Aluminium Speciation in Natural Waters

Application Note

Atomic Absorption

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Background

The existence and ecological dangers of acid rain are familiar to most of us. The actual mechanisms of interaction of acidic precipitation with the environment are less well known. Preliminary studies have suggested that decreasing pH and increasing levels of aluminium in lakes produce a combination toxic to fish. Electron microscopy has shown suffocating accumulations of precipitated aluminium on the gill surfaces of dead and moribund fish from acidic lakes.

It was quickly apparent that toxicity did not correlate with the "total" aluminium levels in lakes and streams and that a fractionation or speciation was required to isolate the toxic chemical forms. Aluminium is electro-inactive so that chemical speciation was necessary. Because of the low levels and often small samples involved, graphite furnace was the analytical method of choice.

Speciation Procedure

Previous workers have developed several procedures involving solvent extraction, ion exchange, calorimetry, flame and graphite furnace atomic absorption (GFAAS) [1,2,3]. None were totally satisfactory for our needs. After much experimentation the following scheme evolved.

Samples are taken in the field and returned to the lab as soon as possible (1–4 hours), where the procedures are begun immediately.

An aliquot is removed and acidified to 0.1% with nitric acid. This is later analyzed as is by GFAAS to provide an estimate of total available aluminium. A second aliquot is extracted and the remainder dialyzed, then extracted as described below. Both extracts are saved for graphite furnace analysis. The extraction of the dialyzate not only provides added speciation information but also conveniently preconcentrates the low level samples.

Fast Reactive Aluminium

A sample volume of 5 mL is pipetted into a 15 mL disposable polypropylene centrifuge tube. Buffer (100 µL), oxine reagent (100 µL) and MIBK (1.5 mL) are added in that order and the tube is capped and shaken vigorously for 7–10 seconds. One mL of the MIBK is immediately drawn off and stored in a tightly capped disposable microcentrifuge tube in a freezer until GFAAS analysis.

Buffer Solution: pH 8.3

NH_4OH (149 mL, 15 N) is mixed with glacial acetic acid (115 mL) and diluted to 500 mL. Excess NH_4OH is added to produce a pH of 9.75. Mixing equal parts of buffer and oxine should produce a pH of 8.3. The buffer is extracted two times with oxine/MIBK to remove any aluminium.

Oxine Solution: 2.5%

2.5 g 8-hydroxyquinoline is dissolved in 5 mL glacial acetic acid and diluted to 100 mL with double-distilled water.

This extraction provides an estimate of inorganic monomeric aluminium and organic aluminium. Further speciation into $[Al(OH)_x^{3-x}]$, (AlF_x^{3-x}), and $[Al(SO_4)_x^{3-2}x]$ can be estimated from dissociation constants and fluoride and sulphate measurements.

Total Reactive Aluminium

Total reactive aluminium is determined as above except the sample/buffer/oxine mixture is allowed to react for at least 3 hours prior to extraction. All the above species are extracted plus amorphous and polymeric aluminium. Further work has shown this fraction to be of limited value and the procedure is not used routinely.

Dialysis

A 5 mL volume of double-distilled water is placed in a 10 cm 1000 molecular weight cut-off Spectrapor 6 dialysis bag supplied by Spectrum Medical Industries Inc., 60916 Terminal Annex, Los Angeles, California, 90054. This in turn is placed in 270 mL of sample. After 20 hours dialysis the contents of the bag are extracted and analyzed for aluminium as above. Bags are precleaned by 1% HNO_3 soaks and several double-distilled water soaks and rinses.

Dialysis separates inorganic aluminium from organic since the organic-aluminium complexes involve mainly humic and fulvic acids which have molecular weights greater than 1000. The fast extraction then separates monomeric from the unreactive relatively non-toxic small polymers.

Graphite Furnace Analysis

Graphite furnace analysis is carried out on both acid preserved waters and MIBK extracts. Analytical conditions for both systems are detailed in Table 1. For the lakes and streams studied, normal ranges and typical values for each fraction are listed in Table 2 and Table 3.

Table 1. Graphite Furnace Determinations – Aluminium

Instrument	Agilent AA-475 and GTA-95 graphite furnace and autosampler
Purge gas	Argon
Sample volume	Water 5 µL, MIBK 2 µL
Mode	Peak height

Stage	Temp °C	Time sec.	Gas flow (L/min)	Read
Dry	75	5	3	
	90	10	3	
	120	5	3	
Ash	1225(ramp)	5	3	
Atomize	2700(ramp)	0.8	0	*
	2700	2	0	*
Clean	2700	2	3	

*Precision data on within run duplicates – µg/L

		Standard deviation (no. of determinations)	
	Range	Water non-dialyzed	MIBK dialyzed
Analysis only	0–15	1.5 (60)	1.6 (57)
	15–50	3.1 (39)	3.4 (56)
Prep & Analysis	0–15	1.3 (11)	2.1 (22)
	15–50	5.6 (18)	–

Table 2. Typical Aluminium Levels in Muskoka – Haliburton Lakes

	µg/L Median	Range
Total Al (except in silicate matrix)	80	10–1500
Fast Reactive Al (monomeric and organic	40	0–500
Dialyzed Al (monomeric)	20	0–300

Table 3. Representative Duplicate Data: Aluminium – µg/L

	Total		Extracted		Dialyzed	
Harp Lake 6	127	127	58	53	12	12
Plastic Lake	20	19	6	8	1	2
12 Mile Lake N	12	10	5	5	5	5
Harp Lake 5	257	233	123	123	19	31
Beach L.	9	8	1	1	2	1

The suggested analytical conditions in the GTA-95 "cookbook", Analytical Methods for Graphite Tube Atomizers, 1982, involved an optional ashing step and atomization at 2500 °C for aluminium determination.

Inclusion of ashing and raising the atomization temperature increased sensitivity without significantly decreasing tube life. Typically the ashing step raised the absorbance of 5 µL of a 100 µg/L standard from 0.28 to 0.45. Raising the atomization temperature further increased absorbance to 0.50. The analytical process was also simplified by arriving at a single program which was adequate for both sample matrices.

As is apparent from Table 1, the analytical precision is quite good, and the precision of the extraction and dialysis procedure is also good.

Note that the calibration curve constructed from 2 µL injections of MIBK extracts displays slightly greater sensitivity than 5 µL injections of aqueous standards (Figure 1). This apparent threefold enhancement in absolute sensitivity results from the 5.0/1.5 or 3.3 fold preconcentration effected by the extraction procedure.

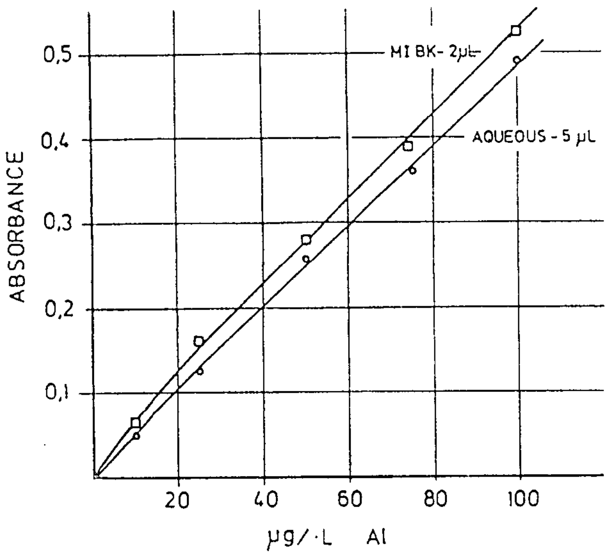

Figure 1. Absorbance

Conclusion

Although the procedures described are somewhat arbitrary, they appear to provide valuable information into the nature and concentration of Al species in natural low alkalinity waters.

An interesting verification of the procedure was obtained by calculations using the known dissociation constants, pH, plus total and free F measurements to yield a "calculated" inorganic monomeric Al which correlates well with the "measured"; that is, dialyzed fraction at pH 5.5. A detailed paper is currently in preparation [4].

Preliminary toxicity work also shows good correlation with the dialyzate levels.

References

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Printed in the USA
November 1, 2010
AA040

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