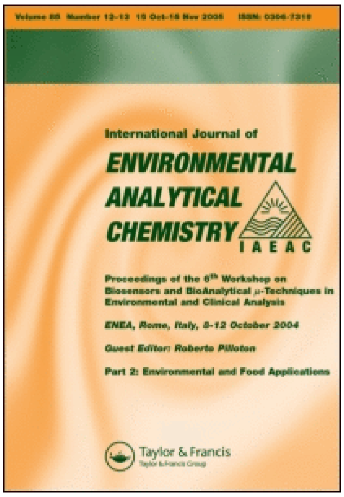

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Apparent Monomeric Aluminum Concentrations in the Presence of Humic and Fulvic Acid and Other Ligands: An Intermethod Comparison Study

Timothy E. Lewis[a]; David E. Dobb[a]; J. M. Henshaw[a]; S. J. Simon[a]; Edward M. Heithmar[b]
[a] Lockheed Engineering and Sciences Company, Environmental Programs, Las Vegas, Nevada, USA [b] Quality Assurance Division, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, USA

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Apparent Monomeric Aluminum Concentrations in the Presence of Humic and Fulvic Acid and Other Ligands: An Intermethod Comparison Study

TIMOTHY E. LEWIS, DAVID E. DOBB, J. M. HENSHAW
and S. J. SIMON

Lockheed Engineering and Sciences Company, Environmental Programs, Las Vegas, Nevada 89109, USA

and

EDWARD M. HEITHMAR

Quality Assurance Division, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada 89114, USA

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The effects of humic and fulvic acids and other ligands on apparent monomeric Al concentration were determined by three analytical methods: 8-hydroxyquinoline/MIBK, pyrocatechol violet, and fluoride complexation kinetics. Citric acid and CDTA were found to cause the greatest reduction. Also, ligands with phenolic and/or carboxylic groups in the ortho position caused significant reduction in apparent total monomeric Al concentrations. Each ligand affected each analytical method in varying degrees. The extent to which each method was affected was dependent upon not only the configuration of the competing ligand, but also the relative stability of the Al/measurement-ligand complex, the pH at which the analytical method operated, and the kinetics of the measurement reaction. These factors must be taken into consideration when interpreting total monomeric Al values generated by different analytical methods, particularly when a large fraction of the monomeric Al pool is comprised of organically-bound forms.

KEY WORDS: Aluminum, organic ligands, 8-hydroxyquinoline, pyrocatechol violet, fluoride complexation.

INTRODUCTION

A possible consequence of acidic deposition is the mobilization of toxic metals from soils and sediments.[1,2] Of particular interest is the mobilization of aluminum from the edaphic to the aquatic environment.[3–6] Decreases in fish populations have been observed in acidified lakes.[7–9] Field and laboratory studies have indicated that Al precedes hydrogen ions as a toxic factor in the pH range 6.0 to 5.0.[10–14] Toxicity is a function of the form in which Al occurs. Controlled laboratory exposures have revealed that the aquo-ions of Al (Al^{3+}), and the somewhat less reactive monomeric hydroxo-complexes, are the forms most acutely toxic to fish, while the polymeric, colloidal, and organically-bound species are innocuous, at least in terms of acute toxicity.[10,11,15]

In response to the aquatic toxicologist's need to quantify the biologically relevant fraction of Al accurately, chemists have devised a myriad of methods for such a purpose. The two most commonly used methods for the determination of monomeric Al species are 8-hydroxyquinoline (8-oxine) extraction[16–18] and reaction with pyrocatechol violet (PCV).[19–21] Methods espoused by one group of scientists have been criticized by another group. The 8-oxine and PCV methods are reported to measure the total monomeric Al in solution. This is comprised of both an organic and inorganic component.[22,23] The two fractions have been separated by cation exchange resins[17,22] and dialysis,[18,23] among other techniques.

Recently, organic and inorganic forms of Al have been selectively extracted at different pH levels by using the 8-oxine method.[18] Another novel approach to quantitating monomeric Al in aqueous systems has recently been developed in our laboratory. It involves the easily measured reaction kinetics of fluoride with Al.[24]

The ability of each measurement ligand (i.e., 8-oxine, PCV, or F) to complex organically bound Al depends on several factors including the strength and stability of the measurement ligand-Al complex, the concentration of the measurement ligand, and the pH at which the measurement ligand is reacted with Al.

The decomposition of dead organic matter releases a great number of water soluble low- and high-molecular-weight organic substances.[25] Humic substances comprise approximately 60 to 80 percent of the dissolved and particulate organic carbon in natural waters.[26] These substances are complex in nature, ranging in molecular weight from a few hundred to thousands of units. The substances with higher molecular weights are often referred to as humic and fulvic acids. These humic substances consist of subunits which are capable of binding Al (III).[27,28] The study presented here compares the effects of various organic ligands on the "apparent" monomeric Al concentration as determined by three analytical techniques: (1) 8-oxine/MIBK, (2) PCV, and (3) the aluminum fluoride complexation kinetic method (AFCK). The ligands examined may exist as individual entities, or they may exist as subunits of humic and fulvic acids in natural waters.[28-31]

MATERIALS AND METHODS

1. 8-oxine/MIBK Method

Reagents

Phenol red indicator—0.04% (w/v).

8-oxine solution (10 g/L)—8-hydroxyquinoline (99+purity) in 2.5% glacial acetic acid.

8-oxine/sodium acetate (HOx) reagent—30 mL 1.0 M sodium acetate (NaOAc), 150 mL deionized water, and 30 mL 8-oxine.

Buffer solution—2.5 M HCl added dropwise to 21 mL 5 M Ultrex ammonium hydroxide until pH = 8.3; an additional 32 mL of ammonium hydroxide is added, and the solution is diluted to 100 mL.

Methylisobutylketone (MIBK)—analytical grade.

Procedure

Three drops of phenol red indicator were added to a 25 mL aliquot of filtered (0.45 μM) sample, and this was followed by the addition of 5.0 mL of HOx reagent and of 2.0 mL buffer, in order. The mixture was swirled for 5 seconds. The addition of buffer adjusted the pH to 8.3 and turned the solution red. If a red color was not observed, the pH was adjusted rapidly by a dropwise addition of 1.0 M NH_4OH until a red color developed. Ten milliliters of MIBK were added, and the tube was capped and shaken vigorously by hand for precisely 10 seconds with a rapid end-to-end motion. The MIBK layer was transferred to a 10 mL centrifuge tube, and the tube was capped securely. A subsequent Al analyses were performed on a Perkin–Elmer 5000 AA equipped with a Zeeman 5000 graphite furnace.

2. PCV Method

Reagents

Carrier—type 1 water degassed through 0.45 μM filter under vacuum.

Mask—0.11 M hydroxylamine hydrochloride with 0.56 g 1,10-phenanthroline added per liter. Degassed under vacuum.

Buffer—6.0 M hexamethylenetetraamine. Degassed through a Whatman GC/F glass fiber filter under vacuum.

Cation Exchange Column—a glass column packed with Amberlite IR-120 in the 1% hydrogen form.

Procedure

Samples were analyzed for both total monomeric and organically-bound Al using a dual-channel flow injection analyzer (FIA). The sample was loaded into the first sample loop (100 μL). The sample then passed through a cation exchange column at 3.2 mL/min per mL of resin. Effluent from the column filled the second sample loop. Both loops were injected simultaneously by computer prompt. The contents of each loop were injected into the carrier stream and mixed with reagents in sequential order. The intensity of absorbance by the PCV-Al complex at 580 nm was directly proportional to the concentration of PCV-reactive monomeric Al.

3. AFCK Method

Reagents

pH adjustment solution—0.10 M HNO_3 (Instra grade).

Fluoride spiking solution—100 mg/L total fluoride (from NaF stock) with pH adjusted to 3.50.

Procedure

A 20 g aliquot of sample was acidified to pH 3.50. A 200 μL aliquot of fluoride spiking solution was added, and a stopwatch was concurrently started. Free fluoride levels were then recorded between 2 and 5 minutes by using a fluoride ion-selective electrode (calibrated versus 0.1, 1.0, and 10 mg/L standards at pH 3.50). The rate of consumption of fluoride through complexation with reactive Al was then related to the μg/L level by the equation:

$$K(F2/F5-1)/(5-2)=\mu g/L \text{ reactive Al} \qquad (1)$$

where F2 and F5 are fluoride levels at 2 and 5 minutes, respectively, and where K is a constant dependent upon temperature by the equation:

$$K=3.566\times 10^{-8}e^{7720.9/T}. \qquad (2)$$

Precise monitoring or control of the absolute temperature, T, ($\pm 0.1\,^{\circ}$K) was necessary while data were being collected.

4. Preparation of Synthetic Aluminum-Ligand Systems

Organic ligands at various Al:ligand ratios were evaluated in the present study. The chemical structure of the ligands appears in Figure 1. The sodium salts of citrate, salicylate, tartrate, oxalate, and humate (Aldrich) were used. A 50:50 mixture (w/w) of citric acid and sodium citrate was used. This avoided the low or high pH values which would occur if only the acid form or only the sodium form was used, respectively. Fulvic acid was prepared from freshwater sediments by using the methods outlined by Holtzclaw.[32] Additional ligands that were evaluated were malate, maleic acid, tannic acid, and gallic acid. The nominal molar ratios of Al to ligand were prepared in 500 mL volumes from 10 mM of stock ligand solution and from a fixed Al concentration of 100 μg/L. A 10 mg/L stock solution of Al was prepared from atomic absorption standards (Fisher) and was added to the ligand solution. The Al-ligand mixture was mixed for one hour prior to determination of monomeric Al concentration. Total monomeric Al concentrations were determined on each ligand solution in the absence of the Al spike for blank subtraction.

RESULTS

Straight-chain and cyclic carboxylic acids

CDTA (Figure 2a) and citrate (Figure 2b) caused the greatest decrease in apparent monomeric Al. CDTA caused nearly 100%

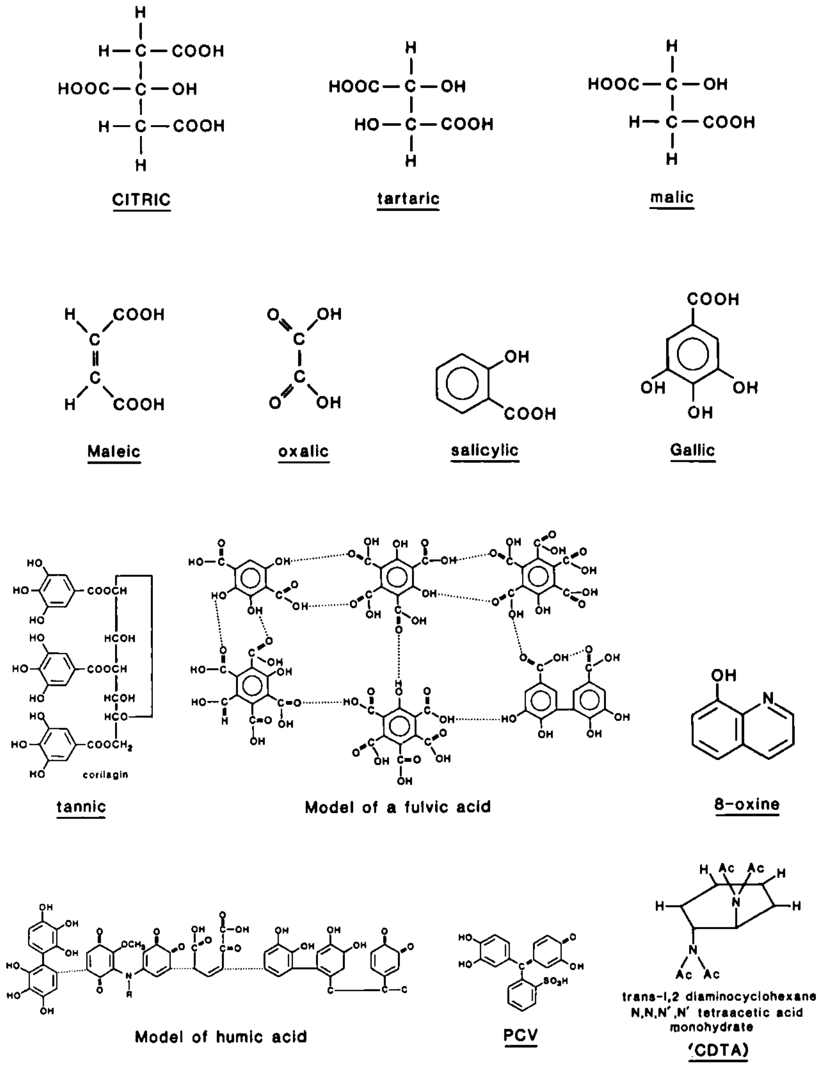
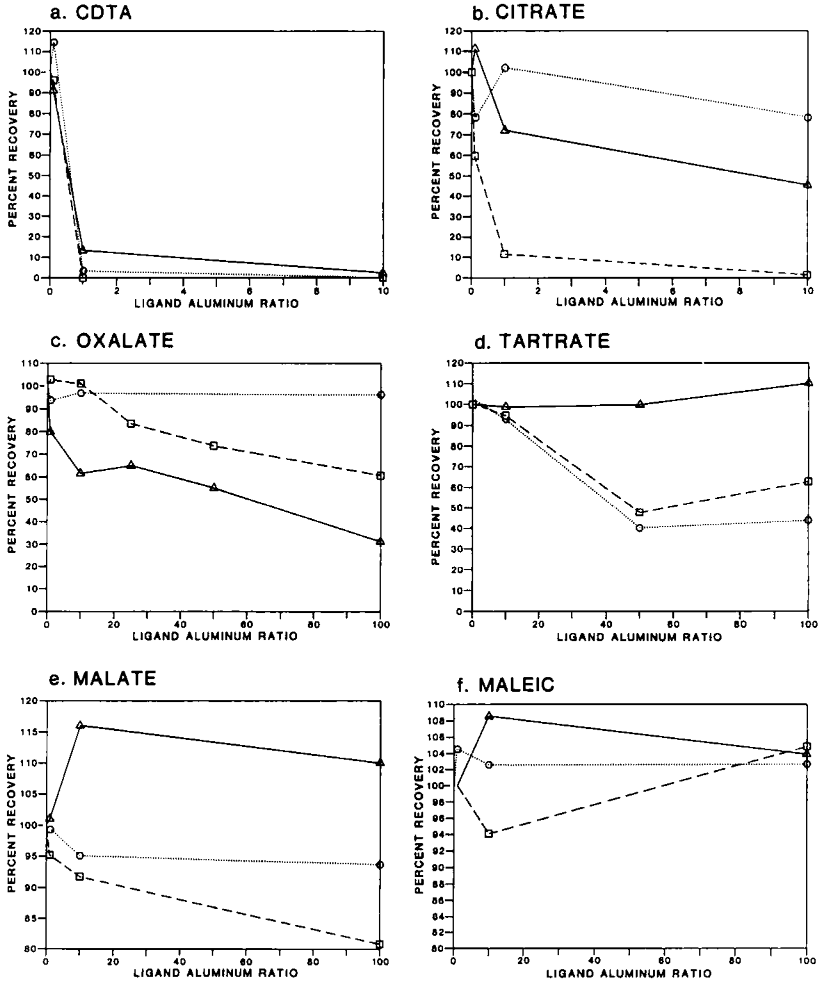


Figure 1 Structure of organic ligands evaluated in aluminum analytical method intercomparison study.

reduction in the recovery of Al by PCV, 8-oxine, and AFCK at an AL:ligand ratio of 1:1. Complete suppression of apparent monomeric Al was observed at 1:10 Al:L ratios. Citrate caused similar yet less profound effects in measurable Al concentrations. Citrate proved



a. CDTA

b. CITRATE

c. OXALATE

d. TARTRATE

e. MALATE

f. MALEIC

Figure 2 Effects of straight-chain and cyclic carboxylic acids on the percent recovery of total monomeric aluminum by three analytical methods; □ = PCV, 0 = 8-oxine, △ = AFCK.

to compete more effectively with PCV for Al binding than with the other two measurement ligands, with nearly 100% reduction in apparent Al concentrations at an Al:L ratio of 1:10. Complete suppression of Al recovery by the 8-oxine extraction procedure was not observed until 1:100.

Oxalate did not significantly reduce apparent Al concentrations in the 8-oxine determination. However, this particular dicarboxylic acid was a significant chelator of Al in the PCV and AFCK systems (Figure 2c). A 20-percent reduction in AFCK-measurable Al was observed at an Al:L ratio of 1:1, with a further 60-percent reduction at 1:100. The effect of oxalate in the PCV system was also significant. Suppression was not detected until a ratio of 1:25 was reached (83.4%). A decrease to approximately 60% of the total monomeric Al at a ratio of 1:100 was observed.

Tartrate and malate are very similar in structure (Figure 1). Neither ligand affected the determination of monomeric Al by the AFCK method. Tartrate, however, caused a significant reduction in apparent monomeric Al concentrations as determined by PCV and 8-oxine (Figure 2d). These reductions were not observed until very low Al:L ratios were attained. Malate caused a slight reduction in 8-oxine and PCV measurement of monomeric Al (Figure 2e). However, these reductions were not greater than the analytical error associated with each method, even at 1:100 Al:L ratios. Maleic acid caused no decrease in apparent monomeric Al concentrations.

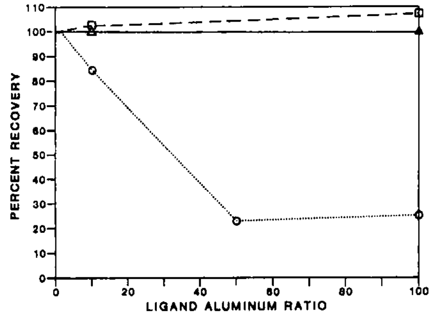
Aromatic carboxylic acids

Salicylate and gallate had an effect on only the 8-oxine determination of monomeric Al. Gallate caused a slightly greater decrease in measurable Al than salicylate. At an Al:gallate ratio of 1:10, only 75 percent recovery of Al was observed (Figure 3b), while 85% recovery was noted for the Al:salicylate system at the same ratio (Figure 3a). At a ratio of 1:100, both ligands caused a significant reduction in apparent monomeric Al concentrations (~25%).

Complex organic acids

Fulvic acid exhibited very little effect on the apparent monomeric Al concentration determined by the three methods (Figure 4a). The changes in Al concentration were within the analytical error of the respective methods. In contrast tannic acid caused a significant decrease in measurable Al at increased ligand:metal ratios in the PCV and 8-oxine methods, but had no effect on the AFCK method

a. SALICYLATE



b. GALLATE

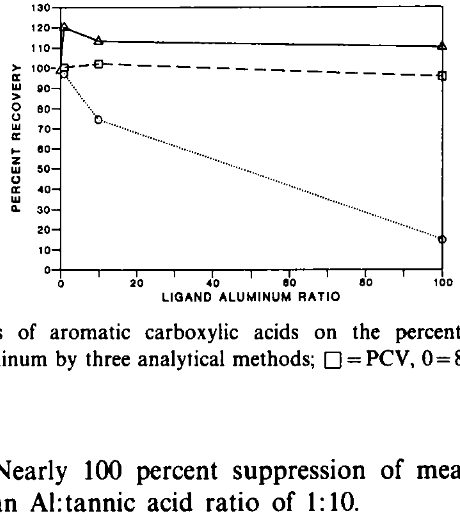


Figure 3 Effects of aromatic carboxylic acids on the percent recovery of total monomeric aluminum by three analytical methods; □ = PCV, 0 = 8-oxine, △ = AFCK.

(Figure 4b). Nearly 100 percent suppression of measurable Al was observed at an Al:tannic acid ratio of 1:10.

Humic acid was difficult to evaluate because of very high Al contamination levels. Approximately 500 μg of Al/g humic acid (dry weight basis) were detected in the starting material as determined by atomic absorption spectrometry. For ratios up to 1:10, blanks were subtracted from the observed percent recoveries. Above an Al:humic ratio of 0:10 for blanks, background concentrations of Al were too great, i.e., out of the linear range of the method. Results indicated that humic acid had a negative interference on the determination of Al by the AFCK method (Figure 4c). For the PCV and 8-oxine methods, humic acid caused only minor reductions in percent recovery.

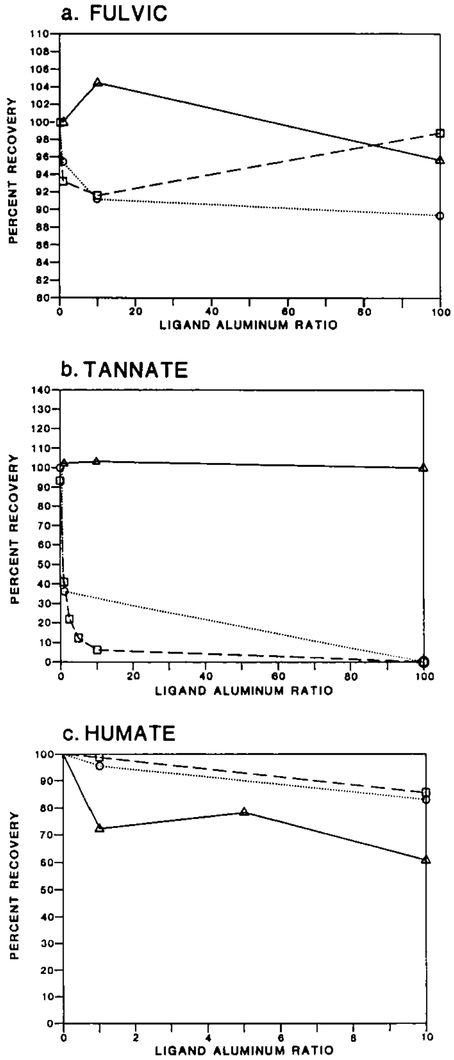


Figure 4 Effects of complex organic acids on the percent recovery of total monomeric aluminum by three analytical methods; □ = PCV, 0 = 8-oxine, △ = AFCK.

Fluoride, PCV, and 8-oxine

The tendency of each measurement ligand to suppress the apparent monomeric Al concentration determined by the other measurement ligands was assessed. This procedure provided a crude estimate of the relative binding strengths of each measurement ligand under the operating conditions of another method. Fluoride caused no reduction in the amount of Al determined by either the PCV or 8-oxine method (Figure 5a). Neither PCV nor 8-oxine affected the AFCK determination of Al. However, PCV and 8-oxine exhibited reciprocity in the reduction of apparent monomeric Al, with each measurement ligand causing decreases in the other method (Figures 5b and 5c). A continuous decrease in percent recovery of monomeric Al by the 8-oxine method was observed at increasing Al:PCV ratios. For the PCV method, 8-oxine caused an initial reduction (~20%) in percent recovery at ratios from 1:1 to 1:50. At 1:100 a substantial decrease occurred with nearly 100 percent suppression of the apparent monomeric Al concentration.

DISCUSSION

Each of three methods examined in the present study reportedly measures "total monomeric" aluminum. However, the results indicate that in the presence of certain naturally occurring organic ligands, the "apparent" total monomeric Al concentration can be drastically underestimated. This could have serious implications for geochemists involved with modeling Al behavior in surface waters. On the other hand, this may not hinder aquatic toxicologists investigating Al toxicity, since a particular method may give values more representative of biologically active Al.

Obviously, the strength of the Al-ligand complex will have a profound effect on the ability of a given analytical method to measure total monomeric Al accurately. The strength of the complex is largely dictated by the conformation and steric factors of the ligand. To establish precise chemical mechanisms for the observed effects of various organic ligands on the apparent Al concentration is beyond the scope of this study. However, some general trends can be discerned from the data.

Motekaitis and Martell[33] and Snitzer[34] found that the proximity of

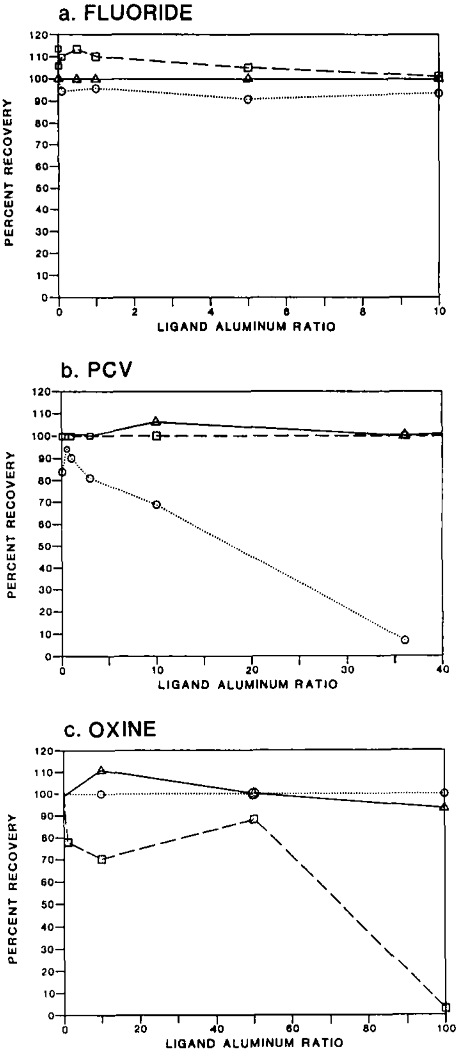


Figure 5 Effects of each measurement ligand on the percent recovery of total monomeric aluminum by three analytical methods; □ = PCV, 0 = 8-oxine, △ = AFCK.

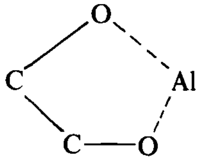
OH and COOH groups in organic acids largely dictates their Al^{3+}-complexing capacity. Hue *et al.*[35] found that organic ligands with structural configurations having two pairs of OH or COOH attached to two adjacent carbon atoms (e.g., citrate and tartrate) or having two COOH groups on the same carbon atom (e.g., oxalate) formed strong complexes with Al^{3+}. The strength of the complex was surmised by the reduction in aluminum toxicity to plant roots. Citrate caused a significant decrease in apparent monomeric Al concentration for the three methods and thereby provided additional evidence of the stability of the Al/citrate complex. Tartrate affected only the two methods that operate at high pH levels. The effects of the pH at which each method operates will be discussed below.

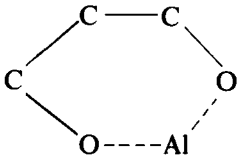
CDTA has replaced EDTA in the TISAB buffer used for total fluoride determinations because of its ability to strongly complex Al. This fact is well demonstrated by the significant suppression of measurable Al caused by CDTA in all three methods.

Weaker chelators, as manifested in increased aluminum phytotoxicity, were ligands having an OH and COOH attached to the adjacent carbon atoms (e.g., malate and salicylate) or having two COOH groups on the same carbon atom (malonic).[35] Apparent monomeric Al concentrations were not affected by the presence of malate or salicylate in any of three methods examined. Ohman and Sjoberg[36] noted the relatively weak complex formed between Al and salicylate. Salicylate has been used as a model ligand for fulvic acid.[23,37] It appears to serve as a valid model since fulvic acid did not reduce apparent Al concentrations in the present study.

Gallic acid has been described as a degradation product of lignin and humic substances.[38] Gallic acid has ortho-diphenolic groups that form a much stronger complex with Al than the ortho-OH/COOH configuration of salicyclic acid.[30,36] Gallate caused a significant decrease in apparent Al concentration as determined by the 8-oxine method only. Ohman and Sjoberg[30] found that 30 μM of gallic acid increased the solubility of kaolinite by an average factor of 5 in the pH range 5–9. If these conditions occurred in a natural sample, total monomeric Al concentrations would be severely underestimated by the 8-oxine method, while the PCV and fluoride methods would not be affected. Tannic acid consists of several subunits of gallic acid. Tannic acid drastically reduced apparent monomeric Al concentrations in both the 8-oxine and PCV methods. The lack of reduction in PCV-determined Al in the presence of gallate and significant reduction in the presence of tannic acid may be due to the greater number of potential Al^{3+} binding sites in tannic acid (i.e., ortho-diphenolic groups).

In general, the relative positions of the OH/COOH or OH/OH groups that complex Al to the greatest extent display configurations that favor the formation of stable 5- and 6-bond ring structures:





In addition to the configuration of the organic ligand, several factors inherent in each method appear to control the amount of monomeric Al observed. The concentration of the measurement ligand in relation to that of the competing organic ligand will undoubtedly affect recovery of Al^{3+}. To illustrate this point, the ability of 8-oxine to measure monomeric Al in the presence of fulvic acid (FA) can be examined. Lalande and Hendershot[18] observed 67 percent recovery of Al at a Al:FA ratio of 1:4. LaZerte[23] used salicylic acid as a model ligand for fulvic acid. He observed 98 to 101 percent recovery at a wide range of Al:salicylic acid ratios. Similarly, we observed 90 to 100 percent recovery at Al:FA ratios up to 1:100. When examining the concentration of 8-oxine used in each case, it is seen that Lalande and Hendershot[18] used 0.32 g 8-oxine/L of sample while LaZerte[23] and we used much higher concentrations, i.e., 1.25 and 1.67 g 8-oxine/L of sample, respectively. Higher concentrations of 8-oxine would tend to shift the equilibrium from FA-bound to 8-oxine-bound Al.

Similar concentration-dependent recovery of organically bound Al can be observed in the PCV system. Royset[21] observed "interference" in the recovery of Al in the presence of FA only at low molarity (1 mM) concentrations of PCV. Even at low PCV levels, Royset did not observe a reduction in apparent Al concentration until FA exceeded 40 mg C/L. We also used 1 mM PCV and observed no significant reduction in apparent monomeric Al up to 1:100 Al:FA ratios.

Another important factor which will influence the ability of an analytical method to measure monomeric Al accurately in the presence of various organic ligands in pH. Conditional stability constants for various organo-aluminum complexes are highly dependent upon pH.[27,33] The less drastic effect of citrate on the recovery of Al by 8-oxine may be pH dependent. Motekaitis and Martell[33] report that at pH levels above 9.0, no citrate remains coordinated with Al^{3+}, since $Al(OH)_4^-$ becomes the thermodynamically preferred species. They also found that above neutral pH, citrate would be totally released and that Al^{3+} would distribute itself between $Al(OH)_3^0$ and $Al(OH)_4^-$, with the occurrence of one or the other of these species being dependent upon the alkalinity. The 8-oxine system operates at pH 8:3, a pH at which the Al:citrate complex is unstable.[33] Citrate, nevertheless, caused a significant reduction in 8-oxine-determined Al, but it was not as profound as the reduction in the PCV and fluoride systems. Ares[39] also noted a decrease in fluoride-reactive Al in the presence of citrate. Motekaitis and Martell[33] reported the increased stability of Al/tartrate complexes with increasing pH. Their findings are supported by the results of the present study where increasing concentrations of tartrate reduced the apparent monomeric Al concentrations in the two methods operated at high pH levels (i.e., PCV and 8-oxine) but not in the low pH method (AFCK).

In a similar study Royset and Sullivan[40] showed that "interferences" from humic and fulvic acid decreased at elevated pH levels for the 8-oxine and the eriochrome cyanine R/CTA methods. These results are in agreement with the present study which showed less interference from humic and fulvic acid for the 8-oxine and PCV methods which operate at higher pH levels, 8.3 and 6.1, respectively. They postulated that the anionic $Al(OH)_4^-$ complex formed at higher pH levels has a lower affinity for the anionic humic compounds than does the cationic forms of Al. At higher pH levels, bound Al may still undergo hydrolysis reactions at open coordination sites on the atom. A similar mechanism may account for the greater interference of oxalate on the AFCK method and increasingly less interference from this ligand on the methods which operate at a higher pH.

The above observations bring another factor into focus, the kinetics of the system. Ohman and Sjoberg[31] found that equilibrium was reached quickly (seconds) in the Al:citrate system at low pH levels but very "sluggishly" at high pH levels (for up to 6 hours). Similarly, James *et al.*[41] observed that the slopes of 8-oxine-measured Al versus time decreased linearly with increasing pH. That is, the reaction rate of Al with 8-oxine decreased with increasing pH.

The complex is thermodynamically unstable at higher pH values because of the competition from OH^-, but the kinetics of the dissociation are slower. The PCV system operates at an optimum pH of 6.1, which would weaken the Al:citrate complex. This factor, in conjunction with the large stability constant for the Al:PCV complex ($B_3 = \sim 60$), would seem to favor the formation of this complex. However, citrate had a profound effect on PCV-determined Al values at Al:citrate ratios as low as 1:0.5. Royset[21] observed the same effect of citrate on PCV-measurable Al in a flow injection analysis system. Despite the favorable conditions for the formation of the Al/PCV complex, the kinetics of the flow injection analysis system may be much faster than the dissociation of the Al:citrate complex at higher pH levels. The pH of the PCV system is not raised to 6.1 until the last mixing coil; the bolus then flows into the colorimeter within two seconds. In the 8-oxine system run at pH 8.3, a 10-second reaction time is used. This extended reaction time may account for the greater recovery of Al in the 8-oxine method than that obtained in the PCV system. Thus, an analytical method that operates at high pH levels would require longer reaction times in order to recover most of the total monomeric Al in a sample containing organic ligands similar to citrate.

In the case of the fluoride method, which operates at low pH (3.5), the Al:citrate complex is more thermodynamically stable.[33] Fluoride ions cannot completely displace the citrate from the aluminum. As noted previously, Ares[39] observed a similar inability of fluoride to complex Al in the presence of citrate.

The present study was performed using synthetic solutions with known organic ligands present. Other studies have noted the effects of organic ligands (DOC) on the concentration of monomeric Al. May *et al.*[42] found that the concentration of 8-oxine-extractable Al was 1.3 times greater than the solubility of Al in equilibrium with gibbsite in Yellow River samples at pH 7.7. In Sherwood Lake water (pH 6.0), 40 times more Al was measured than would be expected, assuming equilbrium with gibbsite. Both waters were high in DOC. The higher pH of Yellow River (pH 7.7) water may have rendered some of the organically-bound Al non-extractable. Furthermore, the nature of the organics may have been different in each surface water, and that difference may be the cause for less Al recovery from the Yellow River sample. The type of ligand present was shown to affect greatly the determination of apparent monomeric Al in the present study. In stark contrast, Driscoll *et al.*[6] observed a negative correlation between Al solubility and DOC levels. This observed phenomenon may be due to a decrease in apparent monomeric Al concentrations at higher DOC levels because the 8-oxine can not efficiently compete with the naturally occurring ligands for Al binding.

CONCLUSIONS

If organically-bound or fluoride-complexed Al^{3+} is not accurately measured by a particular analytical method, then Al equilibria in dilute acidified waters may be seriously misinterpreted. The present study has shown that the nature of the organic ligands present in a particular sample will significantly affect the apparent monomeric Al concentration determined by three different methods. Not only is the configuration of the ligand, and hence the stability of the Al complex important, but also factors inherent in each method are significant. These factors include (1) the pH at which the method operates: (2) the concentration of the measurement ligand (i.e., PCV, 8-oxine, F) relative to the Al:ligand ratio; and (3) the kinetics of the measurement reaction relative to the dissociation kinetics of the Al/ligand complex. It may be entirely possible that one method may not adequately control all of the above factors. Thus, total monomeric Al may be underestimated. The effects of such an underestimation must be considered by the individual data user, e.g., by the geochemist or the toxicologist. Additional research is needed in fine-tuning existing Al speciation methods or in devising new and innovative approaches to solving this problem.

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Notice

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