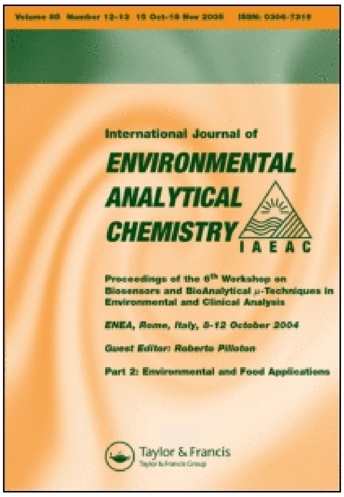

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Automated Measurement of Aqueous Aluminum by the Pyrocatechol Violet Method

J. M. Samaritan[a]; J. D. Wehr[a]; A. Buccafuri[b]; M. Sahn[b]
[a] Louis Calder Center of Fordham University, Armonk, NY [b] Bran + Luebbe Analyzing Technologies, Elmsford, NY, USA

To cite this Article Samaritan, J. M. , Wehr, J. D. , Buccafuri, A. and Sahn, M.(1993) 'Automated Measurement of Aqueous Aluminum by the Pyrocatechol Violet Method', International Journal of Environmental Analytical Chemistry, 50: 3, 173 — 182

To link to this Article: DOI: 10.1080/03067319308027595

URL: http://dx.doi.org/10.1080/03067319308027595

Intern. J. Environ. Anal. Chem., Vol. 50, pp. 173-182
Reprints available directly from the publisher
Photocopying permitted by license only

AUTOMATED MEASUREMENT OF AQUEOUS ALUMINUM BY THE PYROCATECHOL VIOLET METHOD

J. M. SAMARITAN[†]*, J. D. WEHR[†], A. BUCCAFURI[‡] and M. SAHN[‡]

[†]*Louis Calder Center of Fordham University, Drawer K, Armonk, NY 10504 and*
[‡]*Bran + Luebbe Analyzing Technologies, Elmsford, NY 10523-1500, USA.*

(Received, 9 April 1992, in final form, 18 August 1992)

In response to our need for a rapid method of analyzing numerous aluminum samples, we developed an automated procedure for measuring total monomeric aluminum in aqueous samples. Two separate designs for a continuous microflow analyzer are presented which enable detection over a combined range of 20 µg Al/l to 1000 µg Al/l. The best fit to the calibration curve for the high sensitivity manifold is not linear ($r^2 = 0.998$) as previously reported but third order (cubic, $r^2 = 1.000$). The choice of equations for curve fit for the low sensitivity range is less critical as first and third order equations provide comparable fit. Between-sample contamination is less that 3% and reproducibility is high; less than 1% variation for high (200 - 1000 µg Al/l) concentrations and less than 7% for lower (20 - 300 µg Al/l concentrations. Analysis of both water and soil extract samples for aluminum should be facilitated by use of this system.

KEY WORDS: Pyrocatechol violet (PCV), automated colorimetric analysis, aluminum chemistry

INTRODUCTION

Interest in the effects of acidic deposition on aquatic and terrestrial ecosystems has prompted a concomitant development in methodologies for aluminum analysis. Aqueous total monomeric aluminum is generally measured by either the hydroxyquinolone extraction method[1] or pyrocatechol violet colorimetry [2]. The use of pyrocatechol violet (PCV) was proposed by Anton[3] and later modified by Dougan and Wilson [4]. Automation of this latter technique was subsequently developed by Henriksen and Bergmann-Paulsen [5] with an automated analyzer made at their institute. Further modifications to this procedure were made by Rogeberg and Henriksen[6] for the Technicon AutoAnalyzer II. This method has generally been adopted for aluminum analysis by the autoanalyzer; the latest edition of Standard Methods for the Examination of Water and Wastewater [2] includes this as a "proposed" method.

The PCV-based aluminum analysis was also designed for the flow injection autoanalyzer

---

*Corresponding author

(FIA). This equipment was used in the National Surface Water Survey [7, 8, 9] and is also included in Standard Methods [2] as a proposed method for aluminum analysis. The PCV method is similar for both machines except that the reaction time is shorter in FIA and the reagents are more concentrated. The operational principles for each machine differs as segmented (continuous) flow analysis (SFA) introduces an air bubble to separate the samples and FIA prevents inter-sample contamination by eliminating turbulence-induced dispersion between sample parcels.

The Bran + Luebbe TrAAcs 800 is hydraulically scaled-down to the microliter range of sample and reagent volumes as compared to the milliliters required by its predecessor, the Technicon Autoanalyzer II (AAII). This accomplished a reduction in sampling time, reagent consumption, and sample volume required for collection. The rate at which the analytical routine is completed is also faster on this new system bringing it closer to parity with FIA in this regard. Changeover between chemistries requires removal of one manifold and installation of the manifold for the next routine. Changeover between high and low sensitivity capabilities necessitates changing the pump tube configuration according to the schematic while retaining the same manifold on the analytical console. The system is enhanced by computer control and direct printout of sample concentrations.

This paper describes the conversion and modifications of the method of Rogeberg and Henriksen [6] for use on our analyzer for measurement of total monomeric aluminum by the PCV method. This is advantageous for us since it reduced the water sample volume and gave us the ability to rapidly analyze a greater number of samples for aluminum upon return from field collections without long holding times or sample preservation. Sample preservation by the addition of acid may not be desirable since it will cause a change in the speciation of aluminum, may cause an inconsistent rate of release of colloidal aluminum, or dissolve particulates that have passed through after filtration [10]. Arent and Lewis [10] provide a review of the stability of aluminum samples with different treatments.

MATERIALS AND METHODS

This automated method employs a two-channel segmented flow analyzer (Bran + Luebbe Analyzing Technologies, Elmsford, NY) for the analysis of total monomeric aluminum. Design of the aluminum analysis manifold in the present system consists of scaling down the size of the pump tubes, keeping molarities and proportions of reagents to sample similar, and retaining the sequence of reagent additions as in Rogeberg and Henriksen [6]. Table 1 permits comparison of these two SFA methods as well as the FIA techniques for flow rates, concentrations and volumes of reagents.

Dougan and Wilson [4] initially observed that the optimum wavelength for absorbance of the aluminum-pyrocatechol violet complex is at 585 nm. In our system a 590 nm filter was used. Several others [2, 9, 12] also used a 590 nm wavelength filter in their studies. The length of the optical flow cell used by other investigators have ranged from 5 to 20 mm in length[2, 3, 8, 11, 12, 13]. A 10-mm flow cell is used in this and has also been employed on a flow injection system [11, 13].

Table 1 Comparison of flow rates (in parentheses, ml/min) and concentrations of reagents used in the PCV method of aluminum analysis. The molarity of PCV is generally uniform for all applications, however, buffer and iron masking solutions varies with each author.

	Segmented Flow System			*Flow Injection System*	
	TrAAcs	*AutoAnalyzer II*			*LaChat*
REAGENTS	*This study*	*Ref.6*	*Ref. 12*	*Ref. 11*	*Ref. 8*
Sample	(0.534)	(2.50)	(1.00)	(0.8)	(3.5)
Methanamine	2.14 M	2.14 M	1.43 M	3 M	0.6 M
Buffer	(0.258)	(0.80)	(0.80)	(1.0)	(1.8)
Pyrocatechol	1.0 mM	1.0 mM	0.5 mM	5 mM	1.0 mM
Violet	(0.05)	(0.16)	(0.6)	(0.23)	(1.0)
HCl and Wetting Agent	added	added	not added	not added	not added
1,10 phenanthroline	3.6mM	3.6mM	1.5mM	10.0mM	2.8 mM
	(0.025)	(0.10)	(0.32)	(0.32)	(1.0)
Hydroxylamine	1.02 M	1.02 M	0.43 M	0.5 M	0.1 M
	(0.25)	(0.10)	(.32)	(0.32)	(1.0)

The standard configuration of our high sensitivity aluminum manifold (Figure 1) is capable of working in the range of 20 - 300 ug Al/l. The sequence of reagent additions is the same as Rogeberg and Henriksen [6] except that (a) reagents are always followed at each step by a mixing coil in our design and (b) debubbling/rebubbling of the segment is inserted to keep baseline noise low. No accomodation for the ion exchange column is shown.

A second configuration was designed for a manifold intended for low sensitivity analysis, in the range of 200 to 1000 µg Al/l. Figure 2 uses the same coil design as the high sensitivity manifold but a larger HCl/wetting agent pump tube (381 µl) and a smaller sample pump

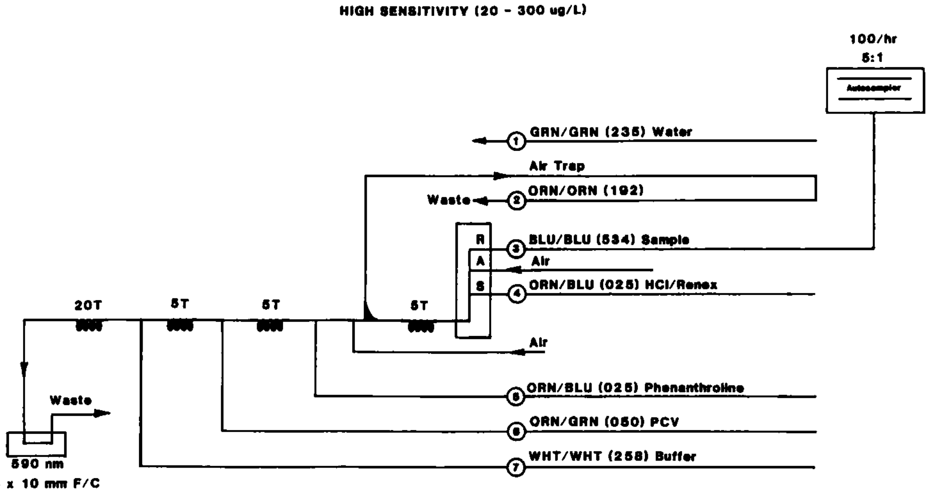

Figure 1 High sensitivity manifold design for the PCV method of aluminum analysis. Pump tube sizes are indicated by the abbreviated color codes and flow rates (µl/min) are contained within parentheses. Sampling rate = 100/hr; sample/wash ratio = 5:1; 20T = 20 turn mixing coil; 5T = 5 turn mixing coil; F/C = optical flow cell.

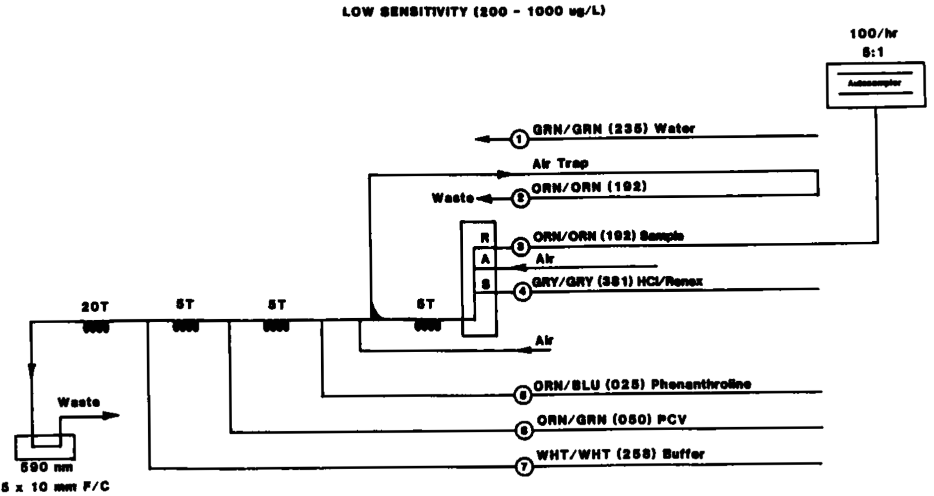

Figure 2 Low sensitivity manifold design for the PCV method (details given in Figure 1).

tube (192 μl) are inserted. This arrangement dilutes samples by 50%, and increases the range of detection to 1000 μg Al/l. The pH of the solution is maintained at 6.1 by lowering the molarity of the HCl/wetting agent solution so that there is not a change in speciation of aluminum by an increase in acid concentration. We prepare the solution by bringing 2.6 ml of 12N HCl up to a final volume of 250 ml with distilled water. As a wetting agent, 2.5 ml of 30% Renex-30 (ICI Americas Inc.) is added to the HCl and the solution degassed by vacuum. The pH of the final effluent is monitored by collection at the waste line and measurement on a pH meter.

The reagents used to perform the aluminum analyses were prepared according to Rogeberg and Henriksen[6] with some modifications. The wetting agent combined with the HCl was changed from 2.5% Brij-35 to 1% Renex-30 (each as 30% solutions) to reduce the baseline noise. The buffer was also changed from 2.3M methenamine to 1M [N-morpholino] ethanesulfonic acid (MES). These modifications are discussed elsewhere[14].

The detectable range can be expanded to even higher aluminum concentrations. We found that 10,000 μg Al/l could be read by changing to an even larger (484 μl) HCl/Renex pump tube (the molarity of this solution must also be changed) and smaller (79 μl) sample pump tube. This illustrates that when dilution of samples is not desired or possible, the range of detection can be manipulated to meet a particular application. We also found that the detection limit could be lowered on the high sensitivity manifold to 10 μg Al/l by setting the base and gain with a standard of 180 μg Al/l (instead of 300 μg Al/l) and doing a gain check with 180 μg Al/l as the highest standard.

A sampling program was written to determine the precision of measurements and the amount of contamination between sample parcels (carryover). A series of aluminum standards ranging in concentration from 30 to 300 μg Al/l and 200 to 1000 μg Al/l were prepared to represent 100, 70, 50, 30, and 10 percent of full scale of detection. We also determined the optimal samples/hour and sample:wash ratio. Using other chemistries as a guideline, we tried combinations of sampling rates (120/h, 100/h, 80/h and 60/h) and sample:wash ratios (3:1, 4:1, 4.5:1, and 5:1) until we found the combination that yielded a carryover factor less than 3.5%.

The instrument detection limit for aluminum analysis on this machine was determined according to the Federal Register [15]. The coefficient of variation, a measure of precision, was determined automatically by the machine for each analysis.

We examined the linearity of absorbance for each sensitivity range (30 - 300 μg Al/l and 200 - 1000 μg Al/l) by utilizing the TrAAcs programming choices for curve fitting. There is a limitation in the number of calibrants (eight) which can be used. The present system permits a fit of calibration curves using linear, quadratic (2nd order), cubic (3rd order) or piecewise (point-to-point) functions. Visual inspection of the calibration curve, reproducibility of the standards when read as samples, and statistical analyses were used to determine the best fit for the calibration curve. These analyses were performed using the SYSTAT statistical package [16].

Different cleaning procedures for use prior to shutdown were evaluated as a part of a standard routine. The options tested were distilled water, 6N HCl, 1N NaOH, 5%HF, and HCl/ETOH [2].

The efficacy of these methods were evaluated on the basis of the carryover attained in the first run following each cleaning routine.

We tested various sampling cups and test tubes for their effects on errors in analysis; based on the coefficient of variation associated with each type. Previous automated systems suffered from high-to-low or low-to-high sample carryover effects on neighboring peaks. The present system was configured to correct for these effects and tested as follows. A test sampling protocol consisted of several possible sampling combinations (e.g., high concentration cup followed by a low concentration cup). Percent carryover was determined for each design. In addition to the standard autoanalyzer polystyrene cups, we tried borosilicate glass tubes (16 × 75 mm) and disposable plastic culture tubes (15 × 75 mm).

RESULTS

The aluminum manifold configurations depicted in Figures 1 and 2 permit the most samples to be run with the least amount of sample-to-sample contamination (carryover). This system can be programmed to run 100 samples per hour (machine maximum is 120/hr) with a 5:1 sample-to-wash ratio without carryover exceeding 3%.

The simplest cleaning routine of distilled water followed by air a few minutes after analysis has commenced is adequate for this system. If any stubborn residue is in the system or blockages occur (the flow cell appears susceptible), a 5% HF solution may be used. The manifold is removed from the analytical console and the solution cautiously pumped through under vacuum pressure with just several slugs followed by distilled water rinsings for a thorough cleaning.

The standard 4.0 mL polystyrene sampling cups introduced the least variation in analytical results (c.v. = 0.69%). We found borosilicate tubes to induce the highest amount of variability in resampling from the same cups (c.v. = 4.4%) when compared to the other types.

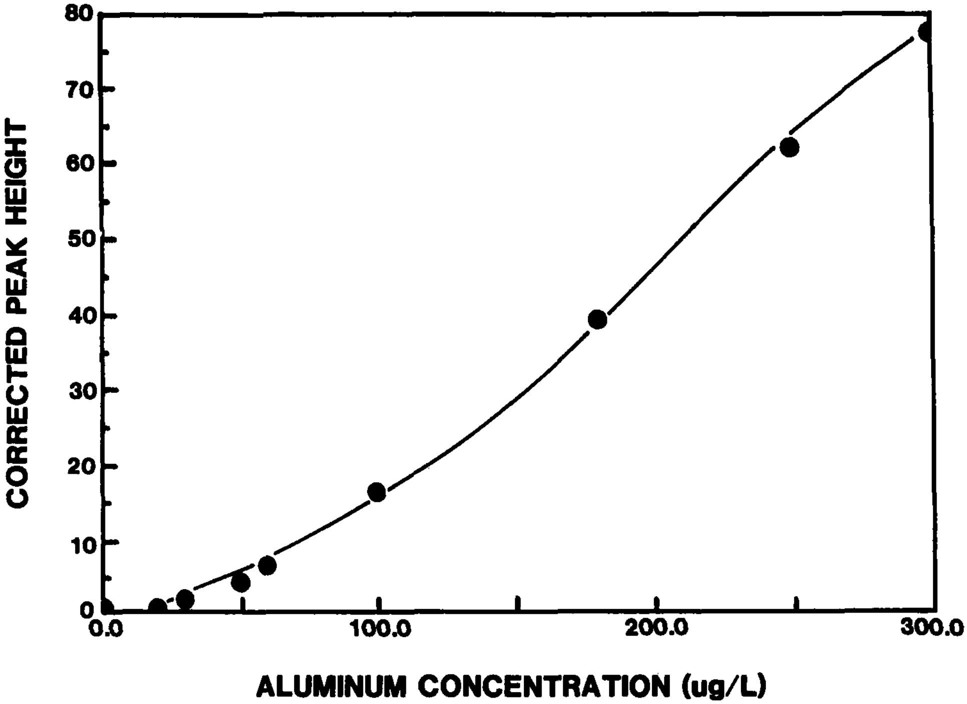

Figure 3a Calibration curve for the high sensitivity manifold (calibrants between 20–300 μg Al/l; curve fit by third order polynomial regression). See Table II for further details.

The calibration curve for absorbance over the range of 0 to 1000 μg Al/l is not linear over the entire detection range. Figures 3a and 3b show the calibration curves obtained for the high and low sensitivity manifolds respectively. A cubic (third order) curve was fit to the data. It is possible to see how others would have chosen to use a linear fit when manually performing this task. The minimum detectable concentration of total monomeric aluminum by this instrument is 20 μg Al/l on the high sensitivity manifold and 200 μg Al/l on the low sensitivity manifold.

The statistical results obtained from ten measurements in the same cup during the test sampling protocol for this method are listed in Table 2a. The coefficient of variation is below 1.5% for the low sensitivity and below 7.0 for the high sensitivity manifold and indicates a high degree of precision in this method. Carryover was 0.7% for the low sensitivity manifold and 1.9% for the high sensitivity manifold.

DISCUSSION

The design of the manifolds for use on our SFA system appears well suited to measuring a broad range of concentrations of total monomeric aluminum which may be present in the environment. Since the definition of aluminum species is still based on operational terms,

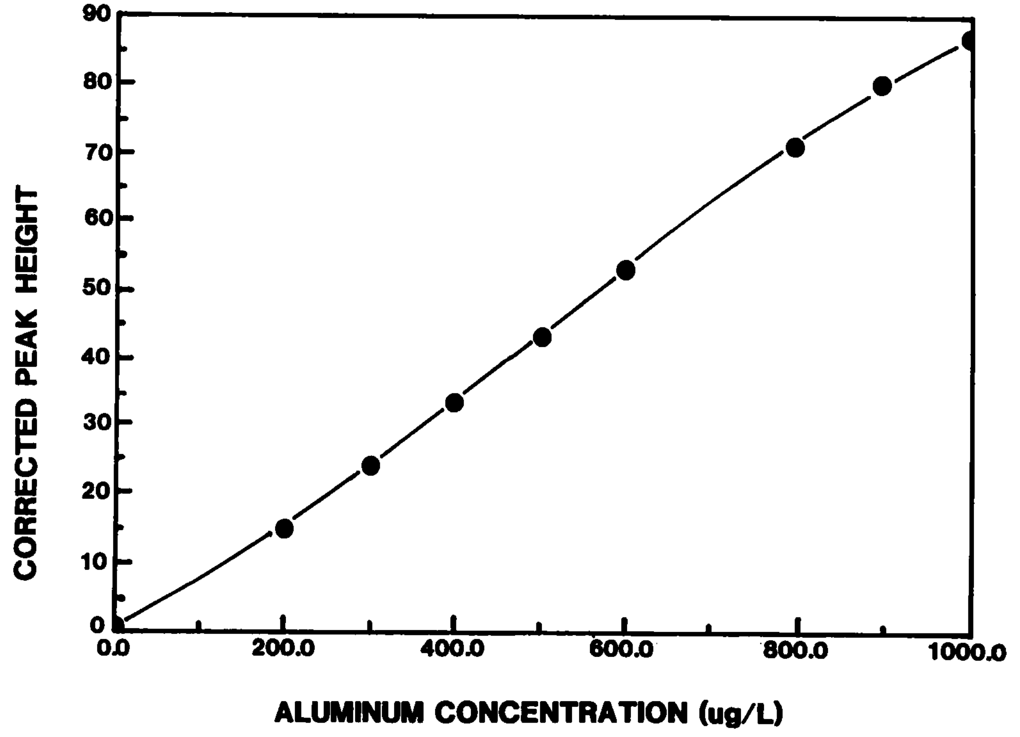

Figure 3b Calibration curve for the low sensitivity manifold (calibrants between 200–1000 μg Al/l; curve fit by third order polynomial regression). See Table II for further details.

we have complied with the common usage. It may be more appropriate to term the fraction of aluminum measured by PCV, however, as catechol reactive aluminum, as suggested by LaZerte *et al.* [12] and Henshaw *et al.* [8]. Critical assessment of the importance of monomeric or polymeric species to the total aluminum pool under consideration is necessary. Polymeric aluminum is generally not of concern in environmental samples, however, users must be aware that the acidification step in this procedure will convert that fraction if present, to monomeric aluminum.

The TrAAcs method of aluminum analysis has faster throughput of samples at 100 per hour when compared to the AutoAnalyzer II which can handle 30 samples per hour [2,6]. This makes this system preferable for intense survey work (the FIA system has a similar advantage) when significant numbers of samples will be collected and storage is undesirable.

Our findings (Table 2) show that the calibration curve for the high sensitivity aluminum analyses most closely fits a third order (cubic) polynomial. The S-shape curve better reflects the distribution of measured values as compared to a line. Regression analyses (Table 2b) produces an $r^2 > 0.999$ and a F-ratio of 7570.97 for the third order polynomial which indicates a better fit than the $r^2 = 0.998$ and F-ratio of 3124.81 for the first order equation. Additionally, the coefficient of variation is lower for replicate sampling with the cubic calibration curve as compared to the linear. Accuracy is also improved when a third order fit is used; the linear

Table 2 Evaluation of the accuracy, precision and best fit for Al calibration curves using high sensitivity (20–300 µg Al/l) and low sensitivity (200–1000 µg Al/l) calibrants (n=10 per concentration). Values in II-a are the average Al concentrations recovered, with error (%) given as coefficients of variation (ND = not determined). Statistics (II-b) based on least squares regression and ANOVA for closeness of fit (P=probability of type I error) for first, second and third order polynomials.

a.	*High Sensitivity*					*Low Sensitivity*				
	60	120	180	240	300	200	400	600	800	1000
Linear	59.4	127.4	185.9	254.4	313.7	204.5	402.3	619.2	814.2	995.0
(1st order)	10%	3.4%	4.4%	21%	6.0%	1.3%	1.2%	0.92%	0.82%	0.72%
Quadratic	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
(2nd order)										
Cubic	61.7	128.2	171.5	249.2	305.3	207.2	412.7	603.0	811.1	1004.0
(3rd order)	1.2%	6.6%	1.6%	1.3%	0.88%	1.3%	0.7%	0.84%	0.52%	0.36%

b.		*High Sensitivity*			*Low Sensitivity*	
	r^2	*F - ratio*	*P*	r^2	*F - ratio*	*P*
Linear	0.998	3124.81	<0.001	0.999	4216.31	<0.001
Quadratic	0.999	3191.46	<0.001	0.999	2122.49	<0.001
Cubic	>0.999	7570.97	<0.001	ND	ND	ND

fit tends to overestimate the concentration of aluminum. The preferred choice of curve fitting techniques is not as critical in the low sensitivity range. The $r^2 = 0.999$ and F-ratio of 4216.31 for the linear is very high and the scatter diagram indicates a much less curved fit. The coefficient of variation for the linear and third order polynomial do not seem very different.

The curve was reported to be linear in the range of 0–300 µg Al/l by Dougan and Wilson[4] for their manual spectrophotometric method. LaZerte *et al.*[12] assert that the calibration for his modified AutoAnalyzer II was nonlinear, but that separate calibrations were necessary for the 0–100 µg Al/l range and the 100–1000 µg Al/l range. Henshaw *et al.*[8] reported a linear calibration curve on a flow injection system from 0–1000 µg Al/l. We recommend that all users run a test of the linearity of absorbance of standards before initiation of sample analyses and a minimum of five standards, preferably eight are used for calibration. Our data suggest that the best fit for high sensitivity analyses should be a third order polynomial.

The detection limit of 20 µg Al/l on the high sensitivity (20–300 µg Al/l) manifold is consistent with others[6]. However, Henshaw *et al.*[8] reports a minimum detection of 7 µg Al/l on the flow injection system. The reasons for the differences in linearity and detection range between the continuous flow and flow injection systems is not known. Explanations for these may lie in the inherent differences in operating conditions or the proportion of sample to reagents in use. Our system sensitivity theoretically can be increased further with a change from a 10-mm to 20 or 50-mm optical flow cell.

The results of a test sampling run (Table 2a) show excellent replication and low carryover achieved with this method. Carryover was almost three times greater when low aluminum concentrations were measured, but this 1.9% is still below the acceptable 3% limit. Variability in carryover between runs can be due to the hydraulic characteristics of the continuous flow systems as well as the chemistry involved in color development.

Table 3 shows the results of analyses performed on freshwater samples. During analysis, the autoanalyzer first presents values extrapolated from peak heights, then it performs a correction for carryover and delivers a final set of values for the run, along with statistics.

Table 3 Values for filtered lake water samples run on the high sensitivity manifold to determine total monomeric aluminum concentrations. These data illustrate the TrAAcs presentation of values before and after correction for carryover. The carryover factor in this run was 2.6%.

Uncorrected Values, µg Al/l	*Corrected Values, µg Al/l*
45.19	46.10
32.96	33.69
26.62	27.35
27.75	28.77
24.65	25.22
23.24	23.70
20.56	20.68

Corrected values represent concentrations corrected for baseline drift, sensitivity (gain) and carryover. Baseline correction is the first applied to the data and is calculated as the difference between the original and final baseline reading. Carryover correction is performed next to adjust for a low concentration slug picking up a residue from a preceeding high concentration slug. Sensitivity correction is performed last to account for several factors which include peculiarities in the chemistry.

Minimizing the use of glassware and employing plastic sample cups in aluminum analysis has been advised, and our results on borosilicate tubes bears this wisdom out. The variability (4.4%) we found to result from the use of glass tubes was also noted as a source of contamination by Peden *et al.* [7]. Taller sample tubes will also reduce noise via reducing the time the sample probe is in air. However, this was not necessary in the present study due to the very low intersample variation achieved; smaller polystyrene sampling cups are satisfactory for analysis.

Analysis of total monomeric aluminum can be reliably performed with the combination of manifold design, sampling speed and wash settings, and use of a more contemporary wetting agent and buffer. The incorporation of an ion exchange column into the design to separate inorganic and organic aluminum fractions is currently being examined.

Acknowledgements

Funding for this study was provided by the National Science Foundation (DIR # 9002145); the Fordham University Research Office (to JDW); and by the Louis Calder Center, Fordham University. The generosity of Bran + Luebbe is greatly appreciated for the donation to the Calder Center of the materials which comprise the aluminum manifold. Mr. Aldo Conetta, Marketing Manager, is thanked for his role in securing this collaboration.

References

1. C.T. Driscoll, *Intern. J. Environ. Anal. Chem.*, **16**, 267–283 (1984).
2. American Public Health Association (APHA). *Standard Methods for the Examination of Water and Wastewater. 17th Edition*. pp. 3-68–3-73 (1989).
3. A. Anton, *Anal. Chem.*, **32**, 725–726 (1960).
4. W.K. Dougan and A.L. Wilson, *Analyst*, **99**, 413–430 (1974).
5. A. Henriksen and I.M. Bergmann-Paulsen, *Vatten*, **4**, 339–342 (1975).
6. E.J.S. Rogeberg and A. Henriksen, *Vatten*, **41**, 48–53 (1985).
7. M.E. Peden, S.A. Amankwah, B.J. Keller, E.C. Krug, and J.M. Peden, *Evaluation of aluminum speciation using synthetic and natural samples: Final Report*. (Illinois State Water Survey Division. SWS Contract Report 463. Illinois Department of Energy and Natural Resources, Champaign, IL., 1989).
8. J.M. Henshaw, T.E. Lewis, and E.M. Heithmar, *Intern. J. Environ. Anal. Chem.*, **34**, 119–135 (1988).
9. U.S. Environmental Protection Agency. *Handbook of Methods for Acid Deposition Studies. Laboratory analyses for surface water chemistry*. (Office of Research and Development: Washington, D.C., EPA 600/4-87/026, 1987).
10. L.J. Arent and T.E. Lewis. In: *The Environmental Chemistry and Toxicology of Aluminum* (T.E. Lewis, ed.) (Lewis Publ., Chelsea, MI, 1989), pp.41–57.
11. O. Royset, *Anal. Chim. Acta*, **185**, 75–81 (1986).
12. B.D. LaZerte, C. Chun, D. Evans, and F. Tomassini, *Environ. Sci. Technol.*, **22**, 110–1108 (1988).
13. LaChat Instruments. QuikChem Method No. 10-173-33-1-A for total reactive monomeric aluminum. Milwaukee: WI, (1988).
14. J.M. Samaritan and J.D. Wehr, In prep.
15. Federal Register 40 CFR 136, App. B. (1990).
16. Leland Wilkinson. SYSTAT: The System for Statistics. Version 4.1. Evanston, IL: SYSTAT, Inc., (1989).