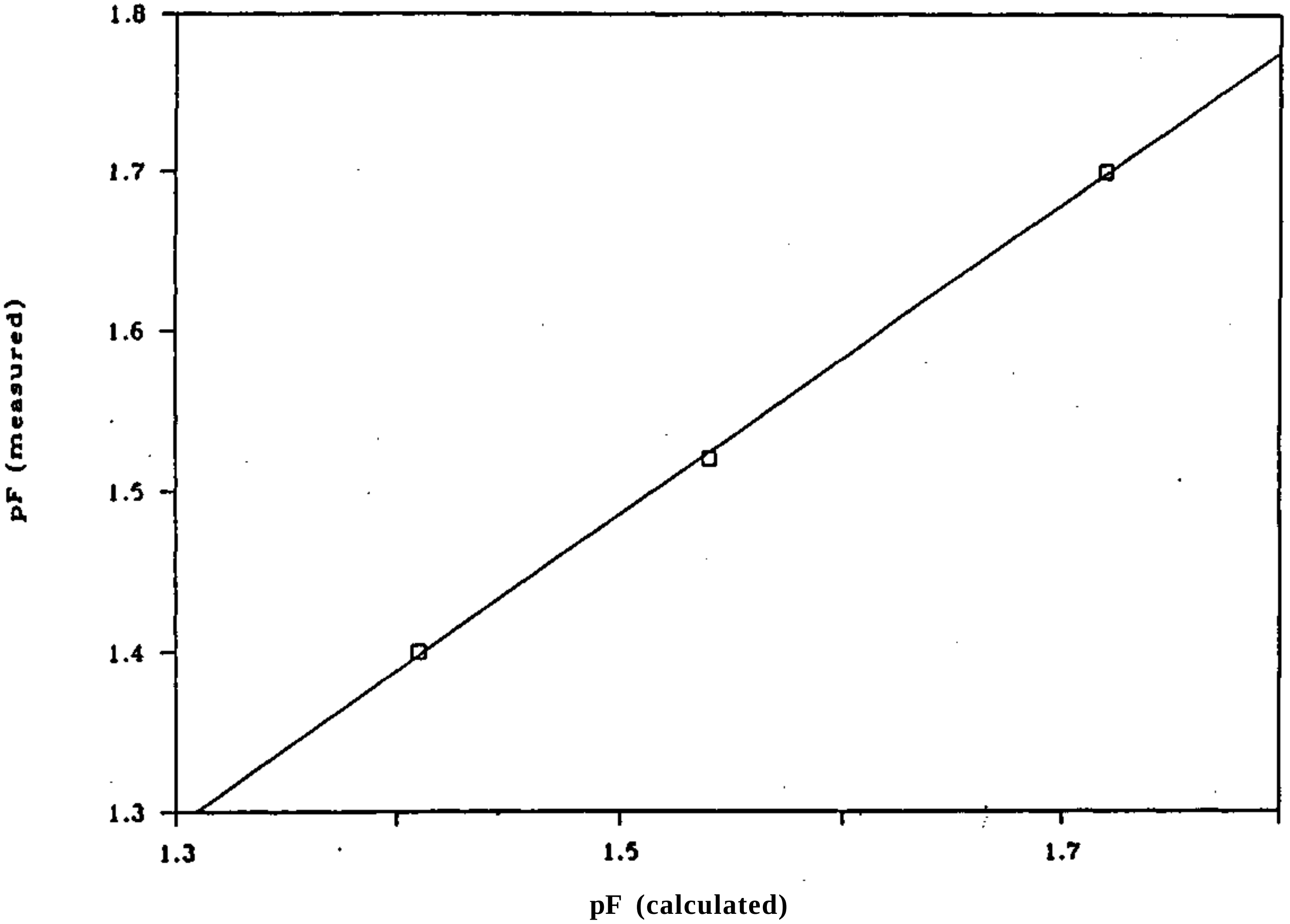

Figure 7. pF (Measured) Versus pF (Calculated)

data sets were well correlated: $R^2 = 0.9998$; pF (measured) = -0.03 + 1.03 pF (calculated). The total and free fluoride measurements were also made on four lake samples. The results are shown in Table 27 and indicate that Bailey and Long Pond samples whose pH values are greater than 6.0 have free fluoride levels greater than the total fluoride when direct measurements are made without the addition of a buffer. These high values are most likely due to hydroxyl ion interferences. Table 27 also shows that the addition of low-level TISAB before analysis provides for a more reliable analysis.

Conclusions

Direct measurements of free fluoride in natural water systems using the fluoride ion-selective electrode are limited to samples in a relatively narrow pH range (5.00 - 7.00). Outside of this range, interferences from hydrogen and hydroxyl ions cause significant errors which would negate the use of the bound/free fluoride computational method for aluminum speciation studies. Low-level TISAB, which will not break down existing fluoride solution complexes, can be used to adjust the sample pH before analysis without altering the free fluoride levels in the samples. This improvement to the method broadens the applicability of the procedure to more diverse sample types. The method detection limit for total fluoride (10 µg/L) and good precision characteristics (2.6% RSD at 20 µg/L) of the method make it a useful corroborative technique for other more direct speciation procedures.

Table 27. Total and Free Fluoride Measurements in Four Lake Samples

Lake Sample	**PH**	**Total Fluoride (mg/L)**	**NSWS Total Fluoride (mg/L)**	**Free Fluoride + Low-level TISAB (mg/L)**	**Free** Fluoride **Direct** Meas. (mg/L)
Bailey Pond	6.24	0.083	0.074	0.075	0.189
Killingly Pond	5.22	0.123	0.125	0.076	0.037
Long Pond	6.98	0.104	0.133	0.099	0.303
Wilbur Pond	4.58	0.083	0.199	0.070	0.035

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PYROCATECHOL VIOLET (PCV) COLORIMETRIC METHOD COUPLED WITH ION EXCHANGE

Background

The pyrocatechol violet method, in conjunction with ion exchange, has recently received greater attention and is more widely accepted than many of the methods examined in this study. One of the reasons for its wide acceptance is the relative sensitivity of the method. In addition, the automated procedure provides a sample analysis rate of 30 per hour. Using a two-channel automated analyzer, both total reactive and non-reactive aluminum species can be determined from a single sample aliquot. The two-channel method of analysis was adopted for the aluminum determinations in Phase II of the NSWS and formed the basis of our comparative studies using synthetic and natural samples. The PCV procedure used is shown in the flowchart provided in Figure 8. The theory behind the PCV - ion exchange procedure is that inorganic monomeric aluminum with a positive charge will be separated from the organically complexed aluminum by passing the solution through a cation exchange column. The sample aliquot that does not pass through the ion exchange column reacts with the PCV reagent to form a colored complex that approximates the total monomeric aluminum in solution. This fraction of aluminum is also described as total PCV reactive. The aliquot that is passed through the ion exchange column is reacted with PCV under the same conditions as the total reactive aliquot and provides an estimate of the organically complexed aluminum. The difference between these two measurements is reported as the inorganic monomeric fraction present in a sample.

Experimental Conditions

A flow injection analyzer (Lachat Instruments, Inc.) was used for the measurements of total PCV reactive and organically complexed aluminum. The

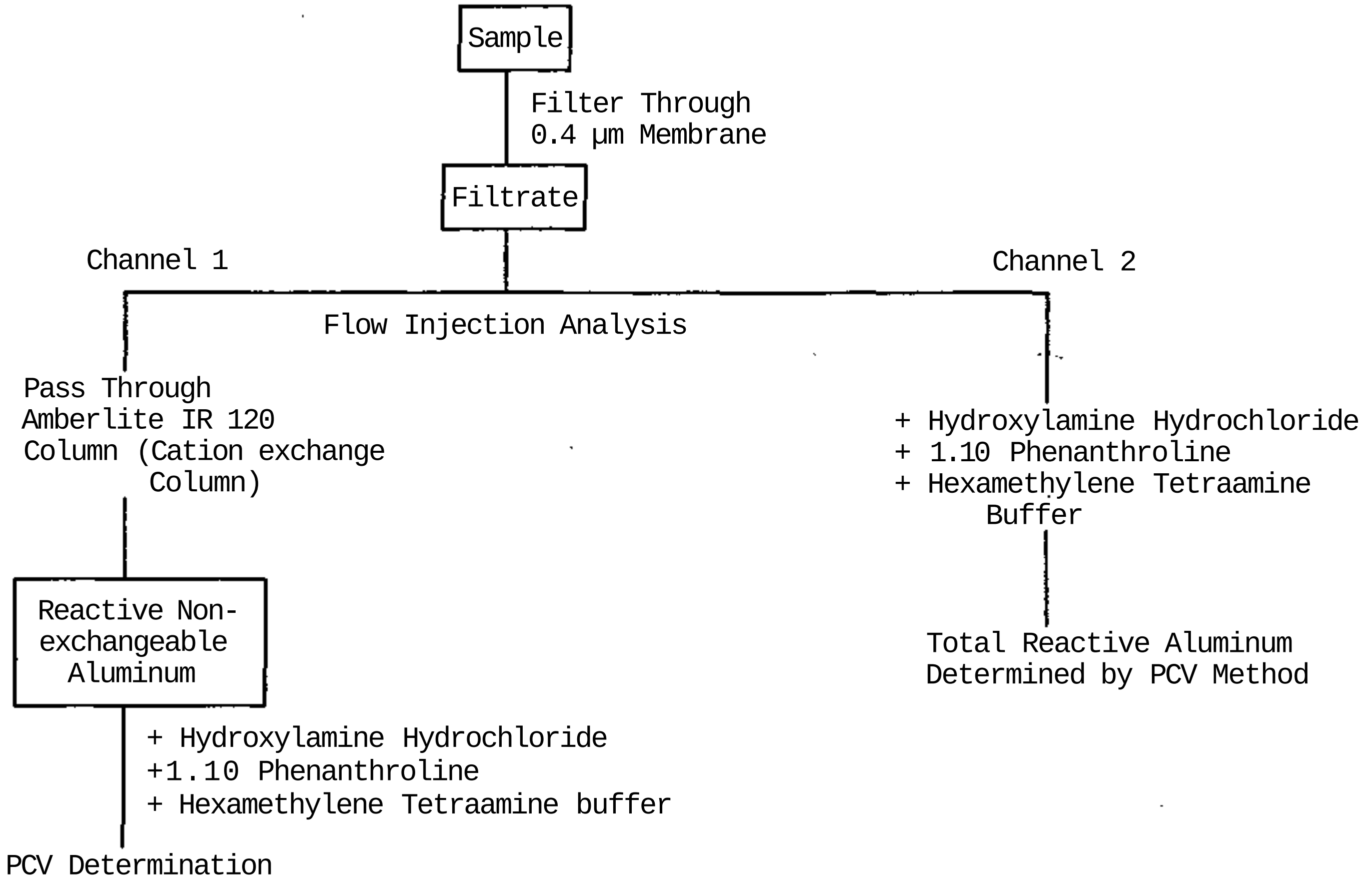


Figure 8. Sample Flowchart for Automated PCV Colorimetry With Ion Exchange Separation

Source: Kerfoot et al., 1986.

reagents and instrument operating conditions were identical to those used by Kerfoot et al. (1987) during Phase II of the NSWS. Instead of a two-channel system, however, a single-channel system was utilized whereby all samples were first measured for total reactive aluminum after calibration of the system. For the determination of organically complexed aluminum, the system was calibrated using the same standards except the ion exchange column was inserted between the sample loop and the first reaction coil. A 200 µg/L aluminum standard solution was inserted at the beginning and end of an analysis sequence to ensure that the ion exchange column was effectively removing all of the inorganic aluminum and that the column capacity was not being exceeded. At the end of a series of analyses, the ion exchange column was removed and the calibration standards checked to verify that instrument drift had not affected the initial calibration.

When the system was first put into operation, the effluent from the flow cell was monitored to ensure that the pH of the reaction solution was near the optimal color development pH of 6.1 - 6.2. This solution pH was monitored at hourly frequencies as an additional check on the system operation. The use of commonly available reference materials was not possible for the PCV determination because of the low pH (<2.0) of most trace metal reference materials. The buffer solution used in the method was not adequate to increase the pH to the required level of 6.1 - 6.2. This is one of the limitations inherent in the method and must be recognized when analyzing samples outside of the pH range that can be compensated for by the buffer addition. An internally formulated reference solution containing a background matrix that approximated natural water chemistry found in many lakes measured during Phase I of the NSWS was therefore used as a measure of bias.

The sample tubes that were used in the autosampler at the beginning of the comparative studies were manufactured from borosilicate glass. These glass tubes resulted in aluminum contamination of the samples because of the dilute acidic nature of the calibration standards and some of the samples. A change to polystyrene sample tubes eliminated this source of contamination. In order to achieve and maintain a stable baseline response from the colorimeter output, the deionized water carrier was degassed to prevent the introduction of bubbles into the system. Degassing of the reagents was not performed since carrier degassing alone resulted in a stable baseline output.

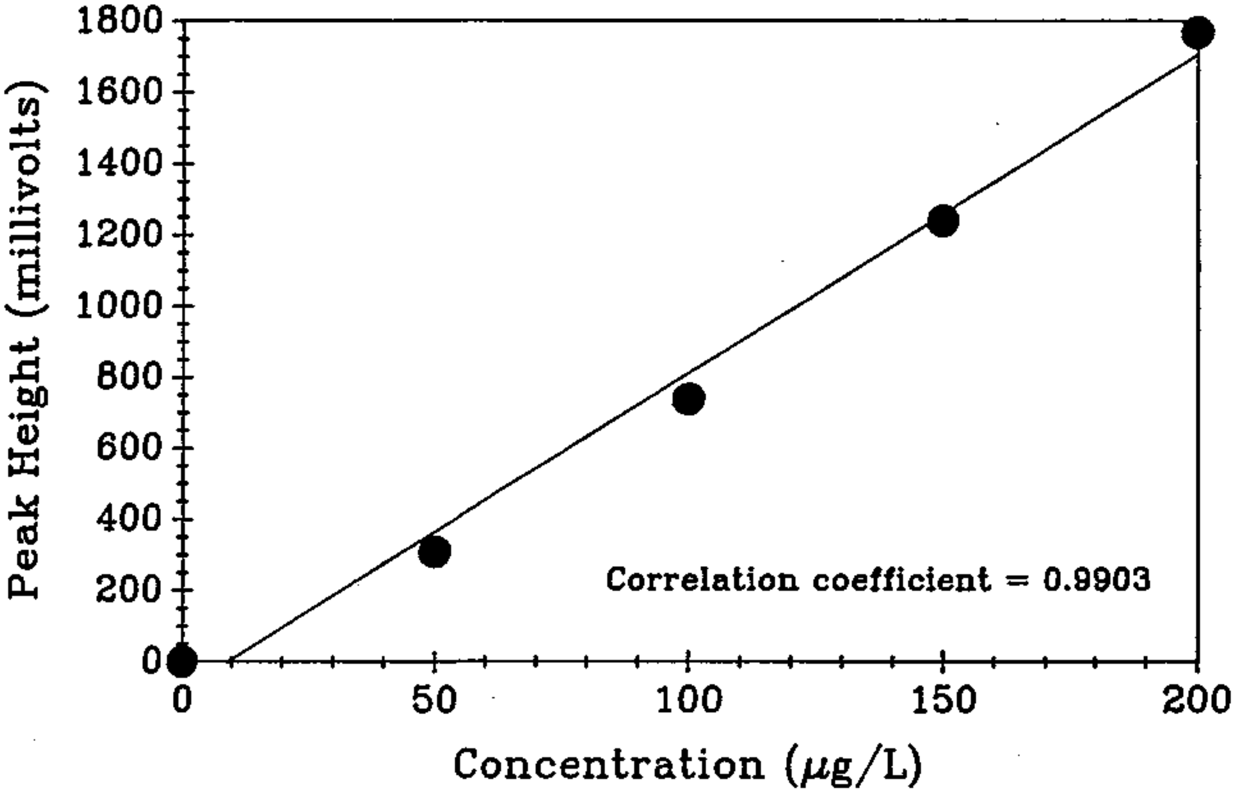
Results and Discussion

The system was calibrated with five standards with the highest standard at 200 µg Al/L. A typical calibration standard is depicted in Figure 8. The concentration versus absorbance curve is linear over the range of 50 - 200 µg/L but is non-linear between 0 and 50 µg/L. This characteristic of the PCV reaction has been previously reported by LaZerte et al. (1988) and is evident in our studies as well. In order to achieve the most accurate results below 50 µg/L, a second calibration for low level samples is required. The calculated within-run precision of the total PCV determinations in this study was 5% RSD at 20 µg/L, and 1% RSD at 200 µg/L. For the non-reactive organically complexed fraction, the precision was approximately 6% (RSD) at 15 µg/L. These precision statistics are in good agreement with those reported from the Phase II NSWS laboratory. A summary of the precision data is presented in Table 28.

Table 28. PCV Precision Data For Natural and Synthetic Samples

Solution Type	N	Nominal Concentration (µg/L)	Measured Mean Concentration (µg/L)	Standard Deviation (µg/L)	%RSD
Total Reactive Standard	12	**20**	**19.8**	1.03	**5.2**
Total Reactive Standard	10	200	199.1	2.08	**1.0**
Non-reactive Killingly Pond	6	**15**	14.3	**0.88**	**6.2**

Figure 9. Total Reactive Aluminum Calibration
Flow Injection Analysis
Pyrocatechol Violet Colorimetry



As mentioned previously, estimates of bias were difficult to obtain using the PCV procedure because of the pH sensitivity of the colorimetric reaction. In an effort to address this area, synthetic reference materials were developed. These contained known amounts of aluminum in the presence of a solution matrix that approximated natural waters of low buffering capacity, mildly acidic pH, and with complexing ligands present. The target concentrations for these solutions were derived from the median concentration values measured during Phase I of the NSWS. A more complete summary of the solution compositions was provided in the First Progress Report for this study (Peden et al., 1987). The aluminum speciation results obtained on these synthetic solutions are summarized in Table 29. Varying amounts of aluminum and dissolved organic carbon were added to these synthetic solutions in an attempt to develop reference materials that would be useful for determining the bias of various speciation techniques. The data in Table 29 indicate that the PCV method accurately determines total reactive aluminum in solutions with and without the presence of organic complexing ligands. When 5 mg/L of dissolved organic carbon are added to the solutions, however, the fraction of non-exchangeable aluminum increases. This is consistent with the theory that the organic humic and fulvic acids are complexing with the aluminum in solution. Additional work in this area is needed to evaluate the long term stability of these solutions, particularly in terms of the non-exchangeable organically complexed fraction. The results obtained thus far are encouraging and indicate that the continued development of synthetic solutions containing complexing ligands in a mildly acidic solution is worthwhile.

The PCV results obtained from the analysis of natural lake waters used in the intercomparison study are tabulated in Table 30. Included in Table 30 are the data for dissolved organic carbon concentrations for each of the lakes studied. Little Cherry Patch, Wilbur, and Brandy Ponds are noteworthy because

Table 29. Bias Determination of PCV Method

Sample Type	Calculated Total Al (µg/L)	Measured Al Total Reactive PCV (µg/L)	Measured Al Non-exchangeable (µg/L)	Calculated Al[a] Exchangeable (µg/L)
Synthetic Reference (5 mg/L DOC[b])	100	93	**19**	**74**
Synthetic Reference (5 mg/L DOC[b])	200	200	**50**	**150**
Synthetic Reference (no DOC[b])	80	85	**7**	**78**
Synthetic Reference (5 mg/L DOC[b])	80	87	**46**	**41**

a. Total Reactive - Non-exchangeable

b. 4 mg/L Fulvic Acid; 1 mg/L Humic Acid

Table 30. Automated Pyrocatechol Violet Determination of Total Reactive and Non-exchangeable Aluminum

Lake/Pond	Dissolved Organic Carbon (mg/L)[a]	Total Reactive Al (μg/L)	Non-exchangeable Al (μg/L)	Exchangeable Al (μg/L)[b]
Sochia Pond				
Filtered	2	17	9	8
Unfiltered		9	2	7
Killingly Pond				
Filtered	2	185	16	169
Unfiltered		175	10	165
Brandy Pond				
Filtered	8	117	104	13
Unfiltered		141	126	15
Long Pond				
Filtered	4	16	17	-1
Unfiltered		14	11	3
Biscuit Brook				
Filtered	---[c]	78	24	54
Unfiltered		78	21	57
Wilbur Pond				
Filtered	6	157	85	72
Unfiltered		148	85	63
Bailey Pond				
Filtered	5	49	44	5
Unfiltered		40	36	4

a. From Tables 1-9
b. Total Reactive - Non-exchangeable
c. Insufficient Sample

Table 30. Continued

Lake/Pond	**Dissolved Organic Carbon (mg/L)**[a]	Total **Reactive Al (µg/L)**	**Non-exchangeable Al (µg/L)**	**Exchangeable Al (µg/L)**[b]
Follensby Clear Pond				
Filtered	2	7	**7**	**0**
Unfiltered		3	**3**	**0**
Little Cherry Patch Pond				
Filtered	15	71	**63**	**8**
Unfiltered		72	**60**	**8**
Cranberry				
Filtered	4	7	**6**	**1**
Johnson				
Filtered	1	17	**2**	**15**
Delene				
Filtered	7	8	**2**	**6**
Grand Sable				
Filtered	5	41	**30**	**11**
Ostrander				
Filtered	6	47	**3**	**44**
Catract Basin				
Filtered	14	52	**IS**[c]	**IS**[c]
Casey				
Filtered	5	51	**34**	**17**
Annie				
Filtered	4	7	**18**	
Richardson				
Filtered	5	19	**17**	**2**

a. From Tables 1-9
b. Total Reactive - Non--exchangeable
c. Insufficient Sample

of their relatively high dissolved organic carbon concentrations coupled with a large fraction of PCV reactive aluminum in the non-exchangeable fraction. These data are consistent with measurements made using the batch Chelex ion exchange separation and graphite furnace atomic absorption as a the detection technique.

Conclusions

The PCV procedure is fast and exhibits excellent precision and bias characteristics. The color forming reaction is pH dependent, however, which limits the usefulness of the procedure in very acidic solutions (<pH 3.0). When coupled with an ion exchange step, the procedure yields comparable results to graphite furnace determinations preceded by Chelex ion exchange techniques. Results from synthetic reference materials, with humic and fulvic acids added, indicate that the method provides accurate data on inorganic and organically bound fractions of aluminum.

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LUMOGALLION FLUORESCENCE

Background

For fluorescence to occur, a molecule must first absorb radiation at one wavelength and then emit radiation at a later time at a longer, less energetic wavelength (Wehry, 1973). In this method a fluorometric reagent is added to the test solution. The reagent forms a complex with the monomeric, reactive aluminum in solution and the fluorescence of the complex is measured to determine the aluminum concentration. The most sensitive of these fluorometric azo dye reagents in forming complexes with aluminum is lumogallion, 4-chloro-6-(2,4-dihydroxyphenylazo)-1-hydroxzybenzene-2-sulfonic acid (Nishikawa et al., 1967).

As part of the evaluation of this method, the effects of several possibly interfering substances were studied. Of particular interest was the impact that the presence of fluoride, iron, and humic substances had on the measured aluminum concentration. At what concentrations of interfering substances the measurement uncertainties occurred was also explored.

Literature Review

Early fluorometric methods for the determination of aluminum involved the use of 8-hydroxyquinoline, morin, and Pentachrome Blue Black R (PBB) (Burrows, 1977). Table 31 briefly presents some of the conditions and interferences of these methods. The fluorescence of the aluminum salt of 8-quinolinol (8-hydroxyquinoline) in chloroform was used by Goon et al. (1953) for their method to quantitatively determine aluminum in solution. Later Cook (1968) developed a method to determine the aluminum concentration in soil; this method also used the fluorescent complex, 8-hydroxyquinoline aluminum in chloroform. The use of morin in the fluorometric determination of aluminum in the ug/L range has been reported by Fritz (1961). Raggi et al. (1986) used both morin and

Table 31. Determination of A1 by Fluorometric Methods
(from Burrow, 1977)

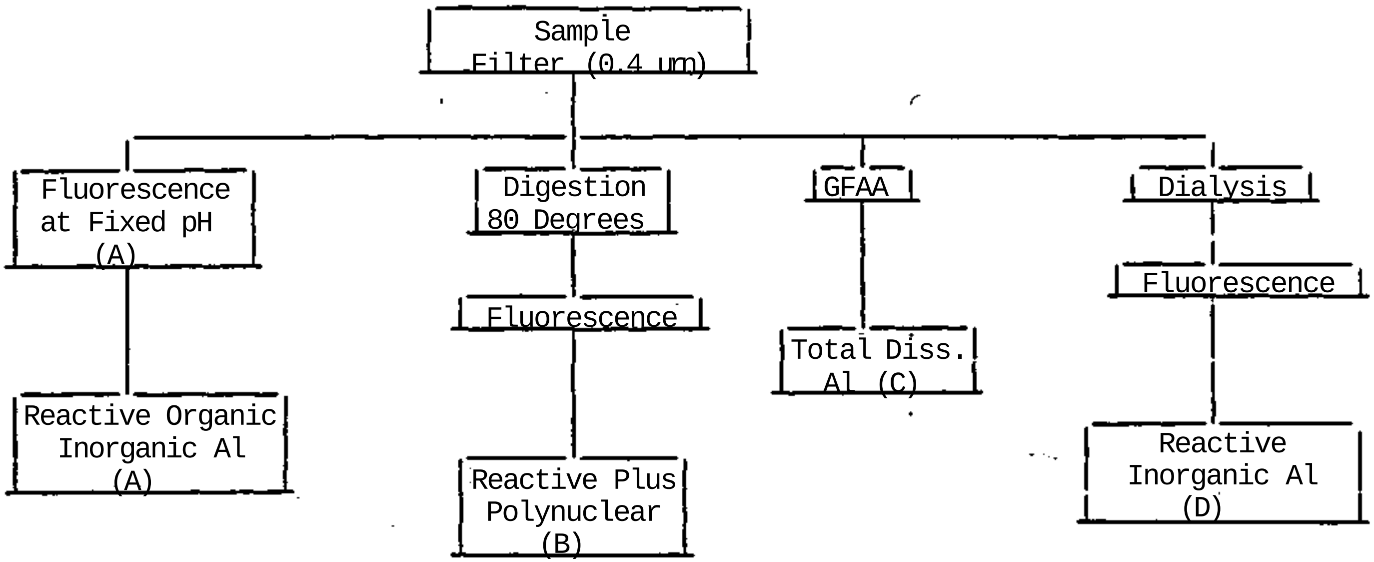
Fluorometric Reagent	Excitation Wavelength (nm)	Emission Wavelength (nm)	Optium PH	Interference (ppb)	Detection Limit (ppb)
Morin	440	525	3.0	Ca(>1000),F"(>5) Fe^{3+}(<100),Mg^{2+}(>200), NH_4^+(>500),PO_4^{3+}(>3) SO_4^{2-}(>1000)	<0.25
Pontachrome Blue Black R.	367	603	5.0	F^-(≥40μg)	0.001-1X
8-Hydroxyquinoline	365	530	8.0	Fe(≥20μg)	-----
Lumogallion	465	555	5.0	Fe(>100),F^-(>300) Humic substances (>5000)	0.12

PBB in the determination of µg/L concentrations of aluminum.

Nishikawa et al. (1967) and Shigematsu et al. (1969) showed lumogallion to be superior to the other fluorometric reagents in terms of sensitivity, precision, and bias. Because of its superior performance characteristics, Hydes and Liss (1976) used lumogallion in the method that they developed for the fluorometric determination of low concentrations of dissolved aluminum in natural waters. Ishibashi and Kina (1972) examined the enhancement of the determination by the addition of surfactants. In 1982, Playle et al. chose it as one of the methods used in their comparison of methods for the determination of aluminum in water. And in 1983, Kramer adopted this method for his aluminum speciation studies. Kramer's method combined with the fluorometer manufacturer's recommended procedures was used for this evaluation.

Experimental Conditions

The procedure for this method is very simple, which makes it very attractive. A pH 5 acetate buffer and the lumogallion are added to the test solutions and the sample vial is shaken vigorously. The vials with the samples are then heated on a water-bath at 80°C for 1.5 hours. The samples are allowed to cool to room temperature before the fluorescence is measured using an excitation wavelength of 465 nm and an emission wavelength of 555 nm. A plot of concentration versus fluorescence was prepared from the analysis of standards prepared by the ISWS. The validity of this concentration curve was checked by the use of a quality control check sample. A blank sample and a quality control sample were analyzed with each set of test samples. Figure 10 is a flow chart that depicts the lumogallion procedure. The method detection limit for this procedure was calculated as 0.12 ug/L (Table 32).



C = Total Dissolved Aluminum
D = Monomeric Aluminum
B-D = Polynuclear Aluminum
C-A = Slow Reactive (Organic/Inorganic)
C-B = Non-reactive Filterable Aluminum
A-D = Reactive Macromolecular Aluminum

Figure 10. **Fluorescence Flowchart for Aluminum Speciation**

(From Kramer, 1983)

Table 32. Method Detection Limit - Lumogallion Method For the Determination of Aluminum

Sample	Al Conc Measured (µg/L)	$(X_i - X)$	$(X_i - X)^2$
1	0.43	0.02	0.0004
2	0.43	0.02	0.0004
3	0.43	0.02	0.0004
4	0.38	-0.03	0.0009
5	0.38	-0.03	0.0009
6	0.35	-0.06	0.0036
7	0.45	0.04	0.0016
Mean, X -	0.41	$\sum (X_i - X)^2$ -	0.0082

$$S^2 - \frac{1}{n-1} \sum_{i-1}^{n-7} (X_i - X)^2$$

$$S - \sqrt{\frac{1}{n-1} \sum_{i-1}^{n-7} (X_i - X)^2}$$

$$- \sqrt{\frac{0.0082}{6}} - 0.037$$

Method Detection Limit - $t_{(n-1,\ 1\ -\ =\ 0.99)}$ X S

- 3.143 X 0.037

- 0.12 µ g/L

Interferences

It has been reported in the literature that fluoride, iron, and humic substances interfere with this method. All three of these potential sources of interference were studied in this evaluation. The results of that work are detailed below.

Varying amounts of NaF were added to a solution containing 5 µg/L aluminum. The lumogallion procedure described previously was followed and the concentration of aluminum in each sample determined from the fluorescence measured. The results from this study are found in Table 33. The literature indicated that the interference from fluoride would begin at fluoride concentrations greater than 300 ug/L. The data in Table 33 confirm this fact. At concentrations of 300 ug/L and less the amount measured aluminum is within experimental error of the target value. Once the fluoride concentration exceeds 300 ug/L the measured value is considerably higher than the target. This could be a problem in some natural waters.

Table 34 presents the data from a similar study investigating the interference of iron. In this instance the interference becomes apparent at 10 ug/L iron, which would be considered a relatively low concentration for many natural waters. This is a more significant source of error. Because the interference results in higher measured concentrations of aluminum than are present in the test sample, it is likely that the iron in also forming a fluorescent complex with the lumogallion that is being measured, at least in part, with the aluminum.

Finally, the data from the study of the influence of humic substances on the measured aluminum concentration are presented in Table 35. As in previous method evaluation, both fulvic acid and humic acid additions were studied. The data indicate the probable competition between the humic and fulvic acids and

Table 33. Flouride Interference in Lumogallion Method for the Determination of Aluminum

Fluoride added to Samples as NaF (mg/L)	Target Al Concentration (μgA)	Measured Al Concentration (μg/L)
0	5	5.0
0.05	5	5.1
0.1	5	4.8
0.3	5	5,1
0.5	5	6.0
1.0	5	9.4

Table 34. Iron Interference in Lumogallion Method for the Determination of Aluminum

Iron (as $Fe(NO_3)_3$) added to Samples (μg/L)	Target Al Concentration (μg/L)	Measured Al Concentration (μg/L)
0	5	5.0
10	5	5.6
20	5	9.0
50	5	7.1
100	5	9.0
10	0	1.2

Table 35. Humic Acid and Fulvic Acid Interferences in Lumogallion Methods for the Determination of Aluminum

Fulvic acid Added to Samples (mg/L)	Target Al Concentration (μg/L)	Measured Al Concentration (pg/L)
0	15	14.4
2	15	14.7
5	15	14.4
10	15	12.2

Humic Acid Added (mg/L)	Target Al Concentration (μg/L)	Measured Al Concentration (μg/L)
2	15	13.6
5	15	9.9
10	15	7.1

The ratio of fulvic acid to humic acid in natural waters is approximately 4:1.

the lumogallion for the available aluminum. At least some of the aluminum complexes with the organic acids and is not measured by this method. The data also imply that the competition from humic acid is greater than that from fulvic acid.

Results and Discussion

The interferences described above makes this procedure less than desirable. The presence of fluoride in natural waters is limited so this interference may not be a major concern. However, the presence of iron and humic substances in natural waters is commonplace and presents a real problem in using this method to determine the dissolved aluminum content. It is still important to evaluate the bias and precision of the method for its potential use when the interfering species are absent from the samples.

Bias

Because the specific form of aluminum being determined by this method is unknown, although assumed to be reactive monomeric aluminum, a certified reference material is not available for use in validating the data produced by its use. In this instance, the well characterized Riverine Water Reference Material was used to estimate the accuracy of the determination. For this sample, the total dissolved aluminum present in the sample is 23.5 μg/L, and the amount measured fluorometrically was 25.2 μg/L, which represents a positive bias of 7%. This would certainly be an acceptable uncertainty in measured aluminum.

Bias was also estimated from the analysis of the ISWS synthetic samples. The results of those analyses are given in Table 36. The results are very good with the percent bias ranging from 1% to 12%. These data indicate that in the absence of interfering ions, the method can be used successfully to quantitate

Table 36. Estimates of Bias From Lumogalllon Fluorescence Experiments

Sample No.	Target Aluminum Concentration (μg Al/L)	Measured Aluminum Concentration (μg Al/L)	Bias	
			μg Al/L	%
1	12.5	12.9	+ 0.4	+3.2
2	15	14.8	- 0.2	-1.3
3	50	56	+ 6	+12.0
4	100	101	+ 1	+1.0

Table 37. Lumogalllon Precision Results

Sample	N	Measured Mean Concentration (μg Al/L)	Standard Deviation (μg Al/L)	RSD %
Synthetic I	4	87.3	1.9	2.2
Sochia Lake	4	10.6	0.15	1.4

the monomeric, reactive aluminum present in the samples. The method can be said to be relatively free of any significant bias.

Precision

A synthetic and a natural sample were analyzed to assess the precision of the method. From Table 37, it is apparent the precision for this method is excellent. It ranges from 1.4% for the natural water sample to 2.2% for the synthetic sample. This information combined with the lack of significant bias indicate that use of this method for aluminum speciation would be at least acceptable if not recommended.

Analysis of Lake Samples

Once estimates of bias and precision under ideal conditions, i.e., when no interfering substances were present, had been established, the fluorometric method was used to determine the reactive aluminum in four New England lakes and nine Michigan lakes. To provide an estimate of the amount of humic substances present in these samples, the dissolved organic carbon (DOC) concentrations were also determined. Table 38 and Table 39 contain the data from these analyses.

Because the Oxine and Lumogallion methods should both be used to determine the monomeric species of aluminum and because both methods suffer from the same interference due to the presence of humic substances in the sample, the results of the oxine procedure have been included in these tables of lumogallion lake sample analyses. A comparison of the data from these methods provides two interesting conclusions. The aluminum concentration determined by the lumogallion method is generally lower than that from the oxine method. It is also evident that the presence of humic species will generally result in measured concentrations much lower than expected. This is probably the result of the

Table 38. Lumogallion-Aluminum in Nine Michigan Lakes

Lake Sample	Total Dissolved Al (ug/L)[a]	Lumogallion Aluminum (ugA)	Oxine Extractable Al (ugA)	DOC (mgA)
Delene	<11	2.5	12	6.88
Ostrander	<11	13.9	20	5.76
Annie	17	19.3	18	14.30
Catract	39	5.2	19	14.30
Casey	<11	3.0	13	4.91
Richardson	<11	4.7	7	4.90
Johnson	11	16.1	---	1.28
Cranberry	<11	12.7	---	4.46
Grand Sable	<11	4.7	---	5.37

[a] From Tables 1-9.

Table 39. Lumoga11ion-Aluminum in Four New England Lakes

Lake Sample	Total Dissolved Al (ug/L)[a]	Lumoga11ion Aluminum (ug/L)	Oxine Extractable Al (ug/L)	DOC (mg/L)
Killingly	236	95.5	144	1.57
Bailey	93	59.0	42	4.93
Wilbur	164	48.5	91	5.53
Long	35	6.6	14	4.13

a. From Tables 1-9.

previously discussed competition between organic ligands.

Conclusions

There are several advantages to the lumogallion fluorescence method. The procedure is simple and relatively short. Our assessment of the bias and precision of the method would also make it a strong candidate for addition to the list of preferred speciation methods. But there are problems which diminish its desirability. It does not always distinguish between the different forms of aluminum. More importantly, the interferences from several commonly occurring substances (iron and humic substances) can be quite severe. These interferences are not trivial and eliminate the use of this method when those substances are known or suspected to be present in the sample. When the interferences are absent, the method is quite satisfactory for speciation of the monomeric aluminum in a sample.

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SUMMARY OF RESULTS

The objective of this cooperative research agreement was to compare various analytical methodologies that have been recommended for use in aluminum speciation studies. Aluminum has been show to be toxic to plant and animal life when present in sufficiently high concentrations and in a bioavailable form. As the pH of natural waters decrease to values below 5.0, aluminum bioavailability increases.

Three broad classifications of aluminum speciation procedures have been examined during the course of this study. The first includes the ion exchange and dialysis procedures, which utilize physical separation techniques to speciate inorganic and organic aluminum. The second type of procedure is a computational technique that utilizes the measured concentrations of bound and free fluoride to infer aluminum speciation. Because of the limitations inherent in the fluoride measurement procedure, however, this technique is generally regarded as a useful adjunct to other more direct determinations of aluminum species. The third type of procedure is based on the reaction rates of various aluminum species with either fluorescent dyes (e.g. Lumogallion) or a chelating agent (e.g. oxine extraction). Some of the advantages and limitations of each of these techniques have been discussed in the previous sections of this report.

Table 40 summarizes the data that have been previously presented separately for each technique that has been evaluated. Total dissolved aluminum determinations were made by inductively coupled plasma spectrometry. Also included in Table 40 are data for sample pH and dissolved organic carbon (DOC). These two parameters appear to be the most important indicators of the fraction of aluminum that will be present in an organically complexed form or in an inorganic form. Killingly Pond, for example, is characterized by relatively high concentrations of total dissolved aluminum and low DOC. As a result, most of

Table 40. Comparison of Aluminum Levels in Natural Lake Samples Determined by Different Methods

				Dialysis Al			Pyrocatechol Colorimetry with Ion Exchange			
Lake Sample	pH[a]	Dissolved Organic Carbon (D0C)[a], mg/L	Total Dissolved Aluminum*, Mg/L	Inorganic Monomerlc, Mg/L	Organic, Mg/L	Oxine Extractable, Mg/L	Total Reactive, Mg/L	Non-Exchangeable, Mg/L	Exchangeable, Mg/L	Lummogallion Fluorescence, Mg/L
Johnson	4.81	1.3	11	...	...	...	17	2	15	16
Catract Basin	7.37	14.3	39	...	...	19	52	...	...	5
Cranberry	4.97	4.5	<11	...	...	...	7	6	1	13
Casey	8.75	4.9	<11	...	...	13	51	34	17	3
Annie	5.78	4.2	17	...	...	18	7	18	...	19
Richardson	6.14	4.9	<11	...	...	7	19	17	2	5
Grand Sable	8.11	5.4	<11	...	...	...	41	30	11	5
Delene	6.83	6.9	<11	...	...	12	8	2	6	2
Ostrander	7.06	5.8	<11	...	...	20	47	3	44	14
Follensby Clear	7.17	2.3	<11	9	...	...	7	7	0	...
Sochla	4.52	1.8	<11	12	...	...	17	9	8	...
Brandy	5.08	8.4	69	53	16	...	117	104	13	...
Little Cherry Patch	6.50	14.9	75	12	63	...	71	63	8	...
Wilbur	4.44	5.5	164	107	57	91	157	85	72	48
Killingly	5.10	1.6	236	202	34	144	185	16	169	96
Bailey	6.37	4.9	93	12	81	42	49	44	5	59
Long	6.50	4.1	35	5	30	14	16	17	...	7

a. From Tables 1-9

concentrations of total dissolved aluminum and low DOC. As a result, most of the aluminum present is found in the inorganic fraction. The data obtained from the dialysis results and the PCV - ion exchange results both support this assumption. The oxine extraction and lumogallion results for Killingly Pond appear to underestimate the inorganic aluminum present when compared to the dialysis and PCV results. Possible reasons for these differences are discussed in the methodology descriptions.

Little Cherry Patch Pond, which has a high DOC and a relatively high total dissolved aluminum concentration, is characterized by the large fraction of aluminum that is present in the non-exchangeable or organic form. Once again, the dialysis data and the PCV data are in very good agreement with each other and with the measurements of total dissolved aluminum by inductively coupled plasma spectrometry.

Wilbur Pond, with a moderately high DOC, shows a partitioning between the inorganic and organic forms that is between the two extremes characterized by Killingly and Little Cherry Patch Ponds. The oxine data for Wilbur Pond agrees well with the inorganic fraction determined by dialysis, but the lumogallion data again appear to underestimate the inorganic aluminum present. The lumogallion method is subject to interferences from the presence of iron, fluoride, and humic materials (i.e. , DOC) which may partially explain the results obtained.

The very low concentrations of aluminum found in the lake water samples from Michigan make any statements regarding the comparability of methods uncertain at best. The fact that the PCV measurements of aluminum in the Michigan lakes are, in general, higher than those measured by inductively coupled plasma raises speculation as to a potential source of contamination from the polyethylene bottles that were used to collect the samples. The PCV determinations were made on samples that vere over one year old because the flow injection apparatus was not available until the second year of the project period. Aluminum contamination has been found in new linear polyethylene bottles (Moody and Lindstrom, 1977) that had not been acid leached. Because of the long exposure times of these samples in the plastic bottles, trace levels of aluminum may have leached from the bottle walls. If the sample bottles are pre-leached with acid prior to sample collection, it is extremely important that all residual acidity be removed prior to using the bottles. Residual acids that may remain in the polyethylene matrix can slowly leach into the sample, decrease the sample pH, and change the naturally occurring speciation of aluminum. Based on the results obtained during this study, it is clear that the holding times and type of collection containers used must be carefully controlled to obtain reliable speciation data.

Although our comparative studies were limited in terms of the numbers of samples that were examined, each of the methods has been rigorously evaluated using literature references and our own laboratory investigations. Based on these results, the dialysis and ion exchange techniques appear to provide the most consistent agreement for identifying the inorganic and organic forms of aluminum in natural waters. The aluminum detection methods, after separation of the various species, have also been evaluated. Based on known interferences, sensitivity, ease of use, and method precision, the automated PCV procedure, graphite furnace atomic absorption (excluding MIBK solvent extracts), and inductively coupled plasma spectrometry techniques are all useful for the reliable measurement of aluminum in natural waters. The oxine extraction procedure, followed by graphite furnace determination of aluminum, exhibits poor precision because of the difficulties associated with reproducible delivery of the MIBK solvent to the graphite substrate. Once pipetted into the tube, the organic solvent tends to disperse non-uniformly making the precision of the procedure unacceptably high for trace determinations of aluminum.

Reference

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APPENDIX

LONG RANGE TRANSPORT OF ATMOSPHERIC POLLUTANTS (LRTAP) INTERLABORATORY STUDY NO. L-13, ALUMINUM IN WATER

The Canadian National Water Research Institute, Analytical Methods Division, operates an interlaboratory comparison program designated the Long Range Transport of Atmospheric Pollutants (LRTAP). The LRTAP program involves many different federal and provincial laboratories producing data for various national and regional programs within that country. To assess the comparability of the data being produced, interlaboratory studies were initiated in December 1982. Under the direction of the Quality Assurance and Methods Section, samples were prepared and distributed to 20 laboratories in Canada for analysis. The first set of 16 samples was primarily lake water with one composite precipitation and three synthetic preparations. As the program developed, the number of laboratories participating grew to include several from the United States, and the frequency of the studies expanded to three times per year. Two of the annual studies focus on the routine analysis of both hard waters (lakes, rivers, etc.) and precipitation and the third, on less routine analyses (trace metals, metal speciation, pH).

In August 1983, the ISWS laboratory was first asked to participate in these interlaboratory comparability studies because of our long-standing involvement in precipitation chemistry measurements. Since this first request, the ISWS has regularly participated in the semiannual intercomparisons of "Major Ions, Nutrients and Physical Properties in Water." The parameters included in each study are: specific conductance, pH, nitrate, ammonia, sodium, magnesium, sulfate, chloride, potassium, and calcium. The methods employed for these analyses include electrometric analysis, conductimetric analysis, atomic absorption spectroscopy, ion chromatography, and automated wet chemistry.

In 1986, an interlaboratory study was initiated to assess the comparability of data from LRTAP laboratories who have programs monitoring total aluminum in dilute waters. The secondary objective of this study was to compare data from laboratories who measure various species of aluminum in unpreserved natural waters. The ISWS laboratory was invited to participate in this study because of its project to evaluate aluminum speciation procedures. To meet the study objectives, three series of test samples were developed. The first series of samples (designated A#) were unpreserved filtered natural waters prepared for the determination of total aluminum. The second series (designated B#) were separate aliquots of the same samples prepared for laboratories measuring total as well as various species of aluminum. Laboratories were requested to use the speciation technique that was routinely employed in their programs. The third series (designated C#) of waters were acid-preserved standards for which target concentrations had previously been established. A complete summary of the experimental design and sample preparation is provided in Aspila (1986) .

The ISWS data are presented in Tables 1-4 with the median and mean results reported from all of the study participants. For the total aluminum determinations in all three series of samples, the ISWS results received satisfactory ratings, indicating no analytical bias. Total aluminum was determined on these samples by flame atomic absorption using a nitrous oxide-acetylene combustion mix and CsCl as an ionization supressant. In order to increase the sensitivity of the method, all of the samples were concentrated by a factor of 10 using a 0.2% nitric acid digestion procedure.

Table 3 presents the ISWS results from the paired duplicate samples in the "A" and "B" series samples. The presence of duplicate samples was not known to the participants during the study period, so these data reflect an unbiased estimate of intralaboratory precision for total aluminum. Using the formula for estimating standard deviation from duplicate sample pairs, the ISWS calculated average precision was 5% expressed as the relative standard deviation (RSD). The data contained in Tables 1 and 2 indicate that the interlaboratory precision (expressed as the standard deviation) obtained in this study was characterized by RSD's from 11-40%. This large interlab variance is explained in part by the fact that each laboratory was asked to use the methods that they routinely utilize in performing these analyses. No standard method was provided or recommended to the laboratories. The analytical methodologies used in this intercomparison included most of the procedures that are were evaluated as a part of our methods evaluation work. They included: inductively coupled plasma spectrometry, oxine extraction, graphite furnace atomic absorption, pyrocatechol colorimetry, flame atomic absorption, neutron activation analysis, lumogallion fluorescence, direct current plasma spectrometry, and preliminary dialysis. The large variance that characterizes these data indicates that a rigorous methods validation for total, as well as speciated, aluminum was needed to identify those procedures that will produce comparable and correct results.

The data in Table 4 were obtained from the "B" series samples that were used to evaluate various speciation techniques. The ISWS data were obtained by performing a batch ion exchange procedure using Chelex 100 resin followed by filtration and flame atomic absorption analyses of the filtrate. A second aliquot was analyzed without the ion exchange step and the concentration differences reported as "ion exchangeable aluminum." Only one other laboratory reported an ion exchangeable fraction, determined using Amberlite exchange resin in an automated flow-through system followed by detection using pyrocatechol violet coloriraetry. As Table 4 indicates, the agreement between the two methods is very inconsistent. When data from these two laboratories were included with eight other labs reporting an inorganic monomeric fraction, the results again showed a large variance ranging from 20-76% RSD.

The ISWS participation in this interlaboratory comparison was initiated at the beginning of the project period. Since that time, we have evaluated many of the various procedures that were used in this study in order to identify the sources of the variance found. By performing these procedures in a single laboratory with well characterized natural and synthetic samples, the limitations and strengths of each methodology were quantified.

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Table 1. Results of LRTAP Study 13
Total Aluminum in Water - 1986

Concentration Data (μg/L)

Sample No.	N[a]	Mean	Standard Deviation	Median	ISVS
A1	9	0.9	9.4	3.0	<20
A2	13	12.1	13.6	8.0	<20
A3	20	45.5	17.5	44.4	55
A4	19	63.8	24.8	55.0	55
A5	21	93.3	22.8	91.0	102
A6	20	126.2	28.1	128.5	137
A7	20	132.2	33.0	135.0	149
A8	20	194.8	37.9	208.5	218
A9	21	285.8	61.9	307.0	309
A10	21	377.7	97.6	410.0	432
A11	21	344.4	83.8	353.0	342
B1	15	125.8	21.9	132.0	124
B2	15	204.2	25.0	210.0	229
B3	15	298.8	32.6	305.0	327
B4	15	387.0	60.4	397.0	449
BS	15	348.3	40.9	362.0	370

a. Number of labs used in calculating median and mean concentration data

Table 2. Results of LRTAP Study 13
Total Aluminum in Water - 1986
Preserved Samples

Concentration Data (μg/L)

Sample No.	N[a]	Mean	Standard Deviation	Median	ISWS
C1	8	9.6	14.3	3.4	<20
C2	21	54.0	8.2	53.0	56
C3	22	97.3	13.0	98.0	100
C4	22	344.6	100.1	387.0	357
C5	22	257.6	50.6	255.5	250
C6	22	286.9	51.6	293.0	297

a. Number of labs used in calculating median and mean concentration data

Table 3. Results of LRTAP Study 13
Total Aluminum in Water - 1986

Precision Estimates from Duplicate Measurements

Sample Nos.	Concentration (μg/L)	|Difference|	|Difference|^2
A7	149	25	625
Bl	124		
A8	218	11	121
B2	229		
A9	309	18	324
B3	327		
A10	432	17	289
B4	449		
All	342	28	784
B5	370		
mean (x) -	295		S 2143

Standard Deviation (s) -. $\sqrt{\frac{\Sigma d^2}{2n}}$ - $\sqrt{\frac{2143}{10}}$ - 15 MgA

where d - difference of a duplicate measurement
n - number of duplicate measurements

Relative Standard Deviation (RSD) - $\frac{s.}{X}$ X 100 - $\frac{15}{295}$ X 100 - 5%

Table 4. Results of LRTAP Study 13
Speclated Aluminum in Water - 1986

Concentration Data (μg/L)

Sample No.	ISWS[a]	Inorganic Monomeric[b]	Exchangeable Aluminum[c]
Bl	**35**	**18**	28.8
B2	**72**	87.5	108.5
B3	100	90.3	102.2
B4	136	316.3	316.5
B5	136	90.9	96.8

a. Exchangeable aluminum using Chelex 100; flame atomic absorption was used for aluminum detection.
b. Interlaboratory median values; n — 10
c. Exchangeable aluminum using Amberlite resin followed by pyrocatechol violet colorimetry; one laboratory reporting this method.