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J. M. Henshaw<sup>a</sup>; T. E. Lewis<sup>a</sup>; E. M. Heithmar<sup>b</sup>

<sup>a</sup> Lockheed Engineering and Sciences Company, Las Vegas, NV, USA <sup>b</sup> US EPA, Las Vegas, NV, USA

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# A Semi-Automated Colorimetric Method for the Determination of Monomeric Aluminum Species in Natural Waters by Flow Injection Analysis

J. M. HENSHAW and T. E. LEWIS

*Lockheed Engineering and Sciences Company, 1050 E. Flamingo Suite 120; Las Vegas, NV 89109, USA*

and

E. M. HEITHMAR

*US EPA; P.O. Box 93478, Las Vegas, NV 89193-3478, USA*

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A two-channel flow injection analysis method is presented for the fractionation and determination of monomeric aluminum species in natural waters. The method is based upon the colorimetric reaction of monomeric aluminum with pyrocatechol violet at pH 6.1. The first channel measures total monomeric aluminum, while the second determines the non-exchangeable fraction. The method was found to be linear up to 1.0 mg Al/L with a lower limit of detection of 7.0  $\mu\text{g Al/L}$ . The effects of iron, fluoride and several organic ligands were investigated. The analytical performance of the method was assessed in both the laboratory and as part of a large aquatic chemistry survey. The method was compared with the 8-hydroxyquinoline complexation method for determining monomeric aluminum using 329 natural and quality control samples.

**KEY WORDS:** Flow injection analysis (FIA), colorimetry, pyrocatechol violet (PCV), acidic deposition, aluminum speciation.

## INTRODUCTION

The toxicity of aqueous aluminum has become an important field of research in the past decade. Due to the large charge/radius of  $\text{Al}^{3+}$  it is highly reactive, forming both mononuclear (monomeric) and polynuclear hydrolysis species, as well as numerous complexes with anions in natural waters. The inference has been made that most monomeric inorganic species of aluminum are rapidly reactive while organic and polynuclear species are less reactive, and therefore less toxic.<sup>1</sup> Increased levels of aluminum have been documented for many lakes impacted by acidic deposition. Baker and Schofield<sup>2</sup> demonstrated that mortality of fish in Adirondack lakes was positively correlated with inorganic monomeric aluminum complexes rather than with total aluminum concentration. The presence of organic ligands appears to mitigate the toxicity of monomeric aluminum.<sup>3</sup> Thus, the fractionation and measurement of monomeric aluminum complexes has become central to studies of the environmental chemistry and toxicity of aqueous aluminum.

The U.S. Environmental Protection Agency (EPA) is conducting a field survey of a large number of lakes and streams in the United States. This study, the National Surface Water Survey (NSWS), is intended to assess the extent of acidification of surface waters. A second objective is to quantify the number of lakes and streams which are potentially sensitive to future acidification. The third objective of the NSWS is the chemical characterization of these systems. Due to the toxicity of inorganic monomeric aluminum, and to the relationship between pH and aluminum mobility, the speciation of aluminum is of critical importance to the NSWS.

Perhaps the most common method for the determination of monomeric aluminum is the 8-hydroxyquinoline (8-HQ) method of Barnes.<sup>4</sup> The analysis is based on the assumption that only monomeric aluminum is complexed with 8-hydroxyquinoline at pH 8.3 and extracted into methylisobutylketone (MIBK). Aluminum in the extract is then determined by graphite furnace atomic absorption spectroscopy. This method was modified by Driscoll<sup>5</sup> by including fractionation of inorganic and organic monomeric aluminum compounds with a cation exchange column (CEC). The aluminum fraction recovered after passing through the CEC is operationally defined as organically complexed aluminum. The concentration of inorganic monomeric aluminum is defined as the difference between

the total monomeric aluminum and organically complexed monomeric aluminum species.

The 8-HQ method has some drawbacks when used in a large field survey. First, the method is subject to analyst variability, as the amount of aluminum determined can be affected by the manner and length of extraction. Also, the method is labor intensive and slow; a typical sample throughput is less than 10 samples per hour. Finally, MIBK is a hazardous chemical, creating technician safety and waste disposal problems for the laboratory. The need exists for another method for the analysis of monomeric aluminum species when the sample load is high. The pyrocatechol violet colorimetric method described below has been shown to fill this need.

The colorimetric complexation of aluminum by pyrocatechol violet (PCV) was first described by Anton<sup>6</sup> and used in a batch method for the analysis of aqueous aluminum by Dougan and Wilson.<sup>7</sup> Three PCV molecules react with each monomeric aluminum ion to form a colored complex which absorbs at 580 nm. Optimum color development of this complex has been found to occur at pH 6.1. The method has been adapted to an automated segmented flow analysis system by Rogeberg and Henriksen<sup>8</sup> and has been used extensively in Scandinavia. Royset<sup>9</sup> recently published an adaptation of the PCV method for total aluminum determination using flow injection analysis (FIA). FIA was selected for the NSW method because the throughput is greater for FIA than automated segmented flow. FIA is also simpler because of the absence of the air segment and is therefore easier to maintain in a large survey.

The following is a description of a PCV colorimetric method used in NSW employing a two-channel FIA system to fractionate and quantify monomeric aluminum species. The effects of operating parameters and various potential interferences are examined. The method performance in a large survey is evaluated and compared to that of the 8-HQ method.

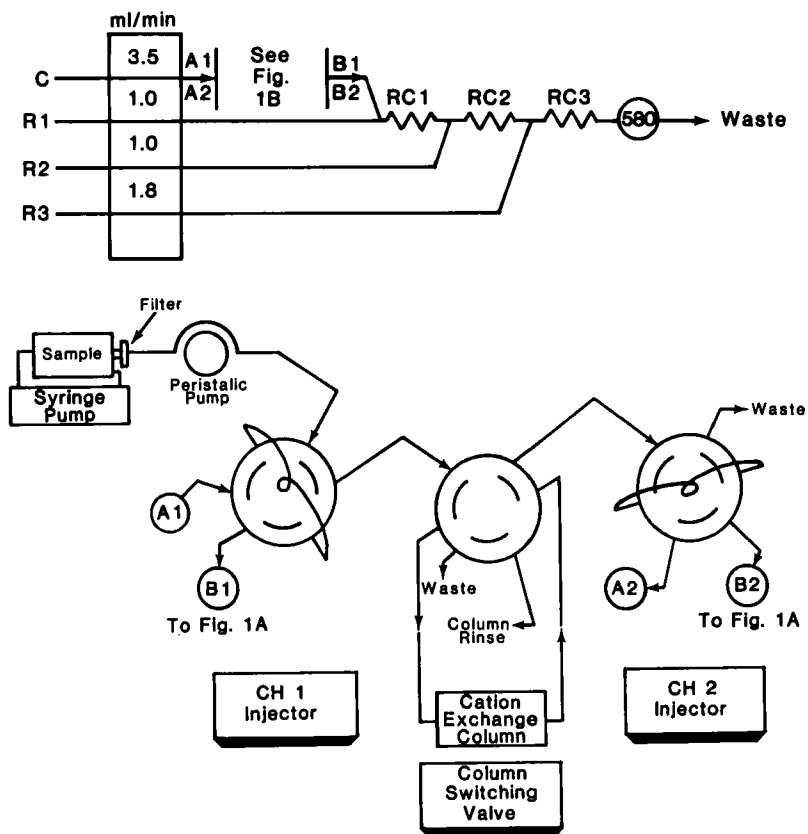
## MATERIALS AND METHODS

### Apparatus

The semi-automated method employs a two-channel FIA system (LaChat Instruments, Mequon, WI) for the analysis of total PCV-reactive (TRx—analogue to total monomeric aluminum) and non-

exchangeable PCV-reactive (NEx—analogue to organically complexed aluminum) monomeric aluminum species (Figure 1).

The chemistries of the two channels are identical except that the NEx fraction first passes through a cation exchange column (CEC) which removes the exchangeable aluminum species<sup>5</sup> before entering the reaction manifold. The concentration of inorganic monomeric aluminum species is defined as the difference between the TRx and NEx fractions. (Figure 1A and B).



**Figure 1** A. Schematic diagram of the PCV-FIA method for the determination of monomeric aluminum species. C: deionized water carrier, R1: iron masking reagent, R2: PCV R3: hexamethylene tetraamine buffer. B. Schematic diagram of the sample introduction configuration of the PCV-FIA method for the determination of monomeric aluminum species.

## Reagents

The reagents used in the method are listed below.

Carrier: ASTM Type II water<sup>10</sup>, degassed under vacuum through a 0.45- $\mu\text{m}$  polycarbonate filter. This water is used in preparing all reagents and standards.

Reagent 1 (iron masking solution): In a 1.0-L volumetric flask, dissolve 7.6 g of hydroxylamine hydrochloride and 0.56 g of 1, 10 phenanthroline in approximately 500 mL of water. Bring to mark with water, degas through 0.45- $\mu\text{m}$  polycarbonate filter and transfer to polypropylene bottle. This solution is stable and is prepared as needed.

Reagent 2 (color reagent): In a 500-mL volumetric flask, dissolve 0.1875 g of pyrocatechol violet in approximately 300 mL water. Bring to mark with water, degas through 0.45- $\mu\text{m}$  polycarbonate filter, and store in a dark glass or polypropylene bottle. This solution degrades with time and exposure to light and should be prepared daily.

Reagent 3 (buffer solution): In a 2.0-L flask, dissolve 168 g of hexamethylene tetraamine in approximately 1.2 L. Bring to mark with water, degas through 0.45- $\mu\text{m}$  polycarbonate filter and transfer to polypropylene bottle. This solution is stable and is prepared as needed.

## Standard and quality control solutions

Aluminum standards were prepared from commercially available AA standards (1000 mg/L). A different source of AA standard was used for the QC solutions. Calibration blank solutions were prepared in Ultrex nitric acid to achieve a pH similar to that of the other standards (approximately 3.5).

## Procedure

A syringe pump pushes the sample through a 0.45- $\mu\text{m}$  polycarbonate syringe filter, over the peristaltic pump, and into the first 100- $\mu\text{l}$  sample loop. The sample then passes through the CEC into the second 100- $\mu\text{l}$  sample loop, and finally to waste (Figure 1B). The sample is injected into the reaction pathway at a fixed time interval controlled by computer. A standard 6-port rotary HPLC injection valve is used for this purpose. As each sample valve is turned, the

deionized water carrier stream flushes the contents of each sample loop into its respective reaction manifold. Following injection of the sample, a third valve controlling sample access to the CEC is switched manually to take the column out-of-line. When the column is out-of-line, deionized water is pumped through the column in a flow opposite to sample flow. This is done primarily to avoid passage of air bubbles, created between sample loadings, through the CEC.

Upon injection, the sample bolus is first mixed with a hydroxylamine hydrochloride (HAHC)/1,10 phenanthroline mask reagent, which eliminates interference from iron (III). Following a mixing coil (Figure 1A, RC1), the bolus mixes with PCV. The bolus passes through a second mixing coil (RC2), and finally a hexamethylene tetraamine (HMTA) solution adjusts the final pH to 6.1, and optimum color development occurs in a third mixing coil (RC3). The transmittance of the PCV-Al solution is measured at 580 nm in a 20-mm flow cell by a colorimeter.

Aluminum standards are injected with the column out-of-line, since the CEC would remove the inorganic aluminum in the standards. A satisfactory synthetic NEx aluminum standard does not exist at the present time. Since the column precedes the sample valve, it does not affect the dispersion of the bolus. A calibration curve is generated from the absorbance peak areas of standard solutions.

A "column-breakthrough" QC solution (75.0  $\mu\text{g Al/L}$ ) is run every ten samples to assess the aluminum removal efficiency of the CEC. This solution is then analyzed again with the column out-of-line, to check the calibration curves of both channels. A quality control limit of  $\pm 10\%$  of the nominal (75.0  $\mu\text{g Al/L}$ ) value is maintained during daily sample analysis. Another form of quality control is the analysis of duplicate pairs of samples, i.e. two samples collected from the same lake. Duplicate precision is defined as the relative difference between the two determinations. A quality control limit of the  $\pm 10\%$  was adopted for duplicate precision.

Big Moose Lake water was used as a laboratory quality control sample. The water was collected in bulk, filtered and refrigerated at 4°C. An aliquot of this sample was analyzed at the beginning and end of each batch of samples. This provided a quality control check on the reproducibility of both channels.<sup>11</sup>

### Interference evaluation

Iron (III) and fluoride were examined as potential interferences. Iron was spiked into solutions containing 0 and 200  $\mu\text{g Al/L}$  at levels of 0, 1000, and 3000  $\mu\text{g Fe/L}$ . Fluoride was spiked into solutions of 0 and 100  $\mu\text{g Al/L}$  at concentrations of 0, 70.3 and 703  $\mu\text{g F/L}$ . The solutions were then analyzed to determine any apparent changes in aluminum concentration.

The effects of several organic ligands were evaluated by spiking them into solutions containing 0 and 100  $\mu\text{g Al/L}$ . The ligands were spiked to a concentration of 37  $\mu\text{M}$ , representing to a molar ratio of 1:10 (Al:ligand) for the 100  $\mu\text{g Al/L}$  solutions. The ligands examined included: CDTA, citrate, fulvate, gallate, humate, mallate, maleate, oxalate, salicylate, tannate, and tartrate. All ligands were obtained from reagent grade sodium salts except for humic and fulvic acids. Humic acid was obtained as a technical grade salt and fulvic acid was extracted from lake sediment following the extraction procedure reported by Holtzclaw *et al.*<sup>12</sup> A formula weight of 10 000 was assumed when preparing the humic and fulvic solutions. Each solution was prepared at least 24 hours before analysis to allow for equilibration.

### Sample collection

During NSW lake sampling operations, 50-mL syringe samples were withdrawn from van Dorn bottles that had been filled at 1.5 m below the lake surface. The syringes were then shipped at 4 °C via overnight express to the laboratory. Analysis by the PCV-FIA method and extraction by the 8-HQ method were performed the day after the sample was collected to minimize holding time.

## RESULTS AND DISCUSSION

### Method development and analytical figures of merit

Some important considerations concerning sample aluminum speciation are addressed in development of the PCV method for the NSW. The speciation and solubility of aluminum is dependent upon solution pH. Therefore, in order to obtain data applicable to the



natural system, it is critical that the pH of the sample remain as stable as possible from the time of collection until reaction with the PCV. Samples exposed to air prior to complexation could suffer changes in carbonate equilibrium, and hence solution pH. In an attempt to maintain the sample pH, samples and the carrier stream were not acidified, a deviation from the Royset FIA application.<sup>9</sup> Also, the syringe samples are injected directly into the FIA and never exposed to air. Røgeberg and Henriksen<sup>8</sup> reported performing analyses with and without an acidified carrier stream. In that study, a buffer containing 300 g/L HMTA with 16.8 mL concentrated  $\text{NH}_4\text{OH/L}$  adjusted to pH 6.1 with 0.1 M HCl was used with the acidified carrier, and a 1:5 dilution of that solution with deionized water was used for the non-acidified carrier stream application. In the method described here, it was determined that pH could be controlled with a solution containing only HMTA, and adjusting the reaction pH by varying the HAHC concentration. The final concentrations of these two reagents were sufficient to buffer sample pH and to mask iron concentrations typically seen in surface waters.

The effects of varying the through-column flow rate on a natural sample (Big Moose Lake, Adirondack Mtns., N.Y.) was examined. The results of this experiment are given in Table 1. Increasing the flow rate from 4.8 to 7.0 mL/min resulted in a slight increase in apparent NEx aluminum. Flow rates greater than 7.0 mL/min did not show a significant change in NEx aluminum concentration. Since slight variations about a flow rate of 7.0 mL/min did not change the apparent NEx aluminum recovery or the method precision, this flow rate was selected.

The conditions listed in Table 2 for the PCV-FIA method are a result of extensive optimization, including both simplex and sequential optimization procedures. These conditions gave the highest possible response while minimizing reagent consumption and tubing maintenance.

Instrumental detection limit of the PCV method, as determined by three times the standard deviation of a low concentration ( $20 \mu\text{g Al/L}$ ) sample analyzed 10 times on each of three nonconsecutive days, is  $7.0 \mu\text{g Al/L}$ . Table 3 shows the precision and bias of aluminum concentrations for synthetic solutions calculated from a calibration curve from 0 to  $350 \mu\text{g Al/L}$ . A calibration from 0 to  $1000 \mu\text{g/L Al}$  remains linear, however the calibration to  $350 \mu\text{g/L Al}$  was typically used to ensure less bias for low concentrations of aluminum.

**Table 1** Effects of through-column flow rate on removal of monomeric aluminum from Big Moose Lake (N.Y.) water

<i>Flow rate (mL/min)</i>	<i>Apparent NEx Al</i>		
<i>(mL/min)</i>	<i>(<math>\mu\text{g/L}</math>)</i>	<i>Std. Dev.</i>	<i>N</i>
4.8	44.2	4.5	6
5.6	44.0	4.4	5
7.0	52.1	3.2	5
7.5	48.0	3.2	5

**Table 2** List of conditions for the PCV-FIA method for the determination of monomeric aluminum species

carrier:	ASTM type II water <sup>10</sup>
Reagent 1:	0.1 M hydroxylamine hydrochloride 2.8 mM 1, 10 phenanthroline
Reagent 2:	1.0 mM pyrocatechol violet
Reagent 3:	0.6 M hexamethylene tetraamine
carrier flow:	3.5 mL/min
R1 pump flow:	1.0 mL/min
R2 pump flow:	1.0 mL/min
R3 pump flow:	1.8 mL/min
sample inlet flow:	7.0 mL/min
column rinse flow:	3.5 mL/min
sample size:	100 $\mu\text{L}$
tubing:	0.5 mm i.d. PFTE
RC1 (length):	12 cm
RC2 (length):	60 cm
RC3 (length):	100 cm
cation exchange column:	PFTE with an inner volume of 7.5 cc
resin:	Amberlite IR-120 (99% Na, 1% H form)
sample throughput:	40 samples/hour

**Table 3** Single-operator precision and bias for the PCV-FIA method using a calibration range from 0 to 350  $\mu\text{g/L Al}$ 

<i>Nominal conc.</i> <i>(<math>\mu\text{g Al/L}</math>)</i>	<i>N</i>	<i>Mean obs. conc.</i> <i>(<math>\mu\text{g Al/L}</math>)</i>	<i>% RSD</i>	<i>bias</i> <i>(<math>\mu\text{g Al/L}</math>)</i>
10	13	9.2	12.0	-0.8
25	10	24.0	8.8	-1.0
50	10	49.4	2.8	-0.6
100	11	99.1	1.3	-0.9
150	2	150.5	2.3	0.5
350	5	350.8	3.4	0.8

Accuracy, as percent spike recovery, was determined for two natural samples spiked with aluminum. Big Moose Lake water was spiked with 300  $\mu\text{g Al/L}$  and Bagley Lake (Cascade Mts., WA) was spiked with 100  $\mu\text{g Al/L}$ . Spike recovery for the samples was 99.6% and 102.3%, respectively.

## INTERFERENCE EVALUATION

The results from the iron interference study are presented in Table 4. Although slight differences in apparent aluminum concentrations were found at 3.0 mg Fe/L, the percent recoveries were within the quality control limits ( $\pm 10\%$ ) established for the method. A concentration of 3.0 mg/L iron greatly exceeds the 4th quintile reported for iron of 0.268 mg/L in a synoptic survey of over 1800 lakes in the eastern U.S.<sup>13</sup>

The results of the fluoride interference study are presented in Table 5. No significant effect on apparent aluminum recovery was observed for 70.3  $\mu\text{g F/L}$ . This is supported by results of a comparison between the formation constants of Al-F and Al-PCV, showing that PCV does not readily release Al to F.<sup>14</sup> A slight effect was seen for 703  $\mu\text{g F/L}$ , however this fluoride concentration is twice the highest value found for the lakes sampled during the field evaluation for this method.

The results of the organic ligand evaluation are presented in Table 6. The values for humate were corrected for aluminum contamination ( $\approx 20 \mu\text{g Al/L}$ ) in the technical grade ligand. No other ligands

**Table 4** Effects of iron upon the PCV-FIA determination of monomeric aluminum species ( $N = 5$ )

<i>Nominal Al conc.</i> ( $\mu\text{g/L}$ )	<i>Nominal Fe conc.</i> ( $\mu\text{g/L}$ )	<i>Apparent Al</i> ( $\mu\text{g/L}$ )	<i>Std. Dev.</i>
0	0	3.3	1.7
0	1000	1.8	2.1
0	3000	6.3	1.4
200	0	198	2.1
200	1000	192	4.8
200	3000	187	2.8

**Table 5** Effects of fluoride upon the PCV FIA determination of monomeric aluminum species ( $N = 7$ )

Nominal Al conc. ( $\mu\text{g/L}$ )	Nominal F conc. ( $\mu\text{g/L}$ )	Molar ratio (Al:F)	Apparent Al conc. ( $\mu\text{g/L}$ )	Std. Dev.
0.0	0.0	0:0	5.1	3.0
0.0	703.0	0:10	0.4	4.8
100.0	0.0	1:0	113.4	3.2
100.0	70.3	1:1	110.0	2.6
100.0	703.0	1:10	101.0	2.7

**Table 6** Effects of organic ligands (10-fold molar excess) upon the percent recovery of total (TRx) and non-exchangeable (NEx) monomeric aluminum

Ligand	% rec. TRx	% rec. NEx
CDTA	0	NA
citrate	0	NA
fulvate	92	0
gallate	102	0
humate	86 <sup>a</sup>	30 <sup>a</sup>
maleate	94	0
mallate	92	0
oxalate	101	15
salicylate	103	0
tannate	0	NA
tartrate	95	0

NA—not analyzed.

<sup>a</sup>—blank corrected.

had detectable aluminum contamination. Fulvate, gallate, maleate, mallate, oxalate, salicylate, and tartrate were shown to have no effect upon the determination of TRx aluminum at the 1:10 (Al:Ligand) molar ratio examined. CDTA, citrate and tannate completely inhibited recovery of TRx aluminum. Humate caused a 14% reduction in TRx recovery. The humate concentration used in this evaluation is much greater than the 4th quintile for dissolved organic carbon reported by Linthurst *et al.*<sup>13</sup> The presence of various organic ligands may cause an underestimation of TRx aluminum.<sup>15</sup>

The ligand effects on channel two, defined as non-exchangeable PCV reactive aluminum, are also given in Table 6. Of the ligands

which do not completely inhibit reaction with PCV, only humate and oxalate formed complexes which passed through the cation exchange column. Any complexes formed with the other ligands were dissociated by the cation exchange resin under the experimental conditions used in this study. The humate complex with aluminum has sufficient stability to pass through the CEC yet is labile enough to allow reaction with PCV. Further work needs to be done on the behavior and strength of organoaluminum complexes present in natural waters.

### Method performance in surveys

Results of the analyses of the Big Moose Lake laboratory quality control samples are presented in Figure 2. The  $\pm 10\%$  quality control criteria (set for synthetic solution accuracy and duplicate pair precision) are also given. The Big Moose data show that the initial acceptance criterion for quality control was an attainable quality control limit for channel one (TRx). However, this limit was too stringent for the lower NEx concentrations measured on channel

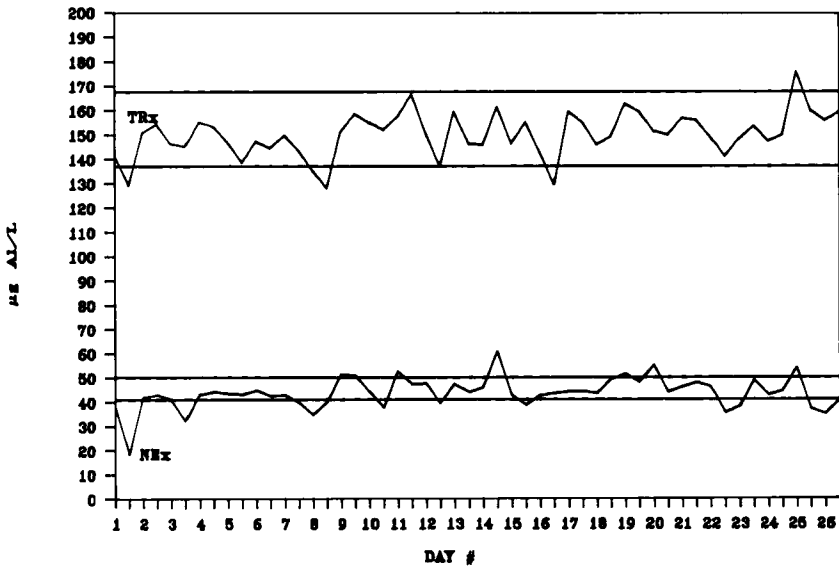


Figure 2 Analytical performance of laboratory quality control sample (Big Moose Lake) with  $\pm 10\%$  quality control limits shown.

two. When 10% of the sample concentration was less than the instrumental detection limit, an acceptance criterion of  $\pm$  the instrumental detection limit ( $7 \mu\text{g Al/L}$ ) was applied. These limits proved much more reasonable for the NEx fraction.

The PCV-FIA and 8-HQ extraction methods were compared using survey data. The Driscoll modification to the method (use of a CEC) was not used in the NSWS. A regression of 8-HQ data versus total PCV reactive yielded an  $R^2$  value of 0.95 and an equation of:

$$8\text{-HQ Al} = 0.76(\text{TRx Al}) - 6.8$$

where all concentrations are in  $\mu\text{g Al/L}$ . The higher total monomeric aluminum concentrations yielded by PCV in the present study was also noted by Sullivan *et al.*<sup>16</sup> employing the Rogeberg and Henriksen<sup>8</sup> method. The authors postulated that PCV may have a higher affinity for certain organoaluminum complexes than does 8-hydroxyquinoline. The duplicate pair (Table 7) and field natural audit (Table 8) data demonstrate the higher recovery of the PCV method.

A regression of monomeric aluminum as determined by the 8-HQ method versus inorganic monomeric aluminum as determined by the PCV method reported here yielded an  $R^2$  value of 0.92 and an equation of:

$$8\text{-HQ Al} = 0.95(\text{TRx} - \text{NEx Al}) + 0.1.$$

This suggests that the fraction of aluminum measured by the 8-HQ method more closely approximates the inorganic monomeric fraction as estimated by the PCV method.

Tables 7-9 present quality assurance data for both methods collected during NSWS. The system detection limits (SDL), calculated as three times the field blank standard deviation added to the mean of the field blanks, gave comparable estimates for the NEx-PCV fraction and the 8-HQ method, but the TRx fraction was much higher (Table 9). The higher SDL for the TRx fraction was not due to a greater standard deviation, but rather to a higher mean ( $10.3 \mu\text{g Al/L}$ ) for the field blanks. The fact that this is not seen in the non-exchangeable fraction suggests that it is attributable to contamination of inorganic monomeric aluminum. This contamination

**Table 7** Duplicate pair precision for the PCV-FIA and 8-HQ extraction methods for determining monomeric aluminum species. All values in  $\mu\text{g Al/L}$ 

Method	TRx Al > 85 $\mu\text{g/L}$ (N = 6)		TRx Al < 50 $\mu\text{g/L}$ (N = 18)	
	Mean	Std. Dev.	Mean	Std. Dev.
TRx	143.1	4.2	25.1	1.8
NEx	46.8	4.1	11.1	1.1
8-HQ	88.7	5.8	9.8	2.3

TRx = Total PCV reactive.

NEx = Non-exchangeable PCV reactive.

8-HQ = 8-hydroxyquinoline extractable.

**Table 8** Field natural audit sample data ( $\mu\text{g Al/L}$ ) from the PCV-FIA and 8-HQ extraction methods for the determination of monomeric aluminum species

Method	FN1	FN2	FN3	FN4
TRx	24.6 $\pm$ 3.4	196.3 $\pm$ 7.7	27.5 $\pm$ 5.9	158.1 $\pm$ 7.9
NEx	15.3 $\pm$ 3.4	52.6 $\pm$ 7.6	12.1 $\pm$ 2.7	41.9 $\pm$ 4.6
8-HQ	13.2 $\pm$ 4.3	137.9 $\pm$ 15.6	9.8 $\pm$ 2.4	114.9 $\pm$ 16.9

FN1-4 = Field Natural audit sample #.

**Table 9** Field and laboratory blank data ( $\mu\text{g Al/L}$ ) from the PCV-FIA and 8-HQ extraction methods for the determination of monomeric aluminum species

Method	Mean	FB	SDL	LOQ	Mean	LB
	FB	Std. Dev.			LB	Std. Dev.
TRx	10.3	4.3	23.2	53.4	12.0	2.0
NEx	1.8	2.9	10.4	30.5	1.5	2.9
8-HQ	3.6	2.5	11.0	28.3	3.0	3.0

FB = Field Blank.

SDL = System Detection Limit = mean FB + 3\*Std. Dev. (FB).

LOQ = Limit of Quantitation (10X s.d.(FB) + mean FB).

LB = Laboratory blank.

was not observed with the 8-HQ method, either due to absence or poor recovery of the contamination. It should be noted that the 8-HQ extraction was performed in a clean air station while the PCV method, although a closed system, was done in a routine laboratory.

Twenty four duplicate pairs were analyzed during the study. These pairs were separated into two groups, those samples with a concen-

tration >85 ppb monomeric Al in one group, and samples containing <50 ppb monomeric Al in the other, to provide estimates of precision for high and low concentration samples. The standard deviation for each group of data was determined from the formula:

$$\text{std. dev.} = \left\{ 1/N \sum_i [(x_{1i} - \bar{x}_i)^2 + (x_{2i} - \bar{x}_i)^2] \right\}^{1/2}$$

where

$N$  = the number of duplicate pairs

$\bar{x}_i$  = the mean of the  $i$ th duplicate pair

$x_{1i}$  = the  $i$ th routine concentration

and

$x_{2i}$  = the  $i$ th duplicate concentration

The data from the duplicate pairs and the field natural audit samples (Tables 7 and 8) reveal that the PCV method (TRx & NEx) has better precision than the 8-HQ method, as evidenced by lower standard deviations for samples of both high and low levels of aluminum. The only sample showing a higher standard deviation for the PCV method was FN3, which could be expected due to the large differences in sample means between the PCV fractions and the 8-HQ extractable aluminum. Calculations of relative standard deviations for all the data would yield results lower for the PCV method than the 8-HQ method.

## CONCLUSIONS

The PCV-FIA method for the fractionation and determination of monomeric aluminum species in natural surface waters has been successfully implemented in a major environmental survey. Despite the apparent differences in affinity for monomeric aluminum compounds, results from the PCV-FIA and the 8-HQ methods correlate well with each other. The PCV method gives better precision and a higher sample throughput. The poorer system detection limit of the TRx fraction can be attributed to contamination by inorganic monomeric aluminum in the laboratory. Characterization of the



effects of various inorganic and organic ligands on the performance of each method is needed. Further work on the cation exchange column is also warranted to better understand which forms of monomeric aluminum are exchanged by the resin.

## NOTICE

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