Illinois State Water Survey Division

ANALYTICAL CHEMISTRY UNIT

SWS Contract Report 436

EVALUATION OF ALUMINUM SPECIATION
USING SYNTHETIC AND NATURAL SAMPLES:
FIRST PROGRESS REPORT

by
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Prepared for:

inorganic Analysis Section
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United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

Champaign, Illinois

December 1987

Illinois Department of Energy and Natural Resources

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ACKNOWLEDGMENTS

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ABSTRACT

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. 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 concentration, and total organic carbon (TOC) content all influence the chemical speciation and subsequent bioavailability of aluminum.

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 used when analyzing historical data sets, interpreting data collected from the NSWS, and conducting future aluminum speciation studies. This project was initiated to address the recommendations of that Workshop.

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.

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

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 is 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 200 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 has been 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 liter 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^+, NH_4^+, SO_4^{2-}, NO_3^-, Cl, and PO_4^{3-}) analyses were performed as well as DOC, color, turbidity, acid neutralizing capacity (ANC), fluoride, iron, and conductivity. Insoluble mass composition was also characterized on the particulates collected on polycarbonate membranes to examine the relative importance of insoluble aluminum to the total sample concentration. These data, combined with the water chemistry data from previous sampling periods, are being 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 the Water Survey 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 needs to be developed that contains the matrix components common to natural waters. We have formulated a set of synthetic solutions that contains 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. The development of stable reference solutions that more closely approximate natural waters is a key element of the methods intercomparison study.

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WATER CHEMISTRY DATA

Tables 1-9 present the chemistry data from the 17 lakes that are being used for the aluminum speciation studies. Each table contains the ISWS measured concentration data as well as the data from earlier sampling periods. The methods used by the ISWS are described in Table 17 of the Experimental Methods Section. Dissolved inorganic carbon (DIC) and pH values are for air-equilibrated samples. Sum of cations and anions values omit those ions whose concentrations are below the method detection limit. Values for HCO_3^- are preferred over those of acid neutralizing capacity (ANC) by the NSWS 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. Inductively coupled plasma (ICP) results for sulfur are reported in Table 10 and compared to ion chromatography values. Agreement between the two methods is excellent for 15 of the 17 lakes examined. A Wilcoxon paired rank sum test performed on the complete data set revealed no significant differences (95% confidence interval) between the Water Survey IC and ICP data. The ICP results for Delene Lake and Catract Basin in Michigan are, however, higher than the ISWS IC results and the IC results obtained during the NSWS. Since the ICP determination measures total sulfur, it is possible that other sulfur species (organo-sulfur compounds) besides sulfate are present in these two lakes.

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 will allow us to more reliably interpret our speciation results in terms of their applicability to existing NSWS aluminum concentration values. A summary of the analytical methods used by the ISWS is presented in Table 11.

Table 1. Adirondack Lakes Survey (ALS)

Parameter	Little Cherry Patch Pond (ALS #020240) (Collection Period)		Brandy Pond (ALS #020115) (Collection Period)	
	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+} (ueq/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
Cations (ueq/L)	1614.8	2010.6	867.5	1130.4
SO_4^{+-} (ueq/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^-	---	---	----	----
Anions (ueq/L)	1443.5	2018.5	691.0	1157.9
Cond. (uS/cm)	187.5	229	105.9	136.8
Color (PCU)	100	---	240	---
P (ug/1)	36	<40	30	<40
Mn "	55	43	55	49
Fe "	460	312	54	451
Al (tot.) "	77	75	183	69
Al (ext.) "	---	---	---	---
DIC (mg/1)	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 Survey Data
b. Illinois State Water Survey Data

Table 2. Adirondack Lakes Survey (ALS)

Parameter	Follensby Clear Pond (ALS #020116) (Collection Period)		Sochia Pond (ALS #020197) (Collection Period)	
	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+} (ueq/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	0.1	26.3	30.1
Cations (ueq/L)	412.8	452.6	57.0	109.1
SO_4^{2-} (ueq/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^- "	---	---	**---**	---
Anions (ueq/L)	392.1	389.6	58.4	63.6
Cond. (uS/cm)	42.7	43.8	14.6	17.3
Color (PCU)	5	---	10	---
P (ug/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 Survey Data
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+} (ueq/1)	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
Cations (ueq/L	87.8	72.3
SO_4^{2-} (ueq/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	---
Anions (ueq/L)	74.7	64.2
Cond. (uS/cm)	9.3	14.7
Color (PCU)	21	---
P (ug/1)	17.0	<40
Mn "	10.0	3
Fe "	20.0	7
Al (tot.) "	12.0	<11
Al (ext.) "	6.0	---
DIC (mg/1)	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

Parameter	Casey Lake (NSWS #2B3-027) Sample Collection Period 10/16/84[a]	6/30/87[b]	Lake Annie (NSWS #2B3-058) Sample Collection Period 10/18/84[a]	7/9/87[b]
pH (air-equil.)	8.69	8.75	6.77	5.78
Ca^{2+} (ueq/1)	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
Cations (ueq/L)	1679.3	1720.0	91.7	79.3
SO_4^{2-} (ueq/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
ANC "	1713.0	1420	32.0	8.8
HCO_3^- "	1500.1	---	24.2	---
Anions (ueq/L)	1593.1	1525.0	78.2	79.2
Cond. (uS/cm)	157.2	158.2	11.4	16.5
Color (PCU)	15	---	15	---
P (ug/1)	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/1)	18.16	---	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

Parameter		Ostrander Lake (NSWS #2B3-071) Collection Period		Catract Basin (NSWS #2B3-028) Collection Period	
		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+}	(ueq/1)	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
Cations (ueq/L)		270.7	237.9	1031.1	956.3
SO_4^{2-}	(ueq/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	---
Anions (ueq/L)		229.1	213.3	967.2	763.4
Cond.	(uS/cm)	22.2	28.8	101.7	90.0
Color	(PCU)	15	---	83	---
P	(ug/1)	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/1)	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

Parameter	Delene Lake (NSWS #2B2-098) Sample Collection Period		Grand Sable (NSWS #2B3-009) Sample Collection Period	
	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+} (ueq/1)	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
Cations (ueq/L)	198.3	194.7	1169.7	1165.6
SO_4^{2-} (ueq/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	---
Anions (ueq/L)	127.7	148.1	1044.3	---
Cond. (uS/cm)	19.6	27.2	102.7	111.0
Color (PCU)	45	---	---	---
P (ug/1)	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/1)	1.29	---	10.64	---
DOC "	10.30	6.88	11.90	5.37
SiO_2 "	0.80	0.41	6.49	0.60

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

Table 7. NSWS Lakes - Michigan Lakes

Parameter		Cranberry Lake (NSWS #2B2-049) Sample Collection Period		Johnson Lake (NSWS #2B1-047) Sample Collection Period	
		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+}	(ueq/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
Cations (ueq/L)		73.3	71.1	130.6	116.5
SO_4^{2-}	(ueq/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	---
Anions (ueq/L)		55.2	---	148.9	127.6
Cond.	(uS/cm)	10.6	14.1	27.9	28.0
Color	(PCU)	25	---	5	---
P	(ug/1)	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/1)	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

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

Parameter	Killingly Pond (NSWS #lD3-029) Sample Collection Period		Wilbur Pond (USFWS #1146) Sample Collection Period	
	11/4/84[a]	3/20/87[b]	12/12/80[c]	3/20/87
pH (air-equil.)	4.97	5.10	3.98	4.44
Ca^{2+} (ueq/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^+ "	10.7	7.9	104.7	36.3
Cations (ueq/L)	200.6	263.7	311.0	186.5
SO_4^{2-} (ueq/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 ~ "	0.9	---	----	----
Anions (ueq/L)	249.0	291.9	234.4	175.8
Cond. (uS/cm)	33.6	41.5	64	33.5
Color (PCU)	5	5	150	50
P (ug/1)	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/1)	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

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Table 9. New England Lakes - NSWS

Parameter	Bailey Pond (NSWS #1D1-020) Sample Collection Period		Long Pond (NSWS #1D3-025) Sample Collection Period	
	11/4/84[a]	3/20/87[b]	11/8/84[3]	3/20/87[b]
pH (air-equil.)	6.78	6.37	7.63	6.50
Ca^{2+} (ueq/L)	101.9	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
Cations (ueq/L)	329.2	448.4	309.1	366.4
SO_4^{2-} (ueq/L)	127.5	152.1	91.4	110.4
Cl~ "	114.4	169.2	52.8	56.4
NO^- "	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	----
Anions (ueq/L)	289.9	394.8	293.4	332.9
Cond. (uS/cm)	38.4	61.2	34.6	42.5
Color (PCU)	80	40	40	45
P (ug/1)	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/1)	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. Comparison of SO. Data Obtained by
Ion Chromatography (IC) and Inductively
Coupled plasma Spectrometry (ICP)
(ueq/L)**

Lake, State	Lake Survey Data[b]	ISWS-IC	ISWS-ICP
Little Cherry Patch, NY	134.6	94.4	109.4
Brandy Pond, NY	92.1	89.4	92.6
Follensby Clear Pond, NY	95.8	104.6	101.3
Sochia Pond, NY	53.5	55.4	56.2
Bailey Pond, CT	127.5	152.1	149.4
Long Pond, CT	91.4	110.4	109.4
Killingly Pond, CT	127.7	139.6	138.5
Wilbur Pond, RI	142.7	122.9	112.5
Richardson Lake, MI	47.9	41.0	46.3
Casey Lake, MI	74.5	81.7	80.6
Lake Annie, MI	43.7	57.9	60.6
Ostrander Lake, MI	77.4	76.3	76.9
Catract Basin, MI	104.8	85.8	324.4
Delene Lake, MI	28.5	38.1	155.6
Grand Sable, MI	104.7	116.7	111.3
Cranberry Lake, MI	46.2	57.1	57.5
Johnson Lake, MI	133.0	117.9	116.3

a. ICP sulfur data are reported as SO_4 for comparison

b. Lake survey data include National surface Water Survey,
    Adirondack Lakes Survey and US Fish and wildlife Survey

Table 11. Analytes and Methods Used for Lake Chemistry Characterizations

Parameter	Method	References 1983 USEPA	References 1986 USEPA	Other	Method Detection Limit
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

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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 Division, samples were prepared and distributed to 20 laboratories in Canada for analysis. The first set of sixteen 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 (lakes, rivers, etc.) and soft (precipitation) waters ana 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/nitrite, 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 soft waters. The secondary objective of this study was to compare data from laboratories who measure various species of aluminum in soft unpreserved natural waters. The ISWS laboratory was invited to participate in this study because of our recently funded program in evaluation of aluminum speciation procedures. To address 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 used 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 tabulated 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 that 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 interlao 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 being 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, lumogallium 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 is needed to identify those procedures that will produce comparable and correct results.

Table 4 presents data 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 colorimetry. 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 established protocols to evaluate the various procedures that were used in this study in order to identify the sources of the variance found. By performing all of these procedures in a single laboratory with well characterized natural and synthetic samples, the limitations and strengths of each methodology will be quantified.

REFERENCE

Aspila, K.I., Draft Summary Report, LRTAP Interlaboratory study No. L-13, Aluminum in Water, National Water Research Institute, Burlington, Ontario, Canada, 1986.

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

Concentration Data (ug/L)

Sample No.	N[a]	Mean	Standard Deviation	Median	ISWS
Al	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
All	21	344.4	83.8	353.0	342
Bl	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
B5	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 (ug/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
	370		
mean ($\bar{X}$) =	295		2143

$$\text{Standard Deviation (s)} = \sqrt{\frac{\Sigma d^2}{2n}} = \frac{2143}{10} = 15 \text{ ug/L}$$

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

$$\text{Relative Standard Deviation (RSD)} = \frac{s}{\bar{X}} \times 100 = \frac{15}{295} \times 100 = 5\%$$

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

Concentration Data (ug/L)

Sample No.	isws[a]	Inorganic Monomeric[b]	Exchangeable Aluminum
B1	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.

BACKGROUND

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. Mononuclear aluminum
    4. Polynuclear aluminum
    5. Organic aluminum

These are diagramed in Figure 1. The total dissolved aluminum is operationally defined as the fraction which passes through a membrane filter with 0.45 um pore size. This fraction is composed of mononuclear aluminum, polynuclear aluminum, and organic aluminum. Part of the dissolved aluminum may also be associated with the colloidal phase of the solution since the 0.45 um pore size membrane filter does not retain colloidal particles.

Particulate aluminum is the fraction which does not pass through the 0.45 um pore size. This is mainly aluminum adsorbed onto the surfaces of solid particles. This may include colloidal aluminum and aluminum adsorbed onto organic substrates of high molecular weight. There is still a controversy over which type of filter pore size to use for fractionation studies since some particulate aluminum will still be detected on a 0.2 um filter after the solution has been passed through 0.45 um filter.

Mononuclear aluminum is composed of all the simple inorganic complexes and the low molecular weight organic complexes of aluminum. The inorganic complexes include the hydrolysis products and the complexes of fluoride, sulfate and phosphate. The hydrolysis product complexes have been studied in detail. Hem and Roberson (1967) have shown that the hydrolysis products of aluminum include $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_4^-$, and $Al(OH)_3$. Recently, Rubin (1985) has disproven the existence of $Al(OH)_2^+$ and has proposed a new scheme to illustrate the hydrolysis of aluminum (see Figures 2 and 3). The speciation of inorganic monomeric aluminum has been shown to be pH dependent. Ma-nahan (1975) has shown that below pH 4.0, $Al(H_2O)_6$ predominates and between pH 4.5 and pH 6.5, the species present include $Al(OH)^{2+}$, $Al(OH)_3$ (S) and fluoride complexes of aluminum. For pH values greater than 7.0, $Al.(OH)_4^-$ is the major ionic form of aluminum present.

With regard to polynuclear aluminum species, there is no agreement as to the forms and structures of the species which are present in aqueous solution. There appears to be substantial evidence for the formation of the polymeric species $Al_2 (OH)_2^{4+}$ and $Al_{13} O_4 (OH)_{24}^{7+}$. Aveston (1965), and later Mesmer and Baes (1971), studied the hydrolysis products of aluminum in acidic solutions at elevated temperatures. Based on their results, it has been concluded that the polynuclear species formed by Al hydrolysis are

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                    ┌─────────────────────┐
                    │ Aluminum Speciation │
                    └─────────────────────┘
                               │
        ┌──────────────────────┼──────────────────────┐
┌───────────────┐      ┌───────────────┐      ┌───────────────┐
│  Particulate  │      │   Monomeric   │      │   Polymeric   │
│ and Colloidal │      │ (Extractable) │      │ (Acid Reactive)│
│   Aluminum    │      └───────────────┘      └───────────────┘
│ (Acid Reactive)│             │
└───────────────┘              │
                ┌──────────────┴──────────────┐
        ┌───────────────┐              ┌───────────────┐
        │   Inorganic   │              │    Organic    │
        │   Monomeric   │              │   Monomeric   │
        │(Fast extractable)│           │(non-exchangeable)│
        └───────────────┘              └───────────────┘
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Inorganic Monomeric (Fast extractable)

$Al(H2O)_6^{3+}$ $Al(F)^{2+}$ $AlSO_4^{+}$

$Al(OH)^{2+}$ $Al(F)_2^{+}$ $Al(SO_4)_2^{-}$

$Al(OH)_2^{+}$ $Al(F)_3$

$Al(OH)_3$ $Al(F)_4^{-}$

$Al(OH)_4^{-}$ $Al(F)_5^{2-}$

$Al(F)_6^{3-}$

Organic Monomeric (non-exchangeable)

Al bound humic acid

Al bound fulvic acid

Figure 1.   Proposed Aluminum Speciation Scheme

Hydrolysis of Aluminum (III)

Increasing pH →

$$Al^{3+} \rightleftharpoons AlOH^{2+} \rightleftharpoons Al(OH)_3(s) \rightleftharpoons Al(OH)_4^-$$

$$Al_8(OH)_{20}^{4+} \qquad AlOOH(s) \rightleftharpoons Al_2O_3(s)$$

Other Polynuclears

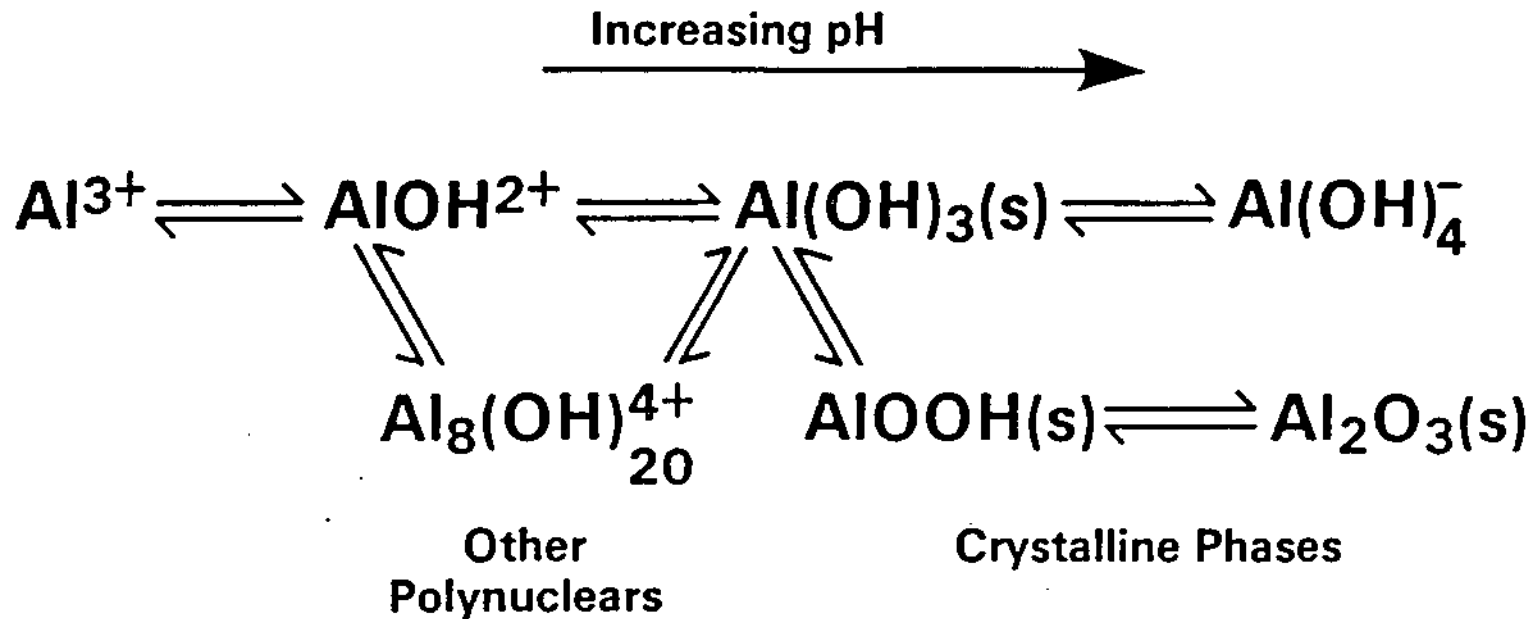**Crystalline Phases**

Figure 2. Aluminum III Hydrolysis Mechanisms
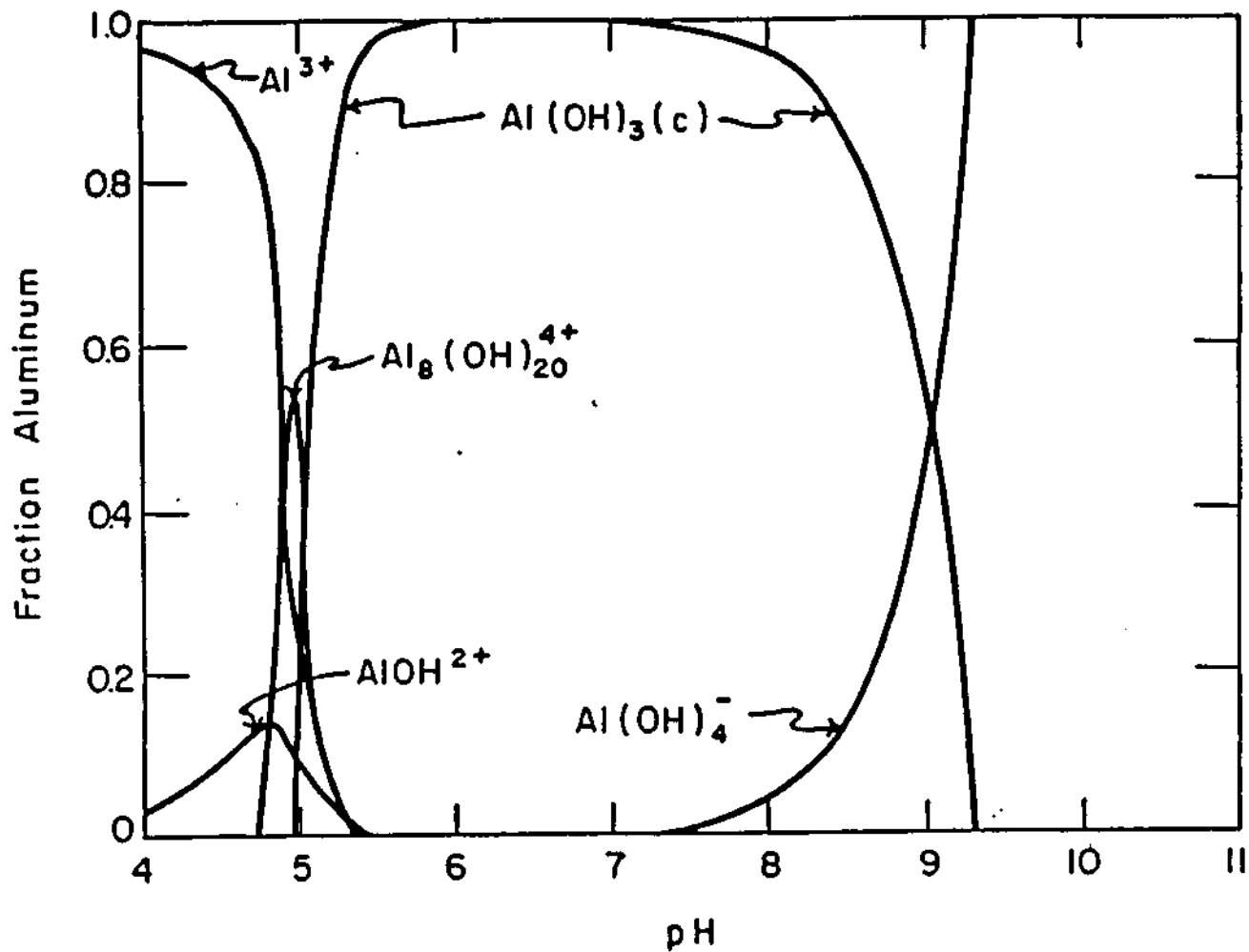(from Rubin, 1985)

Figure 3. Distribution of Hydrolyzed Aluminum (III)
as a function of pH
(from Rubin, 1985)

concluded that the polynuclear species formed by Al^{3+} hydrolysis are $Al_3(OH)_4^{5+}$, $Al_{13}O_4(OH)_{24}^{7+}$, and $Al_2(OH)_2^{4+}$. It can be considered that there are two classes of organo-aluminum complexes. Complexes associated with low molecular weight organics include citric acid, oxalic acid, lactic acid, and some fulvic acids. Complexes associated with high molecular weight organics include polyphenols, carboxylic phenols, aromatic phycarboxylates, and unsaturated cyclic-hydroxyketones. These latter compounds are mainly the components of humic substances.

ANALYTICAL METHODS FOR ALUMINUM SPECIATION

Oxine Extraction

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 forms of Al in aqueous solutions. 8-Quinolinolate extraction methods for the determination of Al plus mononuclear hydroxyaluminum ions, polynuclear hydroxyaluminum ions, and the initial solid phase formed when a base is added to $AlCl_3$ solutions have been reported by Turner (1969).

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 separated from experimental suspensions of clay minerals by solvent extraction followed by spectrophotometric detection of the aluminum 8-hydroxyquinoline complex. The method has been adapted and modified for the determination of labile and total aluminum in soil extracts by Bruce et al. (1983). The most recent method involving 8-hydroxyquinoline is a fast extraction (10-15s) of the aluminum-oxine complex into methyl-isobutyl ketone (MIBK) followed by graphite furnace atomic absorption determination. This method has recently been used in aluminum speciation projects by Lazerte (1984) and later Campbell et al. (1986). In addition, this procedure was used for the Phase I NSWS sampling program. The method of oxine extraction followed for our evaluation study was adapted from Campbell et al. (1986).

Fluorometric Method

Early fluorometric methods for the determination of aluminum involved the use of 8-quinolinol and morin. The fluorescence of the aluminum salt of 8-quinolinol (8-hydroxyquinoline) in chloroform for the quantitative

determination of aluminum has been reported by Goon et al. (1953). The use of morin in the fluorometric determination of aluminum in the ug/L range has also been reported by Fritz (1961). In order to determine soil aluminum concentrations, Cook (1968) developed a procedure based on the fluorescence of the Al salt of 8-hydroxyquinoline in chloroform. Hydes and Liss (1976) have developed a fluorimetric method for the determination of low concentrations of dissolved aluminum in natural waters. In their method, Lumogallion reagent was used. This reagent is superior to the other reagents used in fluorometric studies in terms of sensitivity, precision, and bias. Because of its superior performance characteristics, this method has been adopted by Kramer (1983) in his aluminum speciation studies. Kramer's method was adopted in our evaluation study.

Ion-Exchange Resin

Perhaps the most comprehensive report on the use of ion-exchange resins in aluminum speciation studies is the one by Campbell (1983). The type of ion-exchange resin used in his study is Chelex 100. In his method, the resin was first equilibrated with a synthetic solution containing Ca^{2+}, Mg^{2+}, and H^{+} at concentrations similar to those encountered in the natural waters of interest. Clair and Komadina (1984) adopted the Chelex 100 method to study aluminum speciation in waters of Nova Scotia. The Chelex 100 method has been evaluated by Lacroix et al. (1986) and subsequently adopted with modification to speciate aluminum in acidic rivers of Nova Scotia. The method has also been adopted by Andelman and Kwan (1986) to study the impact of acid rain on aluminum species in streams.

The other ion-exchange resin which has been used for aluminum speciation is Amberlite IR 120. It has been used in a column instead of a batch mode and primarily in automated wet chemical analyzer systems. Rogeberg and Henriksen (1985), in their automated system, used Amberlite ion-exchange resin for the fractionation of aluminum species in fresh waters with subsequent determination by pyrocatechol violet colorimetry. Hans Borg (1986) has reported metal speciation data from acidified mountain streams in central Sweden using Driscoll's method (1980) based on amberlite IR 120. Recently, Backes and Tipping (1987) have evaluated the use of Amberlite 120 for the determination of organically complexed Al in natural acidic waters.

The method involving ion-exchange in current use is based on Campbell's Chelex 100 procedure. This procedure was the one selected for our comparative studies.

Pyrocatechol Violet Colorimetry (PCV)

Pyrocatechol violet is a chromogenic reagent that has frequently been used in the determination of trace concentrations of aluminum. The first use of this reagent for the colorimetric determination of aluminum was reported by Anton (1960). His results indicated that 1 mole of aluminum (III) will complex 1.5 moles of pyrocatechol violet at a pH of 5 and that iron was a major interference. Tanaka and Yamayosi (1964) investigated the critical parameters for the use of the reagent for the determination of aluminum. Meyrowitz (1970) has used this reagent for the direct trace determination of

aluminum in silicate minerals. The method for aluminum determination using the pyrocatechol violet reagent has been evaluated and modified by Dougan and Wilson (1974). Henriksen and Bergmann-Paulsen (1975) have adopted the method in their automated system for measuring aluminum in natural waters. In their method, aluminum reacts with pyrocatechol violet at a pH of 6.0-6.2. The complex formed is measured colorimetrically at 590 nm. Helliwell et al. (1983) have used the method to study the speciation and toxicity of aluminum in a model fresh water. Aluminum speciation at the interface of an acid stream and a limed lake has been studied by Wright and Skogheim (1983). In their method, aluminum was also determined by the PCV technique. The automated procedure for the fractionation and determination of aluminum species in fresh waters reported by Rogeberg and Henriksen (1985) utilizes catechol violet colorimetry as the detector for the aluminum species. Because of its high sensitivity, greater precision, and shorter time of analysis per sample, the automated catechol violet method was selected to replace the oxine extraction technique during Phase II of the NSWS. The method we will evaluate is based on the National Surface Water Survey Analytical Methods Manual by Kerfoot et al. (1986).

Bound/Free Fluoride Method

The use of the bound/free fluoride method in the study of inorganic aluminum speciation has been recent. Driscoll (1980) and later Johnson et al. (1981) were the first to use this technique to determine inorganic aluminum speciation. In their methods, free fluoride was determined by direct measurement using the fluoride ion-selective electrode. David (1984) adopted the bound/free fluoride procedure in his aluminum speciation studies of soil and river water samples. The method has also been evaluated by Lazerte (1984) and Hodges (1987). Currently, it is the only method which is often used to speciate inorganic aluminum in fresh water systems.

Dialysis

Dialysis experiments are performed to supplement the bound/free fluoride method for the determination of inorganic aluminum species. The literature references for dialysis experiments for aluminum speciation are very limited except for those associated with oxine extraction and bound/free fluoriae methods. The method has been evaluated by Lazerte (1984).

Flow charts for the six methods which are being evaluated in our laboratory are shown in Figures 4-9.
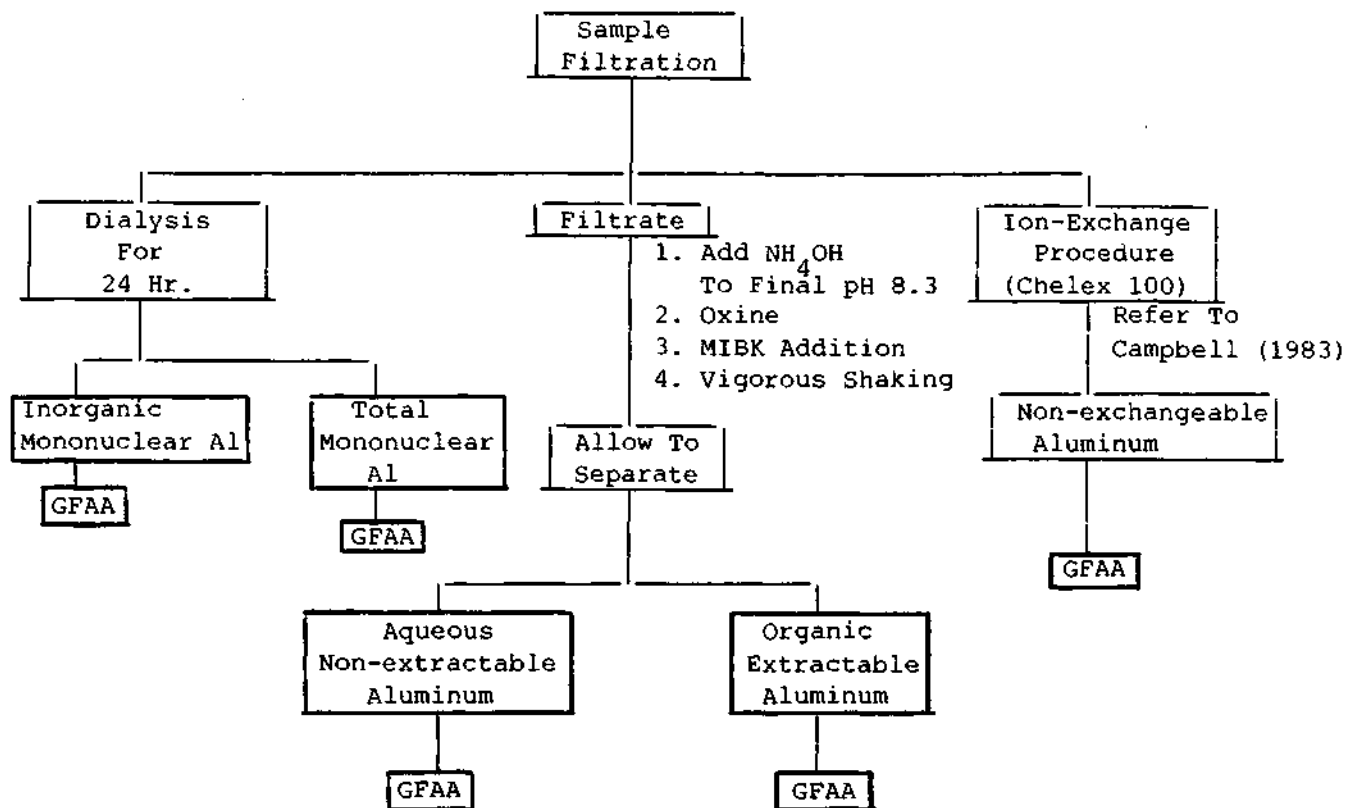
Figure 4.   Oxine Extraction Flowchart for Aluminum Speciation
(from Campbell et al., 1986)

```
              ┌─────────────────────┐
              │     Sample          │
              │ Filter (0.4 um)     │
              └─────────────────────┘
                       │
     ┌─────────────────┼──────────────────────────────┬──────────────────┐
     │                 │                               │                  │
┌──────────────┐ ┌──────────────┐              ┌──────────┐      ┌──────────────┐
│ Fluorescence │ │ Digestion    │              │ GFAA     │      │ Dialysis     │
│ at Fixed pH  │ │ 80 Degrees   │              └──────────┘      └──────────────┘
│     (A)      │ └──────────────┘                   │                  │
└──────────────┘        │                      ┌──────────┐      ┌──────────────┐
     │          ┌──────────────┐               │Total Diss│      │ Fluorescence │
     │          │ Fluorescence │               │ Al  (C)  │      └──────────────┘
     │          └──────────────┘               └──────────┘            │
┌──────────────┐        │                                       ┌──────────────┐
│Reactive Organic│ ┌──────────────┐                             │   Reactive   │
│ Inorganic Al │   │ Reactive Plus│                             │ Inorganic Al │
│     (A)      │   │  Polynuclear │                             │     (D)      │
└──────────────┘   │     (B)      │                             └──────────────┘
                   └──────────────┘
```
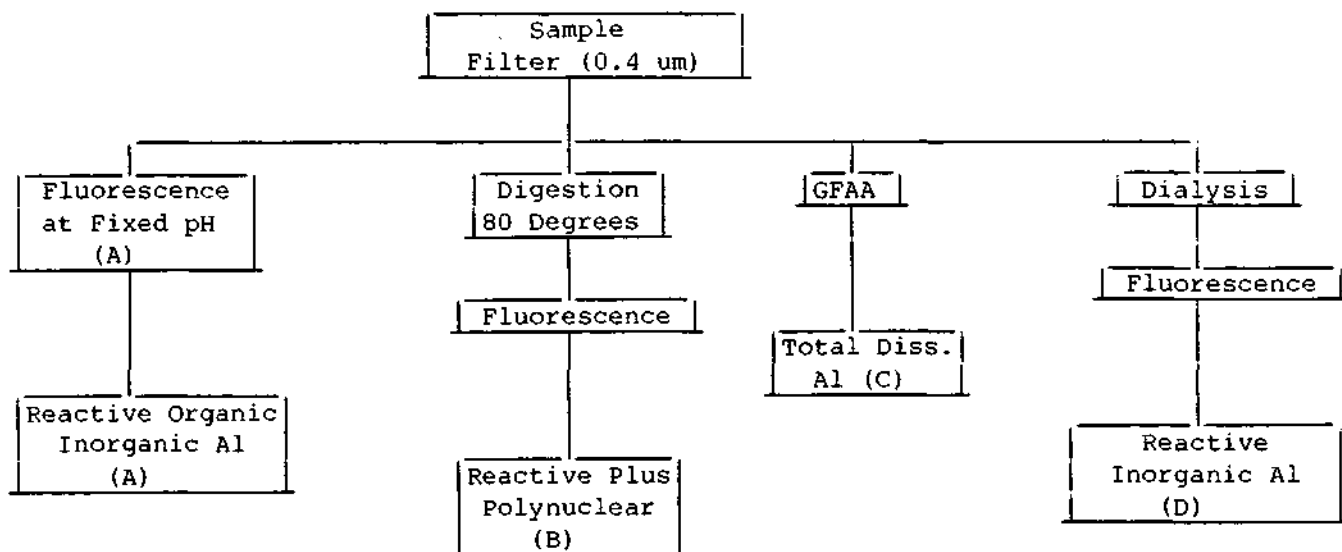
        C   = Total Dissolved Aluminum
        D   = Monomeric Aluminum
      B-D   = Polynuclear Aluminum
      C-A   = Slow Reactive (Organic/Inorganic)
      C-B   = Non-reactive Filterable Aluminum
      A-D   = Reactive Macromolecular Aluminum

    Figure 5.   Fluorescence Flowchart for Aluminum Speciation
                (From Kramer, 1983)

```
                    ┌──────────┐
                    │  Sample  │
                    └────┬─────┘
                         │
              ┌──────────────────────┐
              │  0.4-µm filtration   │
              └──────────┬───────────┘
          ┌──────────────┴─────────────────────────┐
          │                          ┌──────────────┴──────────┐
  ┌───────────────────┐              │                         │
  │  Non-filterable   │      ┌──────────────┐         ┌──────────────────┐
  │  Residue HNO₃     │      │   Filtrate   │         │  Photooxidation  │
  │  Digestion        │      └──────┬───────┘         └────────┬─────────┘
  └─────────┬─────────┘             │                          │
            │                       │                          │
  ┌───────────────────┐     ┌──────────────┐         ┌──────────────────┐
  │   Particulate     │     │   Chelex     │         │     Chelex       │
  │       Al          │     │   exchange   │         │    exchange      │
  └───────────────────┘     └──────┬───────┘         └────────┬─────────┘
                   │                │                          │
          ┌──────────────┐  ┌──────────────┐         ┌──────────────────┐
          │    Total     │  │    Non-      │         │      Non-        │
          │  filterable  │  │ exchangeable │         │  exchangeable    │
          │    Al (A)    │  │   Al  (B)    │         │  inorganic (C)   │
          └──────────────┘  └──────────────┘         └──────────────────┘
```
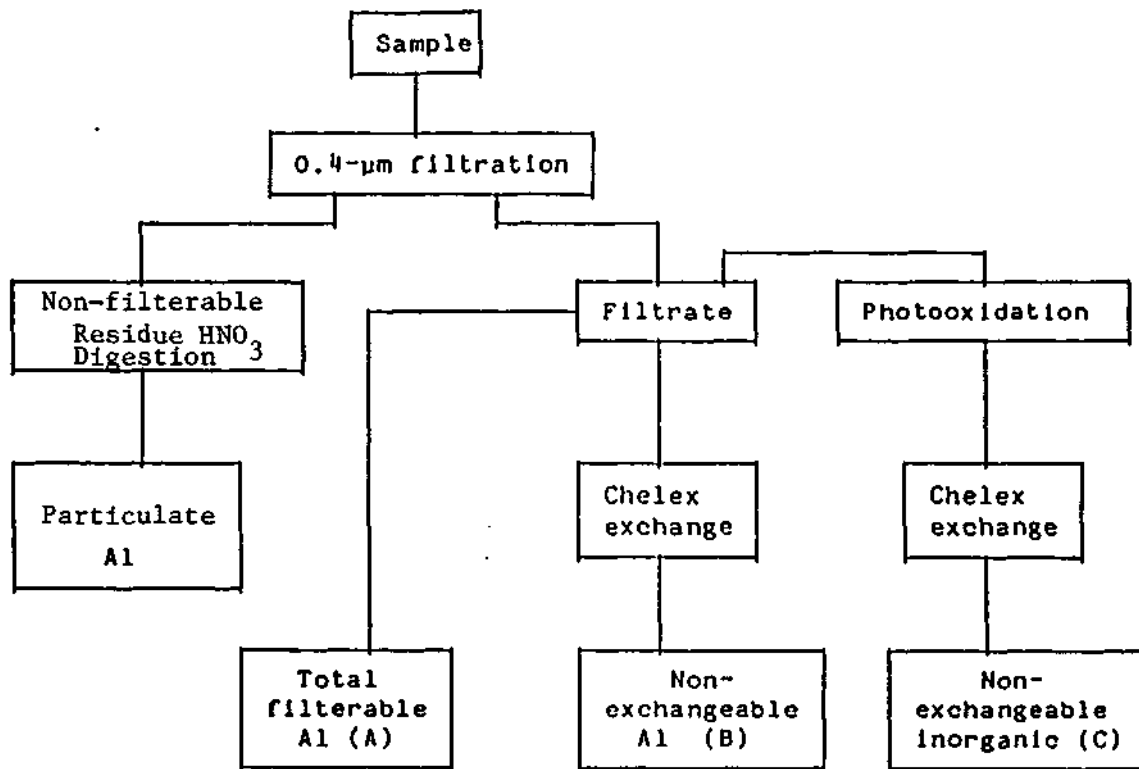
A – D – Exchangeable filterable organic and inorganic Al

B – C – Nonexchangeable filterable organic Al

Figure 6.   Ion Exchange Flowchart for
            Aluminum Speciation
            (from Campbell et al., 1983)

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```
                  ┌─────────────────┐              ┌──────────────────┐
                  │ Sample          │              │ Total Dissolved  │
                  │ Filter 0.4 um   │──────────────│ Al - GFAA        │
                  └─────────────────┘              └──────────────────┘
        ┌──────────────────┼─────────────────────────────────┐
  Adjust pH To        Adjust pH To                            │
  5.0-5.5 With Low    5.0-5.5 With High                       │
  Level TISAB         Level TISAB                  ┌──────────────────────────┐
                                                   │ Oxine Extraction Into    │
  ┌──────────────────┐   ┌──────────────┐          │ Butyl Acetate @ pH 5.5   │
  │ Measure Free F   │   │ Decomplexed F│          └──────────────────────────┘
  │ By ISE           │   │ Plus         │                      │
  └──────────────────┘   │ Free F       │                      │
                         └──────────────┘          ┌──────────────────────────┐
                                │                   │ Extractable Al By        │
                         ┌──────────────┐           │ Spectrophotometric       │
                         │ Measure Total F          │ Measurement @ 395 nm     │
                         │ By ISE       │           └──────────────────────────┘
                         └──────────────┘
```
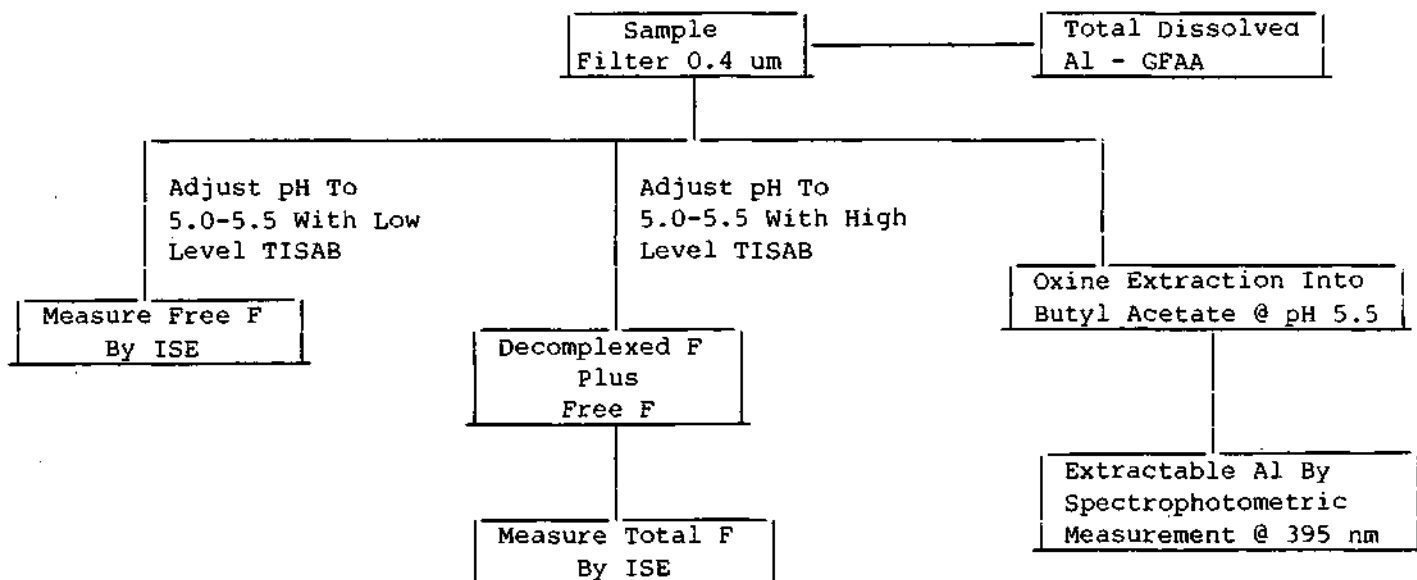
Figure 7. Bound/Free Fluoride Flowchart for Aluminum Speciation
(from David, 1984)
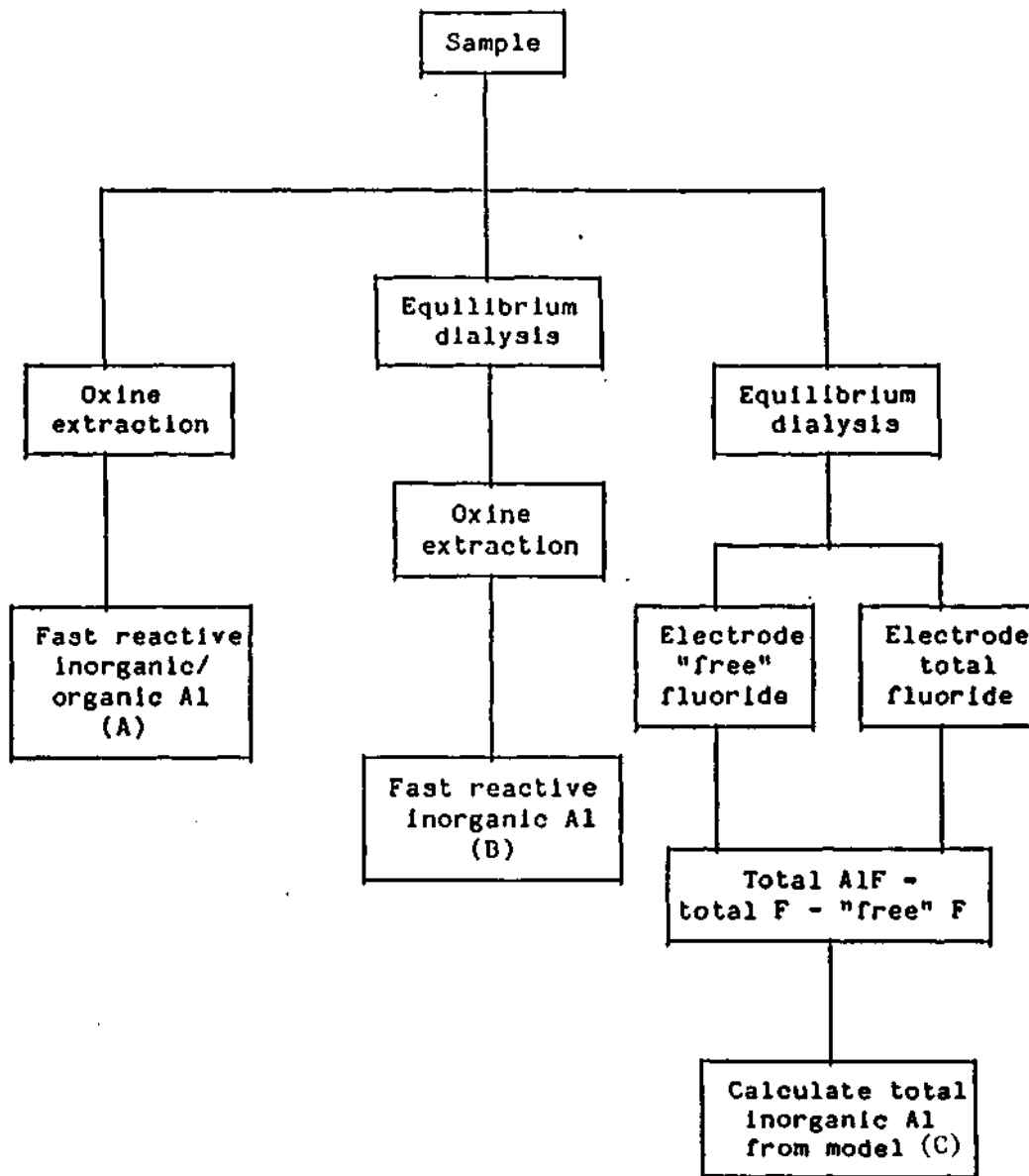
Figure 8. Oxine Extraction Flowchart for
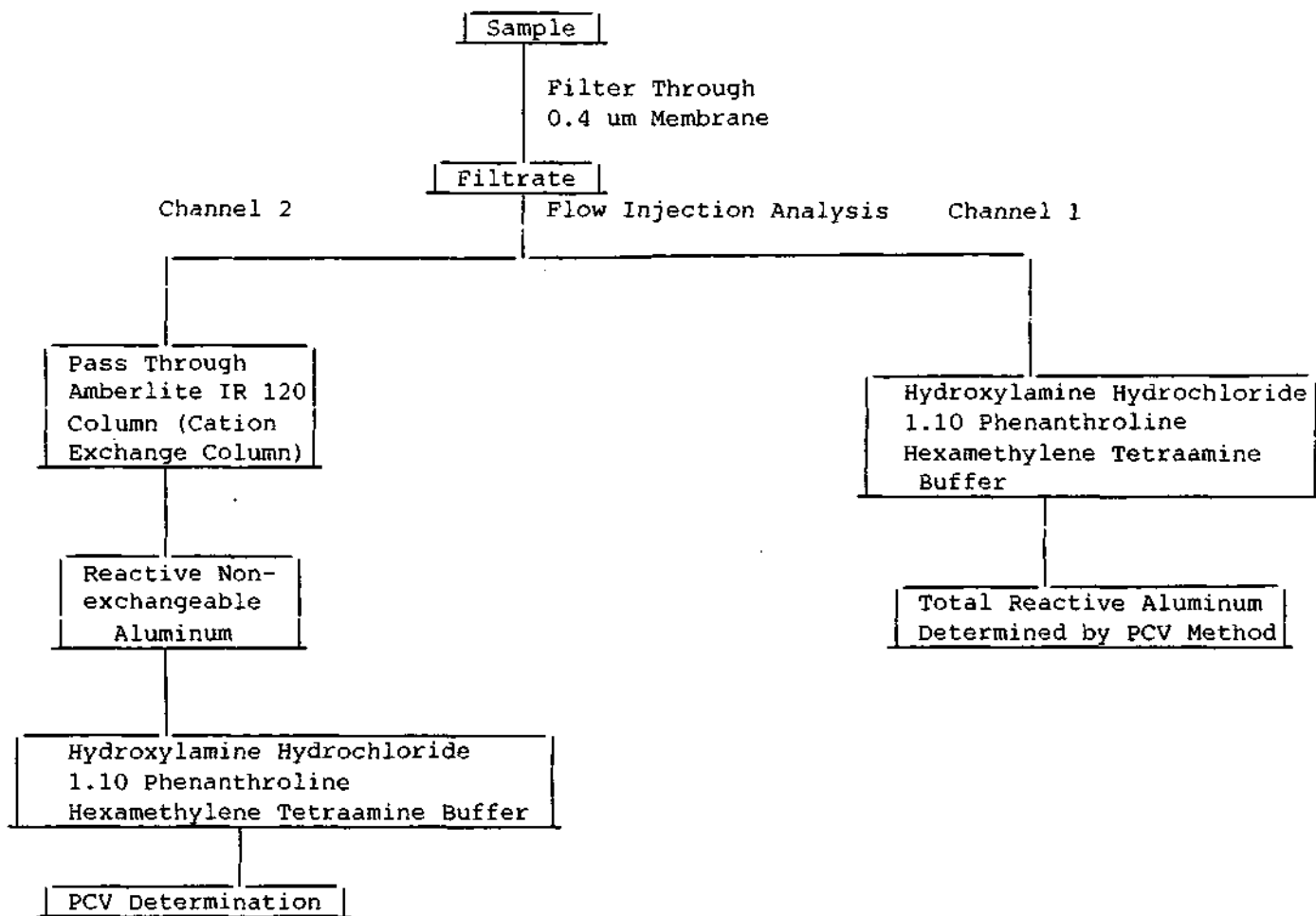Aluminum Speciation
(from LaZerte, 1984)

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```
                        | Sample |
                             |
                        Filter Through
                        0.4 um Membrane
                             |
                        | Filtrate |
Channel 2                Flow Injection Analysis        Channel 1


| Pass Through                                  | Hydroxylamine Hydrochloride
| Amberlite IR 120                              | 1.10 Phenanthroline
| Column (Cation                                | Hexamethylene Tetraamine
| Exchange Column)                              | Buffer


| Reactive Non-                                 | Total Reactive Aluminum |
| exchangeable                                  | Determined by PCV Method|
| Aluminum |


| Hydroxylamine Hydrochloride
| 1.10 Phenanthroline
| Hexamethylene Tetraamine Buffer |


| PCV Determination |
```

Figure 9.   Pyrocatechol Violet Colorimetry Flowchart
             for Aluminum Speciation
             (from Kerfoot et al., 1986)

EXPERIMENTAL CONDITIONS

Oxine Extraction (Figure 8)

Materials:

Polyethylene separatory funnels (125 mLs) were used for the solvent extraction.

30 mL polyethylene bottles were used to collect and store the MIBK extract.

Glass plunger pipets were used to measure the MIBK, NH_4 OH, and the buffer.

Buffer Solution: Add 200 mL concentrated NH_4OH and 115 mL glacial acetic acid to 500 mL deionized water. Stir and adjust the pH to 8.3 with 10 M NH_4OH. Continue to stir until pH is constant for 10 minutes.

8-hydroxyquinoline solution (5%) - 5 grams 8-hydroxyquioline are dissolved in 10 mL glacial acetic acid and diluted to 100 mL with deionized water.

Methyl Isobutyl Ketone (MIBK) - reagent grade

Procedure For Fast Reactive Inorganic/Organic Aluminum:

The following reagents were added in rapid succession:

1. 8-hydroxyquinoline: 2.5 mL/20 mL sample,

2. NH_4 OH: 1.4 mL/20 mL sample,

3. pH 8.3 buffer: 2.5 mL/10 mL sample, and

4. MIBK: 4.5 mL/ 20 mL sample.

The solution mixture in the separatory funnel is then shaken for 10-15 seconds. The organic layer is briefly allowed to separate. The MIBK extract is drawn off for analysis by the graphite furnace atomic absorption spectrophotometer. Standards for the calibration curve were always analyzed at the same time as the sample. The standards used covered the range 0.005-0.100 mg/L.

Fluorometric Method (Figure 5)

Materials:

Lumogallion solution: 0.02% in deionized water.

Buffer solution: sodium acetate plus acetic acid (4 M with respect to acetate), adjusted to pH 5.0.

Standard aluminum solution: Atomic absorption standard aluminum solution, (Fisher Certified 1000 mg/L). Working standard solutions for calibration curve are prepared from this solution.

Procedure For Reactive Inorganic/Organic Aluminum:

50 mL sample aliquots are dispensed into the reaction bottles using a 50 mL measuring cylinder. The reagents, 0.5 mL buffer and 0.3 mL Lumogallion solution, were added. The bottles are shaken well and then heated in the water-bath at a temperature of 80°C for 1 1/2 hours. The bottles are then cooled and allowed to equilibrate to laboratory temperature. Finally, the fluorescence of the samples is measured using an excitation wavelength of 465 nm and an emission wavelength of 555 nm on a Turner Model 112 Digital Fluorometer which has a double beam optical balance. Each set of sample analyses is preceded by blank and quality control sample analyses.

Ion-Exchange Method (Figure 6)

Materials:

Chelex 100 resin: The resin is equilibrated with a synthetic solution containing Ca^{2+}, Mg^{2+}, and H^+ at concentrations of 1.0 mg Ca^{2+}/L, 0.5 mg Mg^{2+}/L, pH 5.0. The resin (1.5 g wet weight) is suspended in dilute nitric acid (500 mL @ pH 5.00), and a concentrated solution of $Ca(NO_3)_2$ (1.25×10^{-20} M) and $MgSO_4$ (1.03×10^{-2} M) is slowly added to the stirred suspension until the concentration of Ca in the bulk solution is 1.0 mg/L as determined by flame atomic absorption.

Atomic absorption standard aluminum solution: 1000 mg/L was diluted to obtain working standard solutions.

Polysulfone filtration apparatus using polycarbonate membranes (0.4 um).

High purity nitric acid (Baker Ultrex).

Procedure:

The method according to Campbell (1983) was followed. As reported by Campbell, the batch method was used to determine exchangeable filterable organic and inorganic aluminum. The procedure is summarized below according to Andelman and Miller (1986):

1. Pour 100 mLs of filtered sample into a 150 mL polyethylene beaker.
2. Turn on stirrer and measure pH of sample.
3. Add 0.5 g of the resin to the sample.
4. At predetermined sampling times, turn off the stirrer, wait about one minute, then remove an aliquot to be filtered and analyzed.
5. Resume stirring the sample and remove additional aliquots using the procedure in step 4.
6. At the end of the experiment, measure the pH of the stirred solution.

All sample aliquots were analyzed by graphite furnace atomic absorption after the addition of HNO$_3$ (1% by volume) and H$_2$O$_2$ (2% by volume).

Bound/Free Flouride Method (Figure 7)

Materials:

The Orion combination fluoride ion-selective electrode Model No. 96-09-00 was used with an Amber Science solution analyzer, Model 4603 with EMF (MV) expansion capability. Temperature was corrected to 25 C using a temperature probe.

All reagents used were analytical grade. Orion application solution TISAB III concentrate with CDTA was used to determine total fluoride.

Low level TISAB was prepared following a recommended method by Orion, Inc.: Add 57 mLs glacial acetic acid and 58 g NaCl to 500 mLs deionized water. The pH of the solution is adjusted to 5.37 using 5 molar NaOH. The final solution is made up to one liter.

Procedure:

A standard method of analysis of fluoride in aqueous media was used from the Orion Inc. Manual. Total time of analysis ranged from 20 to 45 minutes (i.e., when electrode response was about 0.1 mV/minute). Free fluoride was determined by first adjusting the pH of the sample solution to pH 5.0-5.5 with low level TISAB prior to inserting the electrode. For the measurement of total fluoride (free plus decomplexed), a TISAB III solution was added to adjust the pH and decomplex all fluoride compounds. Aluminum concentrations are derived using Al-F stability constants.

RESULTS AND DISCUSSION

Oxine Extraction

Precision:

    The bias and precision of the oxine extraction procedure was studied.
Table 1 shows the results obtained from the analysis of synthetic samples with
and without the addition of fulvic and humic complexing ligands. The matrix of
the synthetic samples was formulated to approximate the median ion
concentrations measured during Phase I of the NSWS. Table 17 lists the target
values for the synthetic formulations. The data from Table 1 suggest that the
oxine extraction procedure is not as precise when used with samples that
contain organic ligands. 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.

Application to Lake Samples:

    Four New England lake samples and six Michigan lake samples were analyzed
using the fast oxine extraction method. The results are shown in Tables 2 and
3. The New England samples have relatively high levels of aluminum when
compared to the Michigan lakes. The results also indicate that not all of the
total dissoved aluminum is extractable by the oxine reagent.

**Table 1. Bias and Precision from
Oxine Extraction Experiments**

Sample No.	Amount Of Al Added (ug/L)	Amount of Al Found (ug/L)[a]
1	50	49
2	50	60
3	50	55
Mean (n=3)		54.7
Standard Deviation (s)		5.5
RSD (%)		10.1

a. Fast reactive, inorganic aluminum (see Figure 8).

Sample No.	Amount of Al Added (ug/L)	Amount of Al Found (ug/L)[a]
1	100	102
2	100	100
3	100	101
4	100	91
Mean (n=4)		98.5
Standard Deviation (s)		5.1
RSD (%)		5.1

a. Fast reactive, inorganic aluminum (see Figure 8).

Table 1., Continued

Sample No.	Amount of Al Added (ug/L)[a]	Amount of Al_b Found (ug/L)	Total Dissolved Al (ug/L)[c]
1	80	36	90
2	80	42	
3	80	57	
4	80	43	
Mean (n=4)		44.5	
Standard Deviation (s)		8.9	
RSD (%)		20.0	

a. Synthetic reference solution with humic (1 mg/L) and fulvic (4 mg/L) acid added.
b. Fast reactive, inorganic aluminum (see Figure 8).
c. Determined by graphite furnace atomic absorption.

Table 2. Oxine Extractable Aluminum in Four New England Lakes

Lake Sample	Total Dissolved Al (ug/L)[a]	Oxine Extractable Al (ug/L)[b]	pH
Bailey	93	42	6.19
Killingly	239	144	4.91
Long	35	14	6.13
Wilbur	164	91	4.47

a. Determined by graphite furnace atomic absorption.
b. Fast reactive, inorganic aluminum (see Figure 8).

Table 3. Oxine Extractable Aluminum in Six Michigan Lakes

Lake Sample	Total Dissolved Al (ug/L)[a]	Oxine Extractable Al (ug/L)	pH
Delene	60	12	6.83
Ostrander	37	20	7.06
Catract	106	19	7.37
Casey	92	13	8.75
Annie	35	18	5.78
Richardson	14	7	6.14

a. Determined by graphite furnace atomic absorption.
b. Fast reactive, inorganic aluminum (see Figure 8).

Ion Exchange Resin (Chelex 100)

The exchange rate of dissolved aluminum in deionized water with Chelex 100 resin was studied. The results are shown in Table 4. The results show that after 15 minutes, the inorganic aluminum has been taken up by the resin. This agrees with the results obtained by Campbell et al. (1983). After a contact time of 60 minutes no detectable amount of the inorganic aluminum was present in a 50 ug/L Al solution.

The pH changes associated with the exchange of the inorganic aluminum with the Chelex 100 were also examined on natural samples. The results are shown in Table 5. As the table shows, the pH change is less than 0.7 units and within the acceptable limits as defined by Campbell et al. (1983). For acidic (pH 4.50), DOC-rich (5.53 mg/L) Wilbur Pond, equilibrium time was longer than one hour. This suggests that initially non-exchangeable aluminum species, possibly alumino-humics, were being transformed into exchangeable forms.

Precision:

The precision of the Chelex 100 procedure was studied. Table 6 shows the results obtained. The precision obtained from samples without the presence of humic acids, expressed as percent relative standard deviation, was comparable to the results obtained from the oxine extraction procedure. When comparing the two sets of data with the humic acids present, the Chelex exchange technique shows slightly better precision (20% RSD versus 13% RSD).

Aluminum Speciation by Chelex 100:

After it was proven that the prepared resin could exchange inorganic aluminum, the method was applied to natural water systems. Tables 7 and 8 show the results obtained for the four New England and nine Michigan lakes. In most cases, the ratio of dissolved organic carbon (DOC) to total dissolved aluminum correlated well with exchangeable aluminum. The higher the ratio, on average, the lower the proportion of exchangeable to total dissolved aluminum.

Table 4. Exchange Rate of Dissolved Aluminum in Deionized Water with Chelex 100 Resin

Time, (min.)	50 ug/L Al + 0.5 g Chelex 100	100 ug/L Al + 0.5 g Chelex 100	Blank 100 ug/L Al without Chelex 100
0	50	84	84
15	0.004	<.004	78
60	<0.004	0.016	78
120	<0.004	<0.004	84

Table 5. Chelex 100 Results from Four New England Lake Samples

Time, (hrs.)	Lake	pH	Non--exchangeable Aluminum (ug/L)
	Bailey Lake		
0		6.21	58
1		6.20	53
2		5.06	53
	Killingly Pond		
0		5.07	33
1		4.52	20
2		4.68	21
	Long Pond		
0		6.44	35
1		6.57	37
2		6.26	26
	Wilbur Pond		
0		4.50	111
1		4.69	103
2		4.57	48

Table 6. Precision Results from Chelex 100 Procedure

Synthetic Samples 200 ug/L Al, 0.5 mg/L humic acid. 2.0 mg/L fulvic acid	Non-exchangeable Al Measured (ug/L)[a]
1	47
2	57
3	47
Mean (n=3)	50
Standard Deviation (s)	6
RSD (%)	12

a. Determined by graphite furnace atomic absorption.

Natural Samples Biscuit Brook, NY	Non-exchangeable Al Measured (ug/L)
1	40
2	40
3	31
Mean (n=3)	37
Standard Deviation (s)	5
RSD (%) .	13.5

a. Determined by graphite furnace atomic absorption.

Table 7. Aluminum Speciation, pH level, and Dissolved Organic Carbon (DOC) Relationships

Lake Sample	pH	DOC, mg/L	Total Dissolved Aluminum (ug/L)	Non-exchangeable Al (Chelex 100) (ug/L)
Bailey	6.21	4.93	**93**	53
Killingly	5.07	1.57	236	**21**
Long	6.44	4.13	35	**26**
Wilbur	4.50	5.53	164	**48**

Lake Sample	DOC:; Total Al Ratio	Exchangeable Aluminum (ug/L)
Bailey	53.0	**40**
Killingly	7.3	215
Long	118.0	**9**
Wilbur	33.7	116

a. Exchangeable Al is operationally defined as the difference between total filterable (dissolved) Al and no n-exchangeable Al.

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Table 8. Aluminum Speciation Results
Prom Nine Michigan Lakes

Lake Sample	Particulate Aluminum <ug/L>[a]	Total Dissolved Al (ug/L)	Non-exchangeable Al (Chelex 100) (ug/L)	Exchangeable Al (By Difference) (ug/L)	DOC (mg/L)	DOC:Total Dissolved Al Ratio	PH
Delene	14	60	6	54	6.88	0.115	6.83
Ostrander	4	37	9	28	5.76	0.156	7.06
Catract	16	106	45	61	14.30	0.135	7.37
Casey	6	92	19	73	4.91	0.053	8.75
Annie	17	35	10	25	4.16	0.119	5.78
Richardson	2	14	<4	----	4.90	0.350	6.14
Cranberry	1	<11	9	----	4.46	----	4.97
Johnson	<1	11	7	4	1.28	0.116	4.81
Grand Sable	1	<11	16	----	5.37	----	8.11

a. Particulate aluminum concentration is the total aluminum measured on a digested filter that had 5o0 mLs of sample passed through it. Final digestion volume was 20 mLs. The reported concentration data represent the amount of insoluble aluminum in the original sample.

Lumogallion Fluorescence Results

Bias expressed as percent recovery in the aluminum determination by fluorometric method using lumogallion reagent (see Figure 5) was studied using the synthetic samples previously described. The results are shown in Table 9. The percent recovery data range from 98.7 to 112. Based on these results, the fluorometric method for determining aluminum using lumogallion reagent can be said to be free of any significant biases.

Synthetic and natural samples were analyzed on different days to assess the precision of the fluorometric method. The results are shown in Table 10. For the synthetic samples, the precision was found to be 2.2% expressed as percent relative standard deviation and 1.4% for the natural samples. The fluorometric method is therefore very precise.

After the bias and precision had been established, the fluorometric method was applied to the analysis of aluminum in four New England lakes and nine Michigan lakes. The results for reactive inorganic/organic aluminum species are shown in Tables 11 and 12. Included in the tables are the oxine extractable ' aluminum values for comparison. In almost all cases, the lumogallion aluminum results are lower than the oxine-extractable aluminum. Generally, the results indicate that both the lumogallion and the oxine extraction methods do not tell us the specific forms of aluminum which are determined. Total dissolved organic carbon (DOC) may play a role in the forms of aluminum determined by these methods, although there is no general trend in the results obtained so far.

Some background fluorescence was detected in both the samples and in aliquots of deionized water used for blanks. The background fluorescence was always subtracted prior to reporting the fluorescence attributable to the aluminum-lumogallion complex.

Table 9. Percent Recovery Data From Lumogallion Fluorescence Experiments

Synthetic Sample	Amount Added (ug/L)	Amount Found (ug/L)[a]	Percent Recovery	Bias (%)[b]
1	12.5	12.9	103.2	3.2
2	15	14.8	98.7	-1.3
3	50	56	112	12.0
4	100	101	101	1.0
			mean =	3.7

a. Reactive inorganic/organic aluminum (Form A, Figure 5).
b. Bias = % recovery - 100

Table 10. Precision of Lumogallion Experiments

Synthetic Sample	Amount of Al found (ug/L)
1	86
2	87
3	90
4	86
Mean (n=4)	87.3
Standard Deviation (s)	1.9
RSD (%)	2.2

a. Reactive inorganic/organic aluminum (Form A, Figure 5).

Natural Sample (Sochia Lake)	Amount of Al found (ug/L)[a]
1	10.4
2	10.7
3	10.7
4	10.7
Mean (n=4)	10.6
Standard Deviation (s)	0.15
RSD (%)	1.4

a. Reactive inorganic/organic aluminum (Form A, Figure 5).

Table 11. Lumogallion-Aluminum in Four New England Lakes

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

Table 12. Lumogallion-Aluminum in Nine
Michigan Lakes

Lake Sample	Total Dissolved Al (ug/L)	Lumogallion Aluminum (ug/L)	Oxine Extractable Al (ug/L)	DOC (mg/L)
Delene	60	2.5	12	6.88
Ostrander	37	13.9	20	5.76
Annie	35	19.3	18	14.30
Catract	106	5.2	19	14.30
Casey	92	3.0	13	4.91
Richardson	14	4.7	7	4.90
Johnson	11	16.1	---	1.28
Cranberry	<11	12.7	---	4.46
Grand Sable	<11	4.7	---	5.37

Bound/Free Fluoride Method

     Table 13 shows free fluoride measurements for an EPA Quality Control sample with and without buffer solution addition. The high value of free fluoride from the direct measurement using the fluoride electrode is due to hydroxyl ion interference. The pH of the 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 the addition of a low-level TISAB does not alter the free fluoride concentration in the sample solutions. It rather enhances the accuracy by negating the effect of pH and ionic strength differences from sample to sample.

     Table 14 shows the time of analysis of quality control solutions with and without the addition of low-level TISAB. As is expected, direct measurements of fluoride in aqueous media which have a low conductivity require a longer time to achieve a stable response than the same solution with increased ionic strength due to the addition of a buffer.

     In order to test the reliability of the modified free fluoride measurement method, a correlation experiment was conducted. Aluminum concentrations ranging from 40 ug/L to 150 ug/L were added to a fixed fluoride concentration of 57.6 ug/L at a pH of 4.0. Free fluoride and total fluoride were then measured using low-level TISAB for free fluoride and using TISAB II for total fluoride. The results are shown in Table 15.

     pF (free measured) was then plotted against pF (free calculated from stability constants) to test their correlation. The plot is shown in Figure 4. The plot shows good correlation with R =0.9998 and pF (measured) = -0.03 + 1.03 pF (calculated). It can be seen from Table 15 that the total fluoride values are low by approximately 8-18 ug/L when compared to the Known concentration of 57.6 ug/L. The reason for this is probably due to the ineffectiveness of the TISAB III in completely decomplexing all aluminum-fluoride compounds.

     The total and free fluoride measurements were also made on four lake samples. The results are shown in Table 16. The results show that Bailey and Long Lake 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. Most probably the high values are due to hydroxyl ion interference. The table also shows that addition of low-level TISAB before analysis gave more accurate results.

Table 13. Free Fluoride Measurements

Sample Type	Free Fluoride Measured (mg/L)	True Value (EPA Certified) (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 14. Time of Analysis

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

Table 15. Measured and Calculated Fluoride

Al Added (ug/L)	[F] Total (mg/L) TISAB III	[F] Free (mg/L) Low-level TISAB	[F] Free Calculated (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
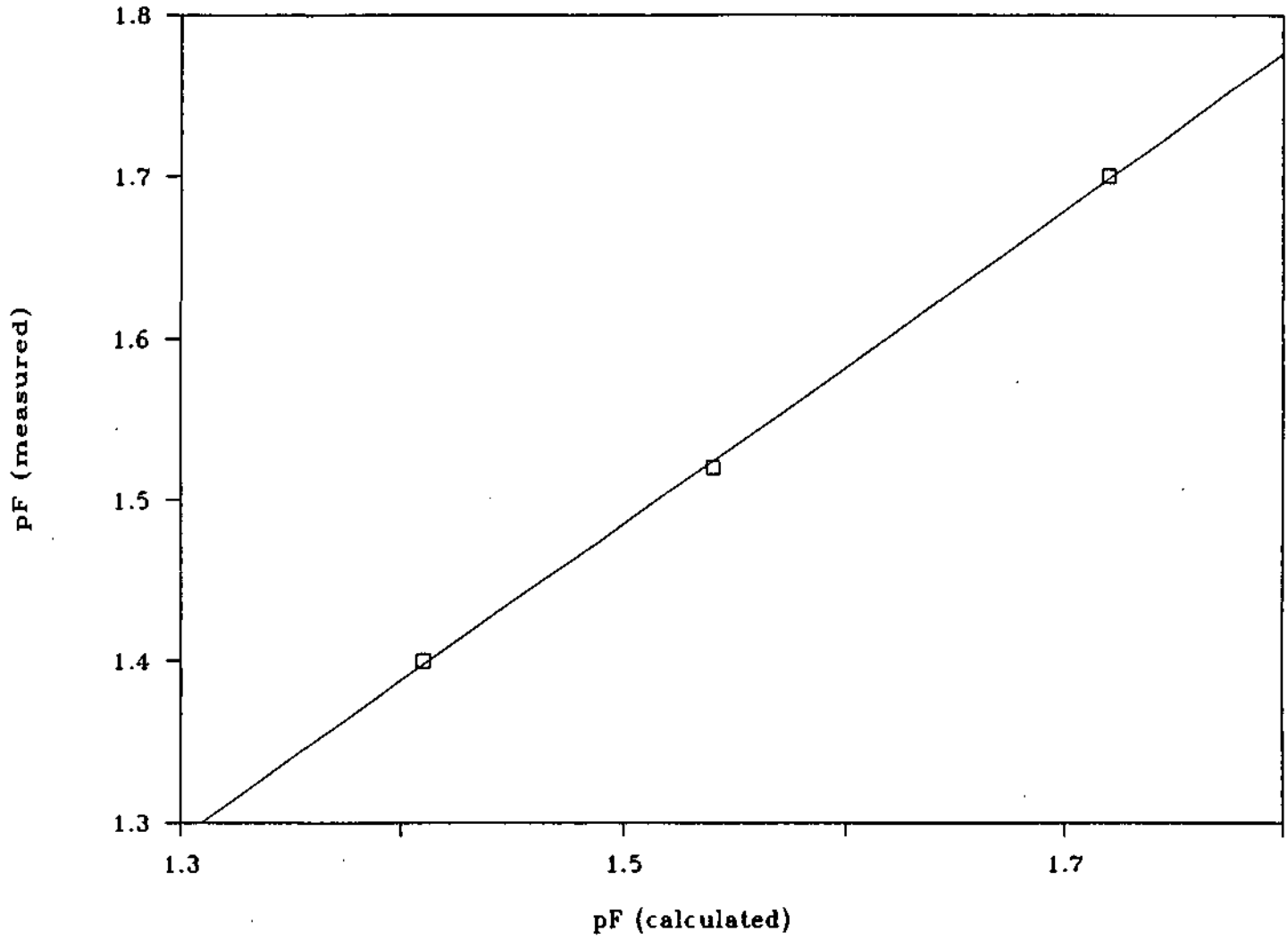
Figure 4. pF (Measured) Versus pF (Calculated)

Table 16. 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 Lake	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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INSTRUMENTATION

GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY

Aluminum concentrations were measured by graphite furnace atomic absorption spectrophotometry (GFAA). An Allied Analytical Systems (Thermo Jarrell-Ash) Model 957, Video 22 atomic absorption spectrophotometer and models IL655 and IL755 graphite furnace atomizers were used for these determinations. Aluminum was measured at the 309.3 nm wavelength with a 0.5 nm bandwidth. Nonspecific background absorption was corrected with a deuterium arc background correction system. The instrument was calibrated using three second peak area integrations.

The furnace atomizers use delayed action cuvettes (DAC's) which have thicker walls at the center than at the ends. This causes a delay in atomization since the cuvette heats more slowly in the center, allowing the sample to be atomized into a hotter environment. It works according to the same principle as the L'vov platform to reduce vapor phase interferences. For most determinations, pyrolytically coated graphite cuvettes were used to retard carbide formation on the furnace surface. Uncoated cuvettes were used for the samples which had been extracted into methyl iso-butyl ketone (MIBK).

Two methods of sample delivery were used: hand pipetting with a plastic tipped Eppendorf pipette (10 uL volume) and an automatic sampling system (Model IL254 autosampler) which uses a nebulizer to deposit the sample in an aerosol form.

Initial furnace settings and conditions are given in Table 1. These are manufacturer-recommended settings for ultra-pure water and for waste waters. Quality control sample (QCS) results revealed problems with the analysis of surface waters under these conditions. Results for USEPA QCS and the SLRS-1 Riverine Water Reference Material for Trace Metals are shown in Table 2. The SLRS-1 is a river sample prepared by the Division of Chemistry, National Research Council of Canada. It was collected in the St. Lawrence River close to Quebec City, filtered and acidified with nitric acid (pH 1.6). The 184% mean recovery for the SLRS, when compared to the mean recoveries of 92% and 94% for the USEPA samples clearly indicate interferences from the river-water matrix. Further evidence of these interferences is demonstrated by the variability of results between GFAA and inductively coupled argon plasma spectrometry (ICAP) analyses of the same samples (Table 3). Although a paired t-test shows no significant difference between the data sets, the calculated means differ by 34.3%.

The USEPA recommends a 1300°C ash temperature in their GFAA Method 202.2 (USEPA, 1983). This method was used in the National Surface Water Survey (Hillman et al., 1985). Several authors have also recommended ashing in the 1200-1250°C range (Carrondo et al., 1979, Maruta et al., 1976, and Persson et al., 1977). Increasing the ash to 1300 C did not improve the SLRS recovery data in this study, where mean aluminum recoveries were 191% (n=3).

Playle et al. (1982), in their comparison of methods for determinations of aluminum in water, used an 800°C ash. A 1985 study by Noller et al., recommended using an ashing temperature of 1500°C to eliminate chemical interferences. This temperature increase resulted in remarkable improvement for the SLRS recoveries in our study. At the same time, however, it reduced the recovery on the USEPA QCS to 25%. Only by carefully adjusting the temperature between 1450-1500°C, were the recoveries for both sample types within acceptable limits (Table 4). The ash temperature settings were adjusted until the "correct" known values were achieved. Obviously, this subjective manipulation is not appropriate for routine analyses since the matrix of natural water samples will be varied. Comparisons of ICAP analyses with GFAA analyses at 1450-1500°C ashing temperatures are shown in Table 5. As the results for sample No. 020240 show, the magnitude of interferences can vary, possibly due to cuvette deterioration. Spike recovery data for samples analyzed by GFAA at the higher ash temperatures are presented in Table 6.

To further complicate the whole issue, the GFAA aluminum analyses conducted by the National Research Council of Canada to determine the SLRS certified value of 0.0235 mg Al/L were performed using a 900°C ash temperature (Sturgeon, 1987).

The GFAA analyses involved samples of varying nitric acid concentrations. The samples, standards, and QCS samples, however, were always matched for acid concentrations. We are avoiding the multiple standard addition method since the calibration curve often becomes nonlinear as the cuvette ages. Also, relatively poor precision characterizes GFAA aluminum analyses. Small errors, therefore, can be greatly magnified in multiple standard addition calculations. Further investigations are underway involving uncoated cuvettes and possible matrix modifiers to improve the performance of the GFAA procedure.

The method detection limit (MDL) of 0.0035 mg Al/L was calculated from 17 determinations (5 different days) of aluminum concentrations in a 0.0100 mg/L aluminum standard, according to the method of Glaser et al. (1981).

Samples which were extracted into MTBK were analyzed using the furnace settings in Table 1. The use of uncoated graphite cuvettes improved precision for the highly volatile matrix. The standards had also been extracted into MIBK. Bias and precision data for these standards are presented in Table 7.

INDUCTIVELY COUPLED ARGON PLASMA SPECTROMETRY

Twelve elements were measured by inductively coupled argon plasma spectrometry (ICAP). The instrument used was a Jarrell-Ash Atom Comp 1100 simultaneous ICAP with a vacuum tank spectrometer housing which provides analyses in the ultraviolet wavelength range. The sample is aspirated into a fixed cross-flow nebulizer and dispersed into aerosol form by an argon gas stream. A peristaltic pump is used for sample delivery to the nebulizer.

The ICAP was optimized according to manufacturer's instructions. Background correction and inter-element corrections were used where necessary. These correction factors were determined by the use of a spectrum shifter which uses a fixed entrance slit and refractor plate to provide for wavelength scanning.

Each reported value is the mean of five integrated exposure periods. Method detection limits (MDL's) were determined according to the method of Glaser et al. (1985). The MDL's and quality control data are shown in Tables 8 and 9. The biases and precisions for most elements are within acceptable limits. However, the MDL's for ICAP are too high to obtain useful data for aluminum, manganese, nickel, and phosphorus.

**Table 1. Initial Furnace Atomizer Settings for
GFAA Aluminum Determinations**

Stage	Temperature (°C)	Time (seconds)
Dry[b]	70	5
	110	45
Ash	950	20
	1100	35
Atomize	2600	0
	2600	5

a. Purge gas: argon
b. When the autosampler was used, the dry stage
    setting was 150°C for 5 seconds.

Table 2. GFAA Quality Control Data for Aluminum Using an 1100°C Ash

Sample	Certified True Value (ug/L)	N	Mean Recovery (ug/L)	Bias (ug/L)	Standard Deviation (ug/L)	RSD (%)
SLRS–1	23.5	9	43.3	+19.8	4.3	9.9
1/20[a]	36.5	10	34.2	−2.3	1.6	4.7
1/40[b]	18.2	10	16.8	−1.4	1.5	8.9

a. USEPA Trace Metals WP284 , concentration 2 at a 1:19 dilution
b. USEPA Trace Metals WP284 , concentration 2 at a 1:39 dilution

Table 3. Comparison of GFAA and ICAP Data for Digested Filtered Lake Samples (7% HNO_3, 1.5% H_2O_2)

Sample	ICAP Analyses Al (ug/L)	GFAA Analyses Al (ug/L)	Difference GFAA-ICAP (ug/L)	Difference[c,d] (%)
Synthetic (80 ug/L)	95	90	5	5.4
Biscuit Brook, NY	332	176	156	61.4
Delene Lake, MI	69	60	9	14.0
Ostrander Lake, MI	62	37	25	50.5
Catract Basin, MI	114	106	8	7.3
Casey Lake, MI	64	92	−28	−35.9
Lake Annie, MI	83	35	48	81.4
Richardson Lake, MI	37	14	23	90.2

a. $1100^{\circ}C$ ash

b. % Difference = $\dfrac{\text{Difference}}{\dfrac{\text{ICAP + GFAA}}{2}}$ X 100

c. The mean of the Differences = 34.3%

**Table 4. GFAA Quality Control Data for Aluminum
Using a 1450-1500° Ash**

Sample	Certified True Value (ug/L)	N	Mean Recovery (ug/L)	Bias (ug/L)	Standard Deviation (ug/L)	RSD (%)
SLRS-1	23.5	8	24.6	+1.1	3.4	13.8
1/20[a]	36.5	11	38.4	+1.9	5.7	14.8
1/40[b]	18.2	2	19.6	+1.4	0.7	3.8

a. USEPA Trace Metals WP284, concentration 2 at a 1:19 dilution
b. USEPA Trace Metals WP284, concentration 2 at a 1:39 dilution .

Table 5. Natural Water Samples
Chelex 100 Experiment
2% H_2O_2 and 1% HNO_3

Aluminum (ug/L)

Lake I.D. Number	GFAA ANALYSES[a]		ICP ANALYSES	
	Date	Al	Date	Al
2B2-049	10/06/87	13.3	10/16/87	<11
	10/14/87	9.1		
2B1-047	10/06/87	8.9	10/16/87	<11
	10/14/87	5.6		
2B3-009	10/06/87	16.3	10/16/87	<11
	10/14/87	16.2		
020116	10/06/87	11.2	10/16/87	<11
	10/14/87	12.6		
020240	10/06/87	70.2	10/16/76	71
	10/13/87	95		
	10/14/87	105		
020115	10/06/87	47.2	10/16/87	45
	10/13/87	47.2		
020197	10/06/87	7.8	10/16/87	<11

a. 1500°C ash

Table 6.   Chelex 100 Experiment - 1% HNO_3 and 2% H_2O_2
Spike Recoveries - Aluminum

GFAA ANALYSES (ug/L)[a,b]

Lake l.D. Number	Amount Spiked	Spiked Result	Unspiked Result	Calculated Recovery	Deviation From Expected	Percent Recovery
2B2-049	18.2	31.3	11.2	20.1	+1.9	110.4
2B1-047	18.2	27.9	7.2	20.7	+2.5	113.7
2B3-009	18.2	36.1	16.6	19.5	+1.3	107.1
020116	18.2	36.2	12.9	23.3	+5.1	128.0
020240°	18.2	35.6	24.6	11.0	-7.2	60.4
	18.2	35.6	17.5	18.1	-0.1	99.4
SLRS	18.2	42.8	26.9	15.9	-2.3	87.3

a. Samples were spiked immediately prior to analyses. The spikes were
    not put through the Chelex procedure.
b. 1500°C ash
c. Sample 020240 was spiked as a 1:3 dilution.

**Table 7. GFAA Analyses of Aluminum Standards
Extracted into MIBK**

Aluminum (ug/L)	N	Mean Recovery (ug/L)	Bias (ug/L)	Standard Deviation (ug/L)	RSD (%)
0.0	11	0.2	+0.2	4.5	----
20.0	8	19.1	-0.9	2.2	11.7
50.0	11	49.3	-0.7	5.7	11.6

a. A 100 ug/L standard was used to determine the initial curve. After 5 or 6 sample determinations, this standard consistently expanded to overflow readings. All samples were determined at the lower part of the curve,and were diluted with MIBK when necessary.

Table 8. ICAP Quality Control Data

USEPA WP1083[a]

Element	Certified True Value (ug/L)	N	Mean Recovery (ug/L)	Bias (ug/L)	Standard Deviation (ug/L)	MDL (ug/L)
Al	970	6	1036	+66	14.4	11
Ca	1000	6	1010	+10	11.9	2
Fe	1020	6	987	−33	9.3	5
K	10000	6	10800	+800	250	1600
Mg	1000	6	1002	+2	7.4	3
Mn	1020	6	1012	−8	8.7	1
Na	860	6	870	+10	15.0	14
Si	50	6	62	+12	1.0	3
P [b]	1150	6	1110	−40	88	40
S [c]	6670	3	7080	−410	95	20

a. USEPA 1083 ICAP Quality Control Sample (numbers 7 and 9)
b. USEPA Nutrient WP284, concentration 8
c. USEPA Mineral WP1185

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Table 9. ICAP Quality Control Data

SLRS-1[a]

Element	Certified True Value (ug/L)	N	Mean Recovery (ug/L)	Bias (ug/L)	Standard Deviation (ug/L)	MDL (ug/L)
Al	23.5	8	21	-2	4.7	11
Ca	25100	8	28070[b]	+2970	596	2
Fe	31.5	8	33	+2	2	5
K	1300	8	2100	+800	700	1600
Mg	5990	8	5947	-43	137	3
Mn	1.77	8	1	<1	0.5	1
Na	10400	8	9514	-886	189	14

a. SLRS-1 Riverine Water Reference Material for trace metals
b. The mean recovery determined by flame atomic absorption
    spectrophotometry was 27200 ug Ca/L.

FLUOROMETRIC DETERMINATION OF ALUMINUM

The fluorescence of the lumogallion-aluminum complex was measured on a Turner Model 112 Digital Fluorometer which has a double beam optical balance. The method of operation of the instrument followed the manufacturer's guidelines. The method of analysis was also that recommended in the manufacturer's manual. Briefly, the method is summarized below:

1. Prepare a reagent blank and at least five standards which cover the expected concentration range. The solutions are buffered to pH 5.0 using a sodium acetate buffer followed by the addition of 0.3 mL of a 0.02% Lumogallion solution.

2. With the. range selector set to the desired range, insert the reagent blank and set the digital display to zero. Read each standard and the unknowns. All measurements are made at an excitation wavelength of 460 nm and an emission wavelength of 555 nm.

A graph of concentration vs. fluorescence is used to determine the linearity of the concentration range. Table 10 presents the data from the analyses of synthetic and natural samples.

Table 10. Fluorometric Precision Data

Sample Type	N	Mean Conc. (ug/L) Al	Standard Deviation (ug/L)
Synthetic Material	4	87.3	1.9
Lake Sochia	4	10.6	0.15

a. N = number of replicates

It must be noted that it is difficult to develop a quality control standard for the fluorescence determination of aluminum since we do not know the specific forms of aluminum determined by this method. However, when the Canadian Riverine Water Reference Material was used as the quality control standard, the following results (Table 11) were obtained.

Table 11. Fluorometric Bias Data

True Value (ug/L)	Measured Value (ug/L)	Bias (ug/L)	% Bias
23.5	25.2	**1.7**	**7.2**

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SUMMARY OF PROGRESS

1. The initial literature search and review of existing methods that was initiated at the beginning of this project has been completed. So far we have acquired over 200 papers that deal with the aluminum speciation subject or matters closely related to aluminum speciation. The recommended methods to be evaluated have been comprehensively reviewed and have formed the basis of our work.

2. The development of stable reference solutions for organic and inorganic aluminum is an integral part of the aluminum speciation project. Synthetic reference samples have been developed that contain matrix components common to natural waters. The analyte concentrations in these reference samples approximate those found in the northeastern and upper midwestern United States except for pH values which were selected as extreme tests of stability. Target values for the constituents included in these synthetic samples are shown in Table 1. The stability of these solutions in terms of pH and conductivity have been examined for **a** period of six months. The results are shown in Tables 2 and 3.

   All pH >10 samples suffered from instability with respect to pH and conductivity in the order of: FA + HA + Al> FA + HA> inorganic solution. These results are expected as even divalent cations undergo hydrolysis at pH >10. The instability of the HA + FA acidic solution with respect to conductivity is puzzling in light of the other constituents present in solution and the absence of any obvious polymerization reactions. Work continues in this area, and if reproducible, indicate nonstoichiometric reactions of humic and fulvic acids.

3. The evaluation of the bound/free fluoride method has been completed. The analytical shortcomings of this method have been identified and these have been discussed elsewhere in this report. Included in this discussion is a simple method that has been developed for overcoming the analytical problems associated with this procedure.

   Substantial work has been completed on the evaluation of oxine extraction, Chelex-100 ion-exchange and lumogallion fluorescence methods for aluminum speciation. The methods have been used to speciate aluminum in lake samples collected from northeastern and upper midwestern regions of the United States and also from the Adirondack regions of New York. The work on these methods is included in this report.

4. The advantages and limitations of the methods studied based on laboratory and literature investigations to date are shown in Table 4.

Table 1.   Target Concentrations for Synthetic
Lake Water Samples

Parameter	Northeast United States	Upper Midwest United States
Extr. Al (ug/1)	14.3	5.8
Total Al (ug/L)	79.6	45.1
ANC (ueq/L)	286.1	756.0
NH_4 (ueq/L)	3.5	3.8
Ca (ueq/L)	284.0	502.4
CI (ueq/L)	205.8	49.1
Color (PCU)	32.4	48.4
Cond. (uS/cm)	69.5	84.9
DOC (mg/L)	5.0	8.4
F (ueq/1)	3.0	2.5
Fe (ug/1)	95.1	145.8
Mg (ueq/1)	112.2	293.2
Mn (ug/L)	37.5	12.8
NO_3 (ueq/1)	2.5	2.2
pH (pH Units)	6.76	7.09
P (ug/1)	15.4	20.3
K (ueq/1)	18.6	20.0
Si (ueq/1)	2.4	3.9
Na (ueq/1)	205.3	66.3
SO_4 (ueq/1)	133.2	71.6

Table 2. Synthetic Reference Material Results
for Simulated Northeast Lakes

Date	Parameter		FA, HA Added[a]	FA, HA, Al Added[b]
03/23/87	pH	3.63	----	----
	Conductivity	399	----	----
04/04/87	pH	----	3.70	3.57
	Conductivity	----	368	408
04/08/87	pH	3.60	3.70	3.47
	Conductivity	392	360	395
04/14/87	pH	3.53	3.60	3.48
	Conductivity	390	360	402
04/21/87	pH	3.61	3.64	3.51
	Conductivity	383	350	393
04/27/87	pH	3.54	3.60	3.46
	Conductivity	380	340	383
05/11/87	pH	3.56	3.61	3.45
	Conductivity	387	354	399
06/11/87	pH	3.64	3.68	3.50
	Conductivity	380	348	391
06/29/87	pH	3.60	3.70	3.50
	Conductivity	395	204	406
07/27/87	pH	3.62	3.97	3.51
	Conductivity	383	193.8	388
08/28/87	pH	3.67	3.97	3.54
	Conductivity	384	191.5	386
09/22/87	PH	3.70	4.00	3.54
	Conductivity	393	195	391

a. FA = Fulvic Acid, 4 mg/L; HA = Humic Acid, 1 mg/L added
b. FA = Fulvic Acid, 4 mg/L; HA = Humic Acid, 1 mg/L added; Al = Aluminum, 80
    ug/L added

**Table 3. Synthetic Reference Material Results
for Simulated Midwest Lakes**

Date	Parameter		FA, HA Added[a]	FA, HA, Al Added[b]
03/23/87	pH	10.91	----	----
	Conductivity	273	----	----
04/04/87	PH	----	10.74	10.64
	Conductivity	----	231	225
04/08/87	PH	10.68	10.71	10.65
	Conductivity	247	225	213
04/14/87	PH	10.66	10.67	10.38
	Conductivity	242	219	189
04/21/87	pH	10.59	10.62	10.25
	Conductivity	233	211	186
04/27/87	PH	10.48	10.56	9.85
	Conductivity	219	196	166
05/11/87	PH	10.48	10.56	9.93
	Conductivity	219	197	165
06/11/87	pH	10.72	10.85	10.05
	Conductivity	205	191	160
06/29/87	PH	10.65	10.70	9.84
	Conductivity	207	185	164
07/27/87	pH	10.46	10.60	9.16
	Conductivity	195.1	179.6	157.7
08/28/87	PH	10.38	10.55	8.38
	Conductivity	188	173.7	154.6
09/22/87	PH	10.02	9.96	8.00
	Conductivity	176	173	157

a. FA = Fulvic Acid, 4 mg/L; HA = Humic Acid, 1 mg/L added
b. FA = Fulvic Acid, 4 mg/L; HA = Humic Acid, 1 mg/L added; Al = Aluminum, 80
    ug/L added

Table 4. Advantages and Limitations of the Methods Studied

Method	Advantages	Limitations
1. Oxine Extraction	1. Time of analysis is short. 2. The extraction is carried out at a pH of 8.3 and therefore free from fluoride interferences. Atomic absorption determination eliminates Fe interference.	1. Does not indicate the specific forms of aluminum being determined. 2. MIBK and the oxine-Al complexes should have constant contact times for all of the samples. This is very difficult to maintain. 3. The method is limited by the poor precision of the GFAA determination of aluminum. 4. Humic and fulvic acids interfere with the extraction efficiency.
2. Chelex 100 ion exchange	1. Operationally defined forms of aluminum are determined (i.e., organically bound and inorganic aluminum). 2. There are no interferences. 3. Time of analysis is short.	1. The main limitation is with the graphite furnace atomic absorption which has poor precision for aluminum determinations. 2. Must know water chemistry beforehand in order to condition resin. 3. Evidence of complex and poorly understood ion exchange reactions. 4. Accuracy depends on the reliability of the stability constants of the various inorganic complexes.

Method	Advantages	Limitations
3. Lumogallion Fluorometric Method	1. The method is very sensitive and had good precision with a detection limit of 0.05 ug/L. 2. The method of analysis is relatively simple.	1. Specific forms of aluminum are not quantified. 2. The time of analysis is relatively long. 3. There are interferences by organic concentration levels greater than 5 mg/L. Fluoride at high concentrations also interferes.
4. Bound/Free Fluoride Method	1. Low detection limit for fluoride determination. 2. Allows the determination of many inorganic aluminum species by inferential techniques.	1. Direct measurements of free fluoride in natural water systems using fluoride ion-selective electrode has limited application to samples with pH greater-than 6.5. 2. Time of analysis is relatively long. 3. The accuracy of the method depends upon the accurate determination of the stability constants of the various inorganic complexes.

PRELIMINARY CONCLUSIONS

The work completed to date has indicated the following:

1. The bound/free fluoride method for inorganic aluminum speciation is inaccurate due to the potential error associated with the free fluoride measurements. Also, the accuracy of the method is dependent on the reliability of the stability constants of the various inorganic aluminum complexes. A simple method for overcoming the errors associated with the free fluoride measurement is now available, however.

2. The specific forms of aluminum determined by oxine extraction and lumogallion fluorescence methods are not known, making interpretation of the aluminum speciation data obtained by these methods difficult. Both methods suffer from interference with humic and fulvic acids. The lumo-gallion fluorometric method is very sensitive and has good precision but its values usually read significantly less than those obtained by oxine extraction.

3. The Chelex 100 ion exchange method provides information on ionic, non-ionic, organically complexed, and inorganic aluminum. There appears to be a potential for error associated with complex and not well understood ion exchange reactions. Also, as with the bound/free fluoride method, accuracy is dependent on the reliability of the stability constants of the various inorganic aluminum complexes.

4. The water chemistry data we have obtained for four Northeasternlake samples, nine Michigan lake samples, and four lake samples from the Adirondack region of New York compare favorably with the original survey data.

5. Reference solution stability appears to be a function of hydrolysis for alkaline solutions and possibly nonstoichiometric reactions of humic substances for acidic solutions.

6. The LRTAP interlaboratory comparison study showed a large variance in the determination of both total and various species of aluminum. The data support our project results showing that a rigorous methods validation for total as well as speciated aluminum is needed to identify those procedures that will produce comparable and meaningful results for effects research.