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INVESTIGATION OF THE REACTIONS OF AQUATIC ALUMINUM THROUGH FLUOROMETRY USING LUMOGALLION

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by

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Investigation of the Reactions of Aquatic Aluminum Through Fluorometry using Lumogallion

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ABSTRACT

A fluorometric method using lumogallion has been shown to be adequate to measure the degree and and rate of complexation of aluminum at low concentrations, $(1.85 \times 10^{-6} \text{ M})$, by other ligands such as fluoride and citrate, at a pH of 5.2.

The species $H_2PO_4^-$, H_4SiO_4 and SO_4^{2-} do not compete with lumogallion for aluminum at this pH for concentration ratios of less than 100, (competing ion: lumogallion).

A rate law for the destruction of the lumogallion complex by fluoride ion has been determined as

$$-r = -\frac{dC_A}{dt} = \frac{(4.3 \times 10^3) [F^{-}]^{1.8} C_A}{1 - (1.0 \times 10^3) [F^{-}]^{-0.7} C_A}$$

where C_A is the corrected concentration of the fluorescent complex at any time.

This method is proposed to measure aluminum complexes in natural waters.

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LIST OF SYMBOLS:

- t: time after the addition of standard fluoride solution to the digested aluminum- lumogallion solution
- h: the peak height of fluorescence measurement of aluminum-lumogallion complex
- h_o : the peak height of the reference standard (Al)_T = 1.85x10⁻⁶ M ; (lumo.)_T = 5.63x10⁻⁶ M.
- h_{eq}: the peak height resulting from the digestion of a standard aluminum-lumogallion-fuoride solution.

(Taken to represent the equilibrium concentration).

$$C_{AO} = 1.85 \times 10^{-6} (1 - h_{eq}/h_{o})$$
: The corrected, initial concentration of the aluminum-lumogallion complex.

 $C_A = 1.85 \times 10^{-6} (h/h_o - h_{eq}/h_o)$: The concentration of

the aluminum-lumogallion complex at any time,(corrected).
k₁: first overall rate constant;

$$k_1 = t^{-1} (ln(C_{A0}/C_A) + k_2(C_{A0} - C_A))$$

k₂: second overall rate constant;

$$k_2 = \frac{k_1 t}{C_{AO} - C_A} - \frac{\ln(C_{AO} / C_A)}{C_{AO} - C_A}$$

A: intercept; $A = -k_2$ B: slope; $B = k_1 / (C_{AO} - C_A)$ $X = t / (C_{AO} - C_A)$ $Y = ln(C_{AO} / C_A) / (C_{AO} - C_A)$

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INTRODUCTION

1.0 Among the many component fields of geochemistry is the study of the movements, reactions and speciation of chemical elements in nature. One goal of such investigations is the modelling of a system in terms of a geochemical cycle for a given element. That is, one would like to be able to predict and rationalize changes in the concentration and speciation of an element in a given system, as a result of changes in the boundary conditions of the system.

In the case of aluminum in aquatic systems, progress in this area is slow because of the chemical and kinetic inertness of many of its compounds, such as clays, hydroxides and oxides. At pH's between 4 and 10, in the absence of strong complexing chelates, aluminum is very insoluble. The solubility product of gibbsite, (Al(OH),), for example is on the order of 10^{-30} . This helps to explain the low concentrations found in natural waters. Sackett and Arrhenius determined soluble aluminum in ocean water to be in the range 1 to 2 ppb, (1962). Barns (1975) found that the concentrations of monomeric aluminum in thermal springs and oil wells to be in the range 0 to 57 ppb. Unpublished data from this lab indicate conentration of reactive aluminum in acid lakes to be in the range 50 to 300 ppb, while in lakes of pH ca.8 it is on the order of 1 ppb.

Evidence of kinetic inertness is given in a report by Smith and Hem, (1972), for example, who found that precipitated aluminum hydroxide gels may not crystallize and achieve chemical equilibrium for years. 2

In order to predict the concentration of soluble aluminum in some given system, one would like to know 1. which species of aluminum determine. the concentration of aluminum under certain conditions; 2. the equilibria relations of the relevant species; 3. the rate at which the system will achieve equilibrium after a change in the system. A brief review of what has been learned will be given in the next2sections followed by the purpose of this report in the next.

1.1 A SUMMARY REVIEW

The most widespread and by mass, the most important aluminum species in the aquatic environment are the clays, (kaolin, montmorillonite, illite, vermiculite), the chlorites, and the hydroxides, (gibbsite, boehmite, and diaspore). Compilations of thermodynamic data have been prepared, (Robie et al. 1979). Some authors have also published solubility graphs. Roberson and Hem (1968) for example, have published calculated graphs relating to the solubility of gibbsite and cryolite (Na₃AlF₆), in the presence of varying concentrations of fluoride, sulfate and hydroxide, at varying ionic strengths. More specialized studies are to be found only in the journal literature. Turner (1975) has published a formation equilibrium constant for aqueous $Al_2(OH)_2^{+4}$; pK = 6.95 +/- 0.05 at near zero ionic strength. The concentrations of this species were determined for his experiments by a method based on its rate of reaction with 8-hydroxyquinoline, (Turner, 1969). Chen (1973) determined the solubility-products of three-month aged aluminum hydroxide gel in various ionic media. The pK_{sp} 's from extrapolation to zero ionic strength, ranged from 30.36 to 33.15, depending on the 'inert' ion present, $(NH_{\mu}^{+}, Li^{+}, Na^{+}, K^{+}, or Ca^{2+})$. 3

However Paces (1978), has found that based on his own calculations of disequilibrium indices for 112 natural and experimental waters, the solutions are undersaturated with amorphous aluminum hydroxide, microcrystalline gibbsite, amorphous silica, and amorphous aluminuosilicate, and supersaturated with gibbsite and kaolinite. Paces proposed that a reversible, metastable aluminosilicate exists in such solutions which directly controls the aluminum concentration. Such conclusions have been reached by other researchers as well, and have stimulated a search for other aluminum species, in addition to those soluble and crystalline species already known to exist.

In the years 1954 to 1956, L.G. Sillen presented a series of papers in which he derived a series of mathematical methods for interpreting hydrolysis titration data and obtaining best-fit stoichiometries of hydroxide polymers. By similar methods, Brosset et al. (1954). determined the stoichiometry of a hydrolysis product as $Al_6(0H)_{15}^{3+}$. Such structures are of course tentative. But in 1960, Johansson determined the crystal structure of a basic aluminum sulphate, which he prepared in the lab. He found the structure to contain the ion $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$. It was also his conclusion that this ion persists in solution. In 1962 he identified another ion in a crystal structure of a basic aluminum sulfate: Al₂(OH)₂(H₂O)₈⁴⁺. Such studies are not irrelevant in the study of natural aluminum speciation. Alunite, ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) for example is commonly found in weathering pyritiferous, aluminous rocks, as well as in areas of hydrothermal activity.

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More empirical approaches are still being used, however. Hall (1965) has distinguished fresh and aged aluminum hydroxide gels on their capacity to flocculate particles from suspension. In a more recent study Turner, (1976), found that fresh and aged Al-hydroxides could be distinguished on the basis of their rates of reaction with 8-hydroxyquinoline. The aged species reacted 250 times more slowly than the fresh species.

In 1973, Hem et al. released a report on the interaction of aqueous aluminum (at 10^{-5} to 10^{-2} M), with dissolved silica at pH's from 4 to 10 at 25 C. Consistent solubilities of an amorphous colloidal product were obtained after as little as a few months aging. Their calculated free energy of formation was given as -897 +/- 1.0 kcal/mole for the formula $Al_2Si_2O_5(OH)_4$. No X-ray pattern was detected after 4 years aging.

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Operational definitions of various forms have been developed not only in synthetic studies, but also in analytical studies of natural samples. Sackett and Arrhenius (1961) defined three forms of aluminum occuring in ocean water: 1. Al passing through a 0.45 µm filter and reacting directly with the color-reagent, Pontachrome Blue-Black R; 2. Al passing through 0.45 µm filter but only reacting with color-reagent after fuming with sulfuric acid; 3. Al not passing through 0.45 µm filter and reacting with the color-reagent after sodium carbonate fusion,

In 1975 Barns determined that filtration did not adequately distinguish mineral aluminum from soluble aluminum. A method was thus developed in which the reactive forms are complexed with 8-hydroxyquinoline and quickly extracted into MIBK, (methyl-isobutyl-ketone).

A similar extraction method has been used by Turner and his coworkers in synthetic and kinetic investigations, (1969,1975,1976). Extractability of the aluminum from water into toluene with 8-hydroxyquinoline at pH 5, formed the basis of selection between various forms of aluminum in an investigation by May et al.(1979).

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The form of aluminum that occurs on mineral and other surfaces is also relevant in this context. Brown and Hem (1975) prepared a report on the study of adsorption of aqueous aluminum (4.5 x10⁻⁴ M'in 0.01 M NaClO₄ and with an OH:Al ratio from 1,40 to 2.76), onto an assortment of mineral surfaces. Adsorption of monomeric forms was essentially complete after one hour. Polymeric forms also were quickly adsorbed, according to the Langmiur isotherm. In the absence of mineral surfaces, microcrystalline gibbsite, as an aged product, was identified by electronmicroscopy. In 1978, Spolijaric and Crawford determined from adsorption studies of ions onto glauconite that aluminum was retained on glauconite surfaces at low pH's (2-3), and released at high pH'stal (9-10).

In the past decade a new tool for determining the structure of aluminum species in more concentrated solutions has been developed.

In 1971, Akitt et al used ²⁷Al and ³¹P nmr to identify complexes in aqueous phosphoric acid solutions at temperatures from 0 to -50°C. Their interpretation indicated the following possible species: $Al, H_3P0_4^{3^+}$, $Al, H_2P0_4^{2^+}$, $Al, (H_2P0_4)_2^+$, unspecified binuclear complexes, and phosphoric polymers of the type $Al(H_3P0_4)_n$, $n \ge 2$. Addition of F⁻ and the use of ¹⁹F nuclear magnetic resonance, revealed the presence of the known $AlF_n^{(3-n)+}$ species, plus eight fluoro-phosphato-aluminum complexes.

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In a ²⁷Al nmr and ¹H nmr study of the hydrolysis and polymerization of $Al(H_20)_6^{3+}$, Akitt et al (1972) identified and measured the concentrations of several species: $Al(H_20)_6^{3+}$, $Al_2(0H)_2(H_20)_8^{4+}$, $Al_{13}0_4(0H)_{24}(H_20)_{12}^{7+}$, and possibly $Al_8(0H)_{20}(H_20)_x^{4+}$. The sum of these species did not equal the total aluminum in solution, indicating the presence of other species. (Solutions were 0.75 M in aluminum.)

In 1972 Akitt and Greenwood, using ²⁷Al nmr on aqueous aluminum sulphate solutions , found a supphato-aluminum complex and a small amount of dimeric aluminum cation. (Solutions were 0.15 to 1.5 M in aluminum).

In a 27 Al nmr study of Al ions in mixtures of water and trimethylphosphate, Canet et al (1973) identified several species including Al(H₂0)₆³⁺, Al(H₂0)₅(TMPA)³⁺, Al(H₂0)₄(TMPA)₂³⁺ (trans isomer). They found the optimum temperature of measurement to be 40 C.

Measurements of proton chemical shifts of aqueous aluminum salt solutions reveal exchange between three ionic environments and bulk water: " the cationic hydration complex $Al(H_20)_6^{3^+}, \ldots$ its second hydration sphere, and a broken water structure around the anion..." (Akitt, 1973) The primary hydration number was shown to be six. Hydrolysis and acid addition were shown to have a marked effect on the chemical shifts. 8

Toy et al (1973) found that in ²⁷Al nmr measurements of Al-hydroxycarboxylic acid complexes the signal intensity was dependent on pH. Signal broadening was interpreted as indicating polymerization of the Al-chelates.

Admittedly, nuclear magnetic resonance studies require the test solutions to be fairly concentrated. Under such conditions polymer formation is encouraged. For that reason species detected in such studies may not be representative of speciation in dilute solutions. However, since the selection of possible species to explain dilute-solution studies is often rather artificial and arbitrary, species detected by nmr in concentrated solutions constitute a more probable selection group.

Finally, mention should be made of some of the kinetic studies that have appeared in the literature recently. In 1972, Smith and Hem prepared a report on the aging of hydrolysis species of aluminum. Three classes of products were defined according to their rates of reaction with ferron (7-iodo-8-hydroxyquinoline--5-sulfonic acid): monomeric, soluble polymeric and "relatively large, microcrystalline, clearly solid Al(OH)₃ particles."

In 1975 Lind and Hem released a study on the effects of organics on the polymerization and precipitation of aluminum hydroxides. Quercitin, (a flavone) was found to form a complex with aluminum that inhibited the polymerization and formation of gibbsite at concentrations as low as $10^{-5\cdot3}$ M. In the presence of dissolved silica and aluminum, quercitin was found to improve the yield and crystallinity of kaolinite and halloysite. These products were determined by electron-microscopy; no X-ray pattern could be obtained.

1.2 ANALYTICAL METHODS FOR ALUMINUM

A review of colorimetric and fluorometric methods for the detection of aluminum in use prior to 1959, is given by Sandell.

In 1961, Sackett and Arrhenius used a fluorimetric method involving Pontachrome Blue Black R, at pH 5.0 and measurement at 640 nm, for the detection of ppb concentrations of aluminum in sea water. Error was given as $\pm/-$ 0.2 ppb at 1.8 ppb.

In 1974, Dougan and Wilson described a colorimetric method involving Catechol Violet at pH of 6.0 to 6.2, for the measurement of aluminum in the range 50 to 300 ppb in potable waters. Iron interferances were removed by the addition of hydroxylamine-hydrochloride.

Barns introduced an extraction method in 1975. Immediately upon the collection of oil-well water or thermal spring water, the aluminum was complexed with 8-hydroxyquinoline at pH 8.3 and extracted into MIBK. The MIBK solution could then be transported back to the lab , where analysis was done by atomic absorption. Error in the concentration range 2.5 to 50 ppb was estimated at +/- 1 ppb. F- did not interfere at pH 8.3. 10

Also in 1975, Gosink reported the development of a method based on gas chromatography. Aluminum in water samples was complexed with trifluoroacetylacetone at pH 5.5 and extracted into benzene. Detection was with a tritium source electron capture detector. A sample known to contain 32.8 ppb aluminum was found to contain 33.9 ppb +/- 0.9 ppb ; a sample containing 3.28 ppb was found to contain 2.7 ppb +/- 1.9 ppb

aluminum.

A fluorometric method using lumogallion was published by Hydes and Liss (1976) for the measurement of ppb concentrations of aluminum in fresh and sea waters. The natural sample is analysed by standard addition, by digesting the complexed samples in a water bath at 80°C for 1.5 hrs and measuring the fluorescence at 555nm. Error at the 1 ppb level was given as \pm 0.05 ppb. Major interferences of F⁻, Fe and organics were found in the absence of the standard addition analysis.

Caschetto and Wollast (1978) applied the lumogallion method in the analysis of marine sediment interstitial waters. Their error of analysis was given as +/- 0.08 ppb at 2.1 ppb.

In 1979, May et al used an extraction method similar to that of Turner at al (1971,1969), to distinguish forms of aluminum of varying kinetic lability. The sample

would be complexed with 8-hydroxyquinoline for a certain period of time at either a pH of 5.0 or 8.3, (depending on whether the major interfering ion was OH⁻ or F⁻), and then rapidly extracted into toluene. Detection would be done by spectrophotometry. Error was given as +/- 10% at 1.0 ppb. Interferences from other metal ions could be removed by a preliminary extraction of the samples with a chloroform solution of diethyldithiocarbamate.

Note that all the methods described above measure some form of reactive aluminum. Total aluminum can be measured by atomic absorption, using a graphite furnace. Preliminary studies indicate that the use of temperature programming of the graphite furnace can lead to reproducible results for samples up to 150ppb aluminum for a sample size of 50 ul. (Work done in this lab).

1.3 THE PURPOSE OF EXPERIMENTS DONE IN THIS STUDY

In this study it was deemed useful to evaluate one of the methods of aluminum analysis in terms of its potential for deriving useful thermodynamic and kinetic data on the reactions of aqueous aluminum. The fluorescencespectroscopy method of Hydes and Liss (1976) was chosen because it was already being used in this lab for routine aluminum analysis. Any information derived from this investigation could then be directly used to modify the method already in use. Also, the instruments had already been calibrated and tested in routine work, which meant that more time could be spent collecting data more directly related to this study.

1.4 BASIC PRINCIPLES AND INFORMATION

The principle of the fluorescence method is that aluminum in solution, when reacted with excess lumogallion (see figure 1), will fluoresce in ultraviolet light in proportion to the concentration of the fluorescent complex present. The quantity of complex formed depends not only on the concentration of aluminum present, however. Ligands that complex aluminum will compete with the lumogallion for aluminum. This provides a basis for measuring the strength of complexation of aluminum with various ligands, with respect to the aluminum-lumogallion complex. This in turn can lead to

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a better understanding of the speciation of aluminum in natural water systems. By measuring the decrease in the fluorescence of a standard aluminum solution with increasing concentration of competing ligand, the concentrations of the competing aluminum complex can be calculated, and conditional stability constants derived. For the purposes of this set of experiments, the stoichiometries had to be assumed and tested after the data had been collected and analysed.

Figure.1. The Structure of Lumogallion 2(2,4 dihydroxyphenylazo)-4-chlorophenol--6-sulfonic acid



By adding the competing ligand after the aluminum standard has been digested with lumogallion, the decrease in fluorescence can be measured as a function of time. From such data rate constants can be determined.

By measuring the dependence of the rate constants on the concentrations of the other species in the reaction, (such as OH⁻, lumogallion, aluminum), a rate law can be written, which expresses the rate of reaction as a function of the rate constant, k, and the concentrations of the reacting species. A possible rate law may look like this

$$r = \frac{dC}{dt} = k(C)^{c}(D)^{d}(E)^{e} \cdots$$
 (1)

where r is the rate change in concentration of one of the components in the reaction, C,D,E are concentrations of reactants (or products) that affect r, and c,d,e are empirical exponents of the concentration terms C,D,E respectively.

Commonly the temperature dependence of the rate constants is also measured, and is expressed in the form of the Arrhenius Equation:

$$k=Ae^{-E/RT}$$
 (2)

where A is an empirical constant, E is the "activation energy", R is the gas constant and T is the absolute temperature.

Factors which are expected to be important in the lumogallion experiment are the concentrations of total aluminum, total lumogallion, total competing ligand, hydrogen ion, ionic strength and temperature. Also important in this experiment is the stoichiometry of the various complexes in the reaction.

The ultimate aim is to develop a reaction mechanism that is consistent with the kinetic data,

and which attempts to rationalize the chemical processes involved during the reaction.

2.0 EXPERIMENTAL

The fluorometric method used is based on that developed by Hydes and Liss (1976), for the measurement of low concentrations of dissolved aluminum in natural waters. These authors provide absorption spectra for lumogallion and the aluminum-lumogallion complex. They found that maximum fluorescence was developed after 1.5 hours heating in a water bath at 80 C. They also found that the fluorescence decreased with the temperature of the sample during measurement, at the rate of about 1%/ C. Under the specified experimental conditions their calibration curve was linear up to 120 ppb Al and the standard deviation of ten replicate samples of 1.0 ppb Al was 0.05 ppb.

2.1 APPARATUS

In this investigation, a G.K. Turner Associates Model 111 Fluorometer with a flow-through cell and 550 nm filter were used. The samples were fed to the fluorometer with a Gilson Anacol SC30 Sampler and a Technical Instruments Corporation Proportioning Pump. A linear chart recorder was used to collect the data. The samples were prepared in polypropylene, 100 ml wide mouth bottles, that were soaked in 10% HNO₃ in-between runs. Mettler PI200 and H16 balances were used. Volumetric additions were made with Eppendorf microliter pipets. A Texas Instruments SR-56 programmable calculator and Apple II desk computer were used in the statistical analysis.

2.2 REAGENTS

The lumogallion was bottled by Pfalz + Bauer Inc. Solutions of about 0.02% were prepared as stock solutions; (exact concentration= 5.63×10^{-6} M , in the final samples.)

The buffer was prepared with Fisher Reagent ACF glacial acetic acid and Baker Analysed Reagent sodium acetate. (Buffer 3.28 M in acetate).

The stock, 1000 ppm aluminum solutions were prepared from AnalaR aluminum potassium sulfate, and stablized with two drops conc. HN03 per 100 mls.

The rinse solution for the sampling system was 0.01 M HNO $_3$, prepared in distilled, deionized water.

2.3 PROCEDURE

On the day of analysis, prepare a secondary aluminum stock solution, by pipeting 1 ml 1000 ppm stock aluminum solution into a 100 ml polypropylene bottle, and weighing in water to make a 100 g net weight. Into 100 ml polypropyleme bottles weigh 98.0 g water, and dispense 1.0 mls buffer solution from a biuret. Using an Eppendorf pipet, pipet 1.00 mls stock lumogallion and appropriate quantities of secondary stock aluminum into the plasic bottles. For the thermodynamic experiments add at this point appropriate quantities of stock competing ligand. (Error in sample preparation was kept below +/- 2%.) Partially seal the bottles with their screw caps and place into a water bath at about 80 C for an hour; swirl the contents of the bottles occassionally. Retrieve the bottles and allow to cool until they are at room temperature. For the kinetic experiments, add aliquots of stock competing ligand at t=0, swirl and pour an aliquot into the sampling test-tubes. Set sampling time on the sampler to three minutes, and rinsing time to 3.5 min. For the kinetic experiments, note the time after t=0 at which the peaks begin to appear on the chart-recorder.

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2.4 CALIBRATION CURVES

In order to check for linearity, standard aluminum solutions were run, with concentrations varying from 0 to 50 ppb aluminum. (See figure 2.) The blanks, containing all reagents except aluminum, were consistently found to be less than back-ground, (about 2ppb).

Afterwards, peak-heights were normalized with respect to the 50 ppb standard, $(1.85 \times 10^{-6} \text{ M})$, and data listed as h/h_0 .

The maximum error in reading the peak-heights at low levels was 10%, and at 50 ppb was as little as 1%.



3.1 RESULTS OF THE THERMODYNAMIC EXPERIMENT

In table 1 are listed the results of additions of competing ligands to the aluminum-lumogallion system before digestion of the solution at 80 C for 1 hour. The quantity h/h_0 is the ratio of peak height for a solution of 1.85 $\times 10^{-6}$ M aluminum, with and without the competing ligand.

Large excesses of competing ligand were used to test for weak, as well as strong competing complexes. Note that of the group $H_2PO_4^-$, H_4SiO_4 , SO_4^{2-} , only the dihydrogen phosphate ion had any noticable effect on the fluorescence intensity. Polyphosphate ions were not tested.

Fluoride and citrate, though, were the nnly ligands that had a large effect on the fluorescence, and were therefor investigated in more detail.

TABLE.1. The effectiveness of competing ligands in reducing the fluorescence of the aluminum-lumogallion complex

pH = 5.2 ; total acetate =
$$3.28 \times 10^{-2}$$
 M



NOTE: The concentrations of the competing ligand were almost two orders of magnitude greater than the concentration of lumogallion. 22

For the fluoride experiment, the reaction was formulated as :

 $A1-lumo^{2+}_{(aq)} + 6F^{-} \stackrel{K'}{=} A1F_{6}^{3-} + lumo^{-}$, (3) where K' is the conditional stability constant. The stoichiometry of the aluminum-lumogallion complex was selected on the basis of studies by Salikhov and Yampol'kii (1964), which showed that the ratio between lumogallion and the metal ion (in this case gallium), was 1:1. Because the fluoride ion was always in excess over aluminum, it was decided to represent the fluoride complex as $A1F_{6}^{3-}$, though any one or combination of the members of the series $A1F_{n}^{(3-n)+}$ could have been selected, (Cotton and Wilkinson, 1966).

Hydroxide ion was not considered as a part of the reaction, since the experiments were run under conditions of constant pH.

Table 2 lists the solutions of the following mass-balance equations:

$$[AlF_6^{3-}] + [Al-lumo] = [Al)_T$$
, (4)

where
$$[Al-lumo] = h/h_o [Al]_T$$
 (5)

$$[lumo]+[Al-lumo] = [lumo]_{T}$$
(6)

$$[F^{-}] + 6[AIF_{6}^{3-}] = [F^{-}]_{T}$$
 (7)

	$K' = \frac{A1F_6^{3-} lumo}{A1-lumo F^{-6}} $ Al $_{T}$ = 1.85 x10 ⁻⁶ M +/- 2% # i lumo $_{T}$ = 5.63 x10 ⁻⁶ M +/- 2%			pH= 5.2 ; total acetate = 3.28×10^{-2} M		
Al T (M)	fluoride _T (M)	AlF_6^{-3} = Al T- Al-lumo	lumo = lumo _T - Al-lumo	Al-lumo =h/h _o Al _T =	F ⁻ F ⁻ T ⁻ 6 AlF ₆ ⁻³	
0.74 x10 ⁻⁶ +/- 2%	0.50 x10 ⁻⁴ +/- 2%	2.52 x10 ⁻⁷ +/-15%	5.142 x10 ⁻⁶ +/- 2.7 %	0.488 x10 ⁻⁶ +/- 5 %	4.8488 x10 ⁻⁵ +/- 2.5%	
1.11 x10 ⁻⁶	0.50×10^{-4}	4.09 x10 ⁻⁷ +/- 14%	4.929 x10 ⁻⁶ +/- 3.0%	0.701×10^{-6}	4.7546 x10 ⁻⁵ +/- 2.8%	
1.48 x10 ⁻⁶	0.50×10^{-4}	5.66 x10 ⁻⁷ +/- 13%	4.716 x10 ⁻⁶ +/- 3.4%	0.914 x10 ⁻⁶	-5 4.6604 x10 +/- 3.1%	
1.85 x10 ⁻⁶	2.0 x10 ⁻⁵	3.70 x10 ⁻⁷ +/- 30%	4.15 x10 ⁻⁶ +/- 4.5%	1.48 x10 ⁻⁶	1,778 x10 ⁻⁵ +/-6.0%	
	1.0×10^{-5}	2.70×10^{-7}	4.04 x10 ⁻⁶ +/- 4.8%	1.59×10^{-6}	8.38 x10 ⁻⁶ +/- 3.8%	
	0.5 x10 ⁻⁵	2.10 x10 ⁻⁷ +/- 57%	3.99 x10 ⁻⁶ +/- 4.9%	1.64 x10 ⁻⁶	3.74 x10 ⁻⁶ +/- 5.9%	
			4			
	2.0×10^{-4}	1.51 x10 ⁻⁶ +/- 3.6%	5.291 x10 ⁻⁶ +/- 2.5%	0.339 x10 ⁻⁶	1.909 x10 ⁻⁴ +/- 2.1%	
	1.0×10^{-4}	1.17 x10 ⁻⁶ +/- 6.0%	4.963 x10 ⁻⁶ +/- 2.9%	0.667 x10 ⁻⁶	9.296 x10 ⁻⁵ +/- 2.2%	
- -	0.5 x10 ⁻⁴	7.94 x10 ⁻⁷ +/- 11%	4.574 x10 ⁻⁶ +/- 3.6%	1.056 x10 ⁻⁶	4.524 x10 ⁻⁵ +/- 2.4%	

81.4

TABLE, $\mathbf{2}$. CONCENTRATIONS OF SPECIES IN THE EQUILIBRIUM REACTION INVOLVING FLUORIDE

Note that three reactions involving varying aluminum concentrations are also included.

* Note that the stoichiometry of the reaction and complexes are assumed; see text.

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Table 3 lists the resulting K' values for different fluoride and aluminum concentrations. The results are depicted graphically in figures 3 and 4. The constant was found to increase with decreasing fluoride concentration. Deviations from linearity occur in the \log_{10} K' versus \log_{10} [F] curves at \log [F]. A linear-regression on that part of the curve that is linear, resulted in a slope of -4.826 and an intercept of -0.16616. The correllation coefficient for THIS PART OF THE CURVE was -0.999988.

The stability constant can therefor be represented

as

 $K' = 0.6821 [F]^{-4.826}$

(8)
Fluoride _T	(M) Al _T 1	.og ₁₀ fluoride	К •	log ₁₀ K'
0.50×10^{-4}	0.74×10^{-6}	-4.30	2.043 x10 ²⁰ +/- 25%	20.31 +/- 0.10
0.50×10^{-4}	1.11×10^{-6}	-4.30	2.489 x10 ²⁰ +/-25%	20.40 +/- 0.09
0.50×10^{-4}	1.48×10^{-6}	-4.30	2.850 x10 ²⁰ +/- 25%	20.45 +/- 0.10
2.0 x10 ⁻⁵	1.85×10^{-6}	-4.70	$3.284 \times 10^{22} + / - 46\%$	22.51 +/- 0.17
1.0×10^{-5}	0	-5.00	1.981 x10 ²⁴ +/- 57%	24.30 +/- 0.19
0.5×10^{-5}	99	-5.30	1.867 x10 ²⁶ +/- 73%	26.27 +/- 0.24
2.0×10^{-4}	11	-3.70	4.869 x10 ¹⁷ +/- 13%	17.69 +/- 0.06
1.0×10^{-4}	98	-4.00	1.349 x10 ¹⁹ +/- 16%	19.13 +/- 0.06
0.5×10^{-4}	11	-4.30	4.012 x10 ²⁰ +/- 22%	20.60 +/- 0.09

TABLE. \mathfrak{Z} . CONDITIONAL EQUILIBRIUM CONSTANTS FOR THE REACTION INVOLVING FLUORIDE



Al-lumo + citrate = Al-citrate + lumo⁻ Mass-balance equations and solutions are given in table 4. In this experiment the aluminum concentration was kept constant.

The calculated conditional equilibrium constants for various citrate concentrations are listed in table 5 and presented graphically in figures 5 and 6.

In this case K' decreases with decreasing citrate concentration. Deviations from linearity occur in the \log_{10} K' versus \log_{10} [F] curves at low citrate concentrations.

Linear-regression on the linear portion of the curve yielded a slope of 0.2196 and an intercept of 0.25556. The correllation coefficient for the linear portion of the curve was found to be 0.9988. The conditional equilibrium constant could thus be given as

 $K' = 1.8012 [F^{-}]^{0.2196}$ (9)

K' = [<u>Al-citra</u> [Al-lumo [†]	<u>ate][lumo⁻¹]</u> , [Al ⁺²][citrate] , [lu	$]_{\rm T} = 1.85 \times 10^{-6} \text{M}$ +/ mo] $_{\rm T} = 5.63 \times 10^{-6} \text{M}$ +	/- 2% ; pH = /- 2% total	5.2 acetate = 3.28×10^{-2} M
citrate _T (M)	[Al-citrate] =[Al] _T -[Al-lumo]	[lumo] =[lumo] _T -[Al-lumo]	[Al-lumo] = h/h _o [Al] _T	[citrate] =[citrate] _T -[Al-citrate]
2.0 x10 ⁻⁵ +/- 2%	7·7 x10 ⁻⁷ +/-12%	4.55 x10 ⁻⁶ +/- 3.7%	1.08 x10 ⁻⁶ +/- 5.%	1.92 x10 ⁻⁵ +/- 2.6%
1.0 x10 ⁻⁵	5.0 x10 ⁻⁷ +/- 21%	4.28 x10 ⁻⁶ +/- 4.2%	1.35 x10 ⁻⁶	9.50 x10 ⁻⁶ +/- 3.2%
0.5×10^{-5}	3.4 x10 ⁻⁷ +/- 33%	4.12 x10 ⁻⁶ + /- 4.6%	1.51×10^{-6}	4.66 x10 ⁻⁶ +/- 4.6%
2.0×10^{-4}	1.68 x10 ⁻⁶ +/- 2.7%	5.46 x10 ⁻⁶ +/- 2.2%	0.168 x10 ⁻⁶	1.98 x10 ⁻⁴ +/- 2.0%
1.0×10^{-4}	1.51 x10 ⁻⁶ +/-3.6%	5.29 x10 ⁻⁶ +/- 2.4%	0.339×10^{-6}	9.85 x10 ⁻⁵ +/- 2.1%
0.5×10^{-4}	1.23 x10 ⁻⁶ +/- 5.5%	5.01 x10 ⁻⁶ +/- 2.9%	0.623 x10 ⁻⁶	4.877 x10 ⁻⁵ +/- 2.2%

TABLE. 4. CONCENTRATIONS OF SPECIES IN THE EQUILIBRIUM REACTION INVOLVING CITRATE

[citrate](M)	log ₁₀ [citrate]	Κ.	log ₁₀ K'
2.0×10^{-5}	-4.70	0.167 +/- 23%	-0.7773 +/- 0.09
1.0×10^{-5}	-5.00	0.167 +/- 33%	-0.7773 +/- 0.12
0.5×10^{-5}	-5.30	0.200 +/- 47%	-0.6990 +/- 0.17
2.0×10^{-4}	-3.70	0.275 +/- 12%	-0.5607 +/- 0.05
1.0×10^{-4}	-4.00	0.242 +/- 13%	-0.6162 +/- 0.05
0.5×10^{-4}	-4.30	0.204 +/- 16%	-0.6904 +/- 0.06

TABLE. 5. CONDITIONAL EQUILIBRIUM CONSTANTS FOR THE REACTION INVOLVING CITRATE



3.2 RESULTS OF THE KINETIC EXPERIMENT

This section deals with the effects of adding fluoride ion in three concentrations, to the aqueous aluminum-lumogallion system after digestion.

The data analysis is based on procedures presented by Levenspiel (1972) for the interpretation of constant-volume batch-reactor data.

Because the reactions are reversible, and because the equilibrium constants are not infinite, (thermodynamic study), the kinetic reactions had to be treated as 'reversible' reactions. This means that for the purposes of data analysis, the equilibrium concentration of the aluminum-lumogallion complex, previously determined in the thermodynamic experiment, is subtracted from the initial complex concentration, C_{AO} , and from the instantaneous complex concentrations C_A , determined in the kinetic experiment. The terms C_{AO} and C_A are thus defined as,

$$C_{A0} = 1.85 \times 10^{-6} (1 - h_{eq}/h_o),$$
(10)
$$C_A = 1.85 \times 10^{-6} (h/h_o - h_{eq}/h_o),$$
(11)

where h_{eq}/h_o is the equilibrium, reduced fluorescence peak-height of the aluminum-lumogallion-fluoride system. Thus the limit of C_A at infinite time is zero. Plots of C_A versus time are given in figures 10, 11 and 12.

3.2

as

Tests for reversible reactions of simple order were found to be negative. A test for a reversible reaction of mixed order, shifting from high to low order with decreasing concentration of reactant was also found to be negative. The best fit was obtained for a reversible reaction of mixed order, shifting from 0th to 1st order with decreasing concentration of reactant.

> The rate for this model is given by Levenspiel $-r_{A} = -dC_{A}/dt = k_{1}C_{A}/(1+k_{2}C_{A})$, (12)

where k_1 (s⁻¹) and k_2 (moles⁻¹) are empirical rate constants. This rate equation was tested by the integration method, where the integrated equation can be expressed as,

$$\frac{\ln(C_{AO}/C_A)}{C_{AO}-C_A} = -k_2 + \frac{k_1 t}{C_{AO}-C_A}$$
 (13)

A plot of $\frac{\ln(C_{AO}/C_A)}{C_{AO}-C_A}$ versus $t/(C_{AO}-C_A)$ is expected

to yield a straight line if the model fits the data, (t,C_A) . For brevity, the above terms are given the names Y and X respectively. The raw data, t and h/h_o , along with the derived data X and Y are listed in three tables, 7, 8 and 9, one for each initial fluoride concentration tested. Plots of the linear regressions of Y on X are presented in figures 7, 8 and 9.

The intercept of the linear regression line is given the name A = $-k_2$; the slope of the regression line is given the name B = $\Delta \ln(C_{AO}/C_A) / \Delta t$. As a part of the linear regression program, correllation coefficients, r, standard estimates of error, SEE, relative standard estimates of error, SEE/Y, and and standard estimates of error in A and B were also calculated. The statistics for runs at each fluoride concentration are given at the bottom of the corresponding tables, (7, 8 and 9).

Note that the relative standard estimate of error in Y, around 7%, is slightly larger than the estimated error in h/h_0 , (5%).

3.2

- <u>1</u>				54 0
t (s)	h/h _o	C _A (M)	X	Y
(0)	1.00	7.9365 x10 ⁻⁷		
480. +/-1 <i>3</i> %	0.83 +/-5%	4.7915×10^{-7}	1.52623212 x10 ⁹	1604543.27
1980 +/-3.1%	0.76	3.4965 x10 ⁻⁷	4.45945946 x10 ⁹	1846193.48
3540 +/-1.7%	0.72	2.7565 x10 ⁻⁷	6.83397683 x10 ⁹	2041526.28
5580 +/-1.1%	0.67	1.8315 X10 ⁻⁷	9.14004914 x10 ⁹	2401862.52
8280 +/-0.7%	0.66	1.6465×10^{-7}	13.163752 x10 ⁹	2500509.62
8700 +/-0.7%	0.63	1.0915 x10 ⁻⁷	12.7100073 x10 ⁹	2898348 .3 9

<u>TABLE. 6. TEST OF THE RATE EQUATION</u> $[F^{-}]_{T} = 0.5 \times 10^{-4}$ M; pH = 5.2 +/- 0.2; total acetate= 3.28 $\times 10^{-2}$ M; $h_{eq}/h_{o} = 0.571$

B= 9.78401334 x10 - +7- 1.59604402 x10 Correllation Coefficient= 0.950682604 Standard Estimate of Error= 164282.713

SEE/Y =0.0741516208

Fig.7. Plot of the linear regression of Y on X.



TABLE. 7.	TEST OF C	THE RATE EQUATION		
[P ⁻] _T =1.0	x10 ⁻⁴ M;	pH= 5.2 +/- 0.2 ; tot	al acetate = 3.28 x10 ⁻	² ; $h_{eq}/h_{o}=0.366$
t (s)	h/h _o	С _А (М)	X	Y
0	1.00	11.729×10^{-7}		
540. +/-11%	0.771 +/-5%	7.4925×10^{-7}	1.27463708 x10 ⁹	1057858.82
900. +/-6.7%	0.714	6.438 x10 ⁻⁷	1.7010017 x10 ⁹	1133710.97
1680 +/-3.6%	0.629	4.8655 x10 ⁻⁷	2.44773075 x10 ⁹	1281991.58
2520 +/-2.4%	0.582	3.9960 x10 ⁻⁷	3.25876115 x10 ⁹	1392435.73
4860 +/-1.2%	0.448	1.517×10^{-7}	4.75910693 x10 ⁹	2002868.89
6420 +/-0.9%	0.433	1.2395×10^{-7}	6.12040612 x10 ⁹	2142481.85
7980 +/-0.8%	0.418	0.963 x10 ⁻⁷	7.41153525 x10 ⁹	2322657.41
9180 +/-0.7%	0.394	0.518 x10 ⁻⁷	8.18838641 x10 ⁹	2782842.24

A= 721494.828 +/- 154799.81 B= 2.37329845 $\times 10^{-4}$ +/- 0.16028437 $\times 10^{-4}$ r= 0.986591048 SEE= 111827.561 SEE/Y= 0.0633725404



Fig.8. Plot of the linear regression of Y on X.

[F ⁻] _T =2.0	x10 ⁻⁴ M;	pH =5.2 */- 0.2; tota	al acetate = 3.28×10^{-2} M	$h_{eq}/h_{o} = 0.183$
t (s)	h/h _o	C _A (M)	X	Y
0	1.00	15.1146 x10 ⁻⁷		
540. +/-11%	0.61 +/-5%	7.8995 x10 ⁻⁷	0.748440749 x10 ⁹	899314.043
1020. +/-5.9%	0.49	5.6795 x10 ⁻⁷	1.08108108 x10 ⁹	1037404.71
2400 +/-2.5%	0.29	1.9795 x10 ⁻⁷	1.82717929 x10 ⁹	1547628.67
2820 +/-2.1	0.25	1.2395 x10 ⁻⁷	2.03243243 x10 ⁹	1802483.95
3660 +/-1.6%	0.22	0.6845 x10 ⁻⁷	2.53638254 x10 ⁹	2144643.92
4860 +/-1.2%	0.21	0.4995 x10 ⁻⁷	3.32535067 x10 ⁹	2333083.98
5700 +/-1.1%	0.20	0.3145 x10 ⁻⁷	3.85135135 x10 ⁹	2616503.89

TABLE. δ . TEST OF THE RATE EQUATION

A=523764.213 +/- 139641.276 B= 5.65809003 x10⁻⁴ +/- 0.445587499 x10⁻⁴ r= 0.98484 SEE= 123103.221 SEE/Y= 0.0696000447



Fig.9. Plot of the linear regression of X on Y.





Fig.11. Change in the corrected complex concentration with time.



Fig.12. Change in the corrected complex concentration with time.

As a second test of the rate equation, the measured rate was plotted against the rate calculated according to the rate equation,

$$dC_{A}/dt = k_{1}C_{A}/(1+k_{2}C_{A})$$
 (14)

The measured rate was obtained by drawing a line through the points on the C_A versus time curves, (figures 10,11 and 12), and measuring tangents to the curve at points corresponding to times at which data was collected. The error in drawing the curve and reading the tangents was estimated as about 20%.

In order to calculate the rate according to the rate equation, the values of k_1 and k_2 had to be calculated. In order to get estimates of error in k_1 and k_2 , the constants were calculated according to the relations,

$$k_{1} = t^{-1} (\ln(C_{AO}/C_{A}) + k_{2}(C_{AO} - C_{A})), \qquad (15)$$

$$k_{2} = k_{1}t - \ln(C_{AO}/C_{A}), \qquad (16)$$

and

$$e = \frac{k_1 t}{C_{A0} - C_A} - \frac{\ln(C_{A0}/C_A)}{C_{A0} - C_A} , \qquad (16)$$

for each (t,C_A) coordinate. The values for each constant were then averaged for each initial fluoride concentration. The errors listed in table 10 are the sums of relative standard deviations in k_1 and k_2 , for each initial fluoride concentration.

3.2

The results are plotted on graphs in figures 13, 14 and 15, where the drawn-in line represents perfect agreement. Note that deviations from this line occur consistently at higher rates. For initial fluoride concentrations of 0.5×10^{-4} M and 1.0×10^{-4} M, the deviation is towards lower calculated rates, while for the initial fluoride concentration of 2.0×10^{-4} M, the deviation is toward higher calculated rates. $[F^{-}]_{T} = 0.5 \times 10^{-4} M$

t (s)	Rates measured from graph	rate= $k_1 C_A / (1 + k_2 C_A)$
480	-2.870 x10 ⁻¹⁰ +/- 20%*	$-1.527 \times 10^{-10} + / - 26\%^{\#}$
1980	-6.567 x10 ⁻¹¹	-6.982 x10 ⁻¹¹
3540	-3.80 x10 ⁻¹¹	-4.537 x10 ⁻¹¹
5580	-1.63 x10 ⁻¹¹	-2.471 x10 ⁻¹¹
8280	-3.093 x10 ⁻¹²	-2.144×10^{-11}

 $[F]_{T} = 1.0 \times 10^{-4} M$

t (s)	Rates measured from graph	rates= $k_1 C_A / (1 + k_2 C_A)$
540	-4.800 x10 ⁻¹⁰ +/- 20%*	$-3.962 \times 10^{-10} + / - 24 \%^{\#}$
900	-3.065 x10 ⁻¹⁰	-2.820×10^{-10}
1680	-1.818 x10 ⁻¹⁰	-1.697 x10 ⁻¹⁰
2520	-1.158×10^{-10}	-1.252×10^{-10}
4860	-5.000 x10 ⁻¹¹	-3.689 x10 ⁻¹¹
6420	-2.805×10^{-11}	-2.940 ×10 ⁻¹¹
7980	-2.213×10^{-11}	-2,230 x10 ⁻¹¹
9180	-1.750×10^{-11}	-1.155 x10 ⁻¹¹

 $[F]_{T} = 2.0 \times 10^{-4}$

t (s)	Rates measured from graph	rate= $k_1 C_A / (1 + k_2 C_A)$
540	-8.065 x10 ⁻¹⁰ +/- 20%	$-1.607 \times 10^{-9} + / - 58\%^{17}$
1020	-3.164×10^{-10}	-9.644×10^{-10}
2400	-1.689×10^{-10}	2.634×10^{-10}
2820	-1.181×10^{-10}	-1.581×10^{-10}
3660	-5.800 x10 ⁻¹¹	-8.470 x10 ⁻¹¹
4860	-1.560 x10 ⁻¹¹	-6.119 x10 ⁻¹¹
5700	-5.106×10^{-12}	-3.814×10^{-11}

(* estimated error in slopes drawn from hand-drawn concentration/time graghs) (# error in calculated rates defined as the sum of relatives errors in k_1 and k_2)

Comparison of the measured rates and the rates calculated according to the rate equation. $F = 0.5 \times 10^{-4} M$ 2 × 10⁻¹⁰ -rate (calculated) 1 3 ×10⁻¹⁰ 1 2 0 -rate (measured)

Fig.13.

NOTE: The line drawn in is the line for theoretical aggreement.



Fig.15. Comparison of the measured rate and the rate rate calculated from the rate equation

$$F^{-} = 2.0 \times 10^{-4} M$$



In order to build the dependence of the rate equation on fluoride concentration into the rate equation, the logarithms of \bar{k}_1 and \bar{k}_2 were plotted against the logarithm of fluoride concentration. Data are presented in table 11. Curves for \bar{k}_1 and \bar{k}_2 are given in figures 16 and 17, respectively.

Linear regression and solution of the two relations for \overline{k}_1 and \overline{k}_2 yield the following empirical equations:

$$\bar{k}_1 = 4330.8 [F^-]^{1.7921}$$
, (17)
 $\bar{k}_2 = -1038.5 [F^-]^{-0.7273}$. (18)

and

Rounding of the constants and substitution into the rate equation yields,

$$-dC_{A}/dt = \frac{(4.3 \times 10^{3}) [F]^{1.8} C_{A}}{(1 - (1.0 \times 10^{3}) [F]^{-0.7} C_{A}} .$$
(19)

3.2

TABLE. <i>10</i> .	THE	OVERALL	RATE	CONSTANTS	

[F ⁻] _T (M)	k ₁	ln k ₁	^k 2	ln (-k ₂)
0.5×10^{-4}	0.99945755 x10 ⁻⁴	-9.215779638	-1.43549163 x10 ⁶	14.17701795
	+/- 0.1332 x10 ⁻⁴	+/- 0.1257	+/- 0.1876 x10 ⁶	+/- 0.123
1.0 x10 ⁻⁴	2.138296875 x10 ⁻⁴	-8.450330713	-0.794942 x10 ⁶	13.58602523
	+/- 0.2377 x10 ⁻⁴	+/- 0.1054	+/- 0.1057x10 ⁶	+/- 0.125
2.0 x10 ⁻⁴	11.92889171 x10 ⁻⁴	-6.73137704	-0.523764213 x10 ⁶	1 3.16 879689
	+/- 3.752 x10 ⁻⁴	+/- 0.2735	+/- 0.1396 x10 ⁶	+/- 0.236

Fig.16.









4.0 DISCUSSION

First it must be pointed out that all experiments were run under conditions of constant ionic strength and pH, by virtue of the high concentration of acetate buffer, $(3.28 \times 10^{-2} \text{ M})$. The advantage of doing this is that no corrections need be made for varying activity coefficients. The disadvantage of this is that acetate becomes the dominant ion in the system. Even if the stability constant for the formation of an aluminumacetate complex is small, (K= 10^{32} , for a complex of the type AlL²⁺, at pH near 2.7; Kereichuk and Il'cheva), some of the complexed species will form with such an excess acetate concentration. Thus all the results of this investigation are conditional. However, if it is granted that the quantity of aluminum lost to the formation of the acetate complex is constant, then the results should at least be internally consistent.

The effect of such high concentrations of acetate on the rate law and rate constants in the kinetic study can be large if the acetate species are involved with the reaction. For example, Turner and Wan Sulaiman (1970) found that the decomposition of aluminum-hydroxide polymers was dependent on the acetate concentration at a pH of 5.05.

4.1 DISCUSSION OF THE THERMODYNAMIC EXPERIMENT

It ought to be pointed out that some questionable but necessary assumptions were made regarding the massbalance equations. For example, total aluminum concentration was given as being equal to the sum of the concentrations of AlF_6^{3-} and Al-lumo. Some Al-acetate complex was probably also present. Also, almost certainly other members of the series $AlF_n^{(3-n)+}$ are present. This would explain the deviations from linearity of the logK' versus log[F] curve; at low [F] maximum coordination of fluoride around aluminum would not occur, thus altering the products of the reaction and thus the definition of the equilibrium constant.

Further, the stoichiometry of AlF_6^{3-} is probably incorrect, even in that range of fluoride concentrations where the log/log curve is linear. The conditional equilibrium constant calculated from the log/log plot is

$$K' = 0.6821 [F]^{-4.826}$$

indicating that the exponent of either the [lumo] term or the $[F^-]$ term or both are incorrect. This means that the stoichiometries of the complexes Al-lumo and/ or AlF_6^{3-} are also not correct.

Similarly in the case of the citrate experiment, low citrate concentrations result in the formation of citrate complexes of lower citrate/aluminum ratios than those formed at high citrate excess concentrations.

Also, the stoichiometries of the complexes Al-lumo and Al-citrate are suspect.

4.2 THE KINETIC EXPERIMENT

Note that the linear regression of Y on X yielded good results, (figures 7, 8, and 9), with no consistent deviations from linearity either at low or high values of X. This does not prove that the rate law is correct, however. Data for times less than about 500 seconds were not obtainable because of inherent limitations in the apparatus. (The sample must be fed to the flow-through cell via the proportioning pump). In addition to this limitation is the fact that the calculated rates consistently deviated from the line of agreement, (figures 13, 14 and 15), at high measured rates. This might be explained by arguing that the error of measurement of tangents at high slopes, (i.e. high rates), is greater than that for small slopes. It is therefor desirable to have more precise rate data.

The linear regressions of lnk on $\ln[F]$ ought to be regarded with some doubt. If the relationship between lnk and $\ln[F]$ is non-linear, then three points are not enough to define the relation. Even if the relation is linear in the region studied, deviations at high or low values of $\ln[F]$ are not ruled out.

5.0 CONCLUSIONS

1. The lumogallion method is adequate for identifying those ligands found in nature that strongly complex aluminum.

2. With sufficient data, conditional equilibrium constants can be derived for the four the reaction involving the destruction of the aluminum-lumogallion complex by other ligands.

3: By plotting these constants as a function of the competing ligand, it was determined that the stoichiometries of the reactions involving fluoride and citrate are not correct, as assumed in this study.

4. Reactions of aqueous aluminum are considered, on the basis of this study to lend themselves to kinetic investigations, because the reaction half-times are of a convenient length, (a matter of hours).

5. Rate data for the destruction of the aluminumlumogallion complex by an interfering ligand can be obtained in sufficient precision and with sufficient sensitivity by this method in order to yield a reasonable rate-law.

5.1 FUTURE WORK

1. The planned use of a stationary cell in the fluorometer will permit rate data to be collected as soon as 5 seconds after the introduction of the interfering ligand to the aluminum-lumogallion system.

2. A methodical testing of naturally occuring ligands for their capacity to complex aluminum is recommended.

3. A study to develop a mathematical procedure for deriving the stoichiometries of these interfering reactions is also suggested.

4. A study into the rates of reaction of lumogallion with colloidal aluminum species might be considered.

5. A study into the effects of strongly competing ligands on standard-addition curves, obtained using the lumogallion procedure is recommended. REFERENCES

4.

- Akitt, J.W.; Greenwood, N.N.; Lester, G.D. (1971) NUCLEAR MAGNETIC RESONANCE AND RAMAN STUDIES OF THE ALUMINUM COMPLEXES FORMED IN AQUEOUS SOLUTIONS OF ALUMINUM SALTS CONTAINING PHOSPHORIC ACID AND FLUORIDE IONS. J. Chem. Soc. (A) pp2450-2457
- Akitt, J.W.; Greenwood, N.N.; Khandelwal, B.L.; Lester, G.D. (1972) ²⁷Al NUCLEAR MAGNETIC RESONANCE STUDIES OF THE HYDROLYSIS AND POLYMERIZATION OF THE HEXA-AQUO-ALUMINUM (III) CATION J.C.S. Dalton pp604-610
- Akitt, J.W.; Greenwood, N.N.; Khandelwal, B.L. (1972) ALUMINUM-27 NUCLEAR MAGNETIC RESONANCE STUDIES OF SULPHATO-COMPLEXES OF THE HEXA-AQUO-ALUMINUM ION. J.C.S. Dalton pp1226-1229
- Akitt, J.W. (1973) PROTON CHEMICAL SHIFTS OF AQUEOUS ALUMINUM SALT SOLUTIONS J.C.S. Dalton pp1177-1181
- Barnes, R.B. (1975) THE DETERMINATION OF SPECIFIC FORMS OF ALUMINUM IN NATURAL WATER. Chemical Geology 15, pp 177-191
- Brosset, C.; Biedermann, G.; Sillén, L.G. (1954) STUDIES ON THE HYDROLYSIS OF METAL IONS: XI. THE ALUMINUM ION Al³⁺ Acta Chem. Scand. <u>8</u> pp1917-1926
- Brown, D.W.; Hem, J.D. (1975) REACTION OF AQUEOUS ALUMINUM SPECIES AT MINERAL SURFACES Geological Survey Water-Supply Paper 1827-F
- Brown, K.L. (1979) A SIMPLIFIED METHOD FOR SPECTRO-PHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANTS Inorganica Chimica Acta <u>37</u> pp L513-L516

REFERENCES

Cabrera, F.; Talibudeen, O. (1978) THE RELEASE OF ALUMINUM FROM ALUMINOSILICATE MINERALS: I.KINETICS Clays and Clay Minerals <u>26</u> pp 434-440

Cabrera, F.; Talibudeen, O. (1979) THE RELEASE OF ALUMINUM FROM ALUMINOSILICATE MINERALS: II. ACID-BASE POTENTIOMETRIC TITRATIONS Clays and Clay Minerals <u>27</u> pp 113-118

Canet, D.; Delpuech, J.J.; Khaddar. M.R.; Rubini, P. (1973) DIRECT OBSERVATION OF SOLVATED SPECIES BY ²⁷Al NMR. J. Magnetic Resonance <u>9</u> pp 329-330
 Caschetto, S.; Wollast, R. (1979) DISSOLVED ALUMINUM IN INTERSTITIAL WATERS OF RECENT MARINE SEDIMENTS

G.C.A. <u>43</u> pp 425-428

Chen, D.T.Y. (1973) SOLUBILITY PRODUCTS OF ALUMINUM HYDROXIDE IN VARIOUS IONIC SOLUTIONS Can. J. Chem. <u>51</u> pp 3528-3533

Dougan, W.K.; Wilson, A.L. (1974) THE ABSORTIOMETRIC DETERMINATION OF ALUMINUM IN WATER. A COMPARISON OF SOME CHROMOGENIC REAGENTS AND THE DEVELOPMENT OF AN IMPROVED METHOD Analyst <u>99</u> pp 413-430

Dugger, D.L.; Stanton, J.H.; Irby, B.N.; McConnell, B.L.; Cummings, W.W.; Maatman, R.W. (1964) THE EXCHANGE OF TWENTY METAL IONS WITH THE WEAKLY ACIDIC SILANOL GROUP OF SILICA GEL J. Phys. Chem. <u>68</u> #4 pp 757-760

Fowler, D.J. (1975) ALUMINUM COMPLEXES OF 2-METHYL-8-HYDROXYQUINOLINE Master's Thesis, McMaster University (Dept. of Chemistry)

Gavrilova, I.M.; Klyuchnikov, V.M.; Zaitsov, L.M.; Aprakin, I.A.A. (1973) EXTRACTION OF HYDROLYSED ALUMINUM PERCHLORATE WITH TRIBUTYL PHOSPHATE Russian J. Inor. Chem. 18 (6) pp955
- Golub, A.M.; Boldog, I.I. (1974) FORMATION OF ALKALI METAL ALUMINUM DOUBLE PHOSPHATES IN THE PRESENCE OF WATER Russian J. Inor. Chem. <u>19</u> (7) pp 955-958
- Gosink, T.A. (1975) RAPID SIMULTANEOUS DETERMINATION OF PICOGRAM QUANTITIES OF ALUMINUM AND CHROMIUM FROM WATER BY GAS PHASE CHROMATOGRAPHY Anal. Chem. 47 pp165-168
- Greenland, D.J. (1971) INTERACTIONS BETWEEN HUMIC AND FULVIC ACIDS AND CLAYS Soil Science <u>111</u> pp 34-41
- Hall, E.S. (1965) THE ZETA POTENTIAL OF ALUMINUM HYDROXIDE IN RELATION TO WATER TREATMENT COAGULATION J. Appl. Chem. <u>15</u> pp197-205
- Haraguchi, H.; Fujiwara, S. (1969) ALUMINUM COMPLEXES IN SOLUTION AS STUDIED BY ALUMINUM-27 NUCLEAR MAGNETIC RESONANCE J. Phys. Chem. <u>73</u> #10 pp 3467-3473
- Hem, J.D.; Roberson, C.E.; Lind, C.L.; Polzer, W.L. (1973) CHEMICAL INTERACTIONS OF ALUMINUM WITH AQUEOUS SILICA AT 25 C Geological Survey Water-Supply Paper 1827-E
- Hemingway, B.S.; Robie, R.A.; Kittrick, J.A. (1978) REVISED VALUES FOR THE GIBBS FREE ENERGY OF FORMATION OF (Al(OH), aq), DIASPORE, BOEHMITE AND BAYERITE AT 298,15 K AND 1 BAR, THE THERMO-DYNAMIC PROPERTIES OF KAOLINITE TO 800K AND 1 BAR, AND THE HEATS OF SOLUTION OF SEVERAL GIBBSITE SAMPLES G.C.A. <u>42</u> pp1533-1543

REFERENCES

Hydes, D.J.; Liss, P.S. (1976) THE DETERMINATION OF LOW CONCENTRATIONS OF DISSOLVED ALUMINUM IN NATURAL WATERS Analyst 101 pp 922-931

Johansson, G.; Lundgren, G.; Sillén, L.G.; Soderquist, R. (1960) ON THE CRYSTAL STRUCTURE OF A BASIC ALUMINUM SULFATE AND THE CORRESPONDING SELENATE Acta Chem. Scand. 14 #3 pp 769-773

Johansson, G. (1962) THE CRYSTAL STRUCTURES OF Al₂(OH)₂(H₂O)₈.(SO₄)₂.2H₂O and Al₂(OH)₂(H₂O)₈-(SeO₄)₂.2H₂O Acta Chem. Scand. <u>16</u> pp 403-420

Keller, W.D. (1978) DIASPORE RECRYSTALLIZED AT LOW TEMPERATURE American Mineralogist <u>63</u> pp 326-329

- Kereichuk, A.S.; Il'icheva, L.M. (1975) THE FORMATION
 OF ALUMINUM COMPLEXES OF MONOCARBOXYLIC ACIDS
 Russian J. Inor. Chem. <u>20</u> (9) pp 1291-1293
- Lind, C.J.; Hem, J.D. (1975) EFFECTS OF ORGANIC SOLUTES ON CHEMICAL REACTIONS OF ALUMINUM Geological Survey Water-Supply Paper 1827-G
- Malkova, T,V.; Ovchinnikova, V.D. (1972) KINETICS AND MECHANISM OF FORMATION OF THE COMPLEX ML IN THE Al'''-METHYLTHYMOL BLUE SYSTEM Russian J. Inor. Chem. <u>17</u> (6) pp813-816
- May, H.M.; Helmke, P.A.; Jackson, M.L. DETERMINATION OF MONONUCLEAR DISSOLVED ALUMINUM IN NEAR-NEUTRAL WATERS Chem. Geol. 24 pp 259-269
- Mesmer, R.E.; Baes, C.F. Jr. (1971) ACIDITY MEASUREMENTS AT ELEVATED TEMPERATURES.V. ALUMINUM ION HYDROLYSIS Inor. Chem. <u>10</u> #10 pp 2290-2296

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Pačes, T. (1978) REVERSIBLE CONTROL OF AQUEOUS ALUMINUM AND SILICA DURING THE IRREVERSIBLE EVOLUTION OF NATURAL WATERS G.C.A. <u>42</u> pp 1487-1493

Reesman, A.L.; Pickett, E.E.; Keller, W.D. (1969) ALUMINUM IONS IN AQUEOUS SOLUTIONS Am. J. Sci. <u>267</u> pp99-113

- Ross, G.J.; Turner, R.C. (1971) EFFECT OF DIFFERENT ANIONS ON THE CRYSTALLIZATION OF ALUMINUM HYDROXIDE IN PARTIALLY NEUTRALIZED AQUEOUS ALUMINUM SALT SYSTEMS Soil Science Society of America Proceedings <u>35</u> (1971)
- Sackett, W.; Arrhenius, G. (1962) DISTRIBUTION OF ALUMINUM SPECIES IN THE HYDROSPHERE- I. ALUMINUM IN THE OCEAN G.C.A. 26 pp 955-968
- Salikov, V.D.; Yampol'kii, M.Z. (1964) SPECTRO-PHOTOMETRIC STUDY OF LUMOGALLION AND ITS COMPLEX WITH GALLIUM Zh. Analit. Khim. <u>20</u> (12) pp 1299 (See Chemical Abstracts 64:10390b)
- Smith, R.W.; Hem, J.D. (1972) EFFECTS OF AGING ON ALUMINUM HYDROXIDE COMPLEXES IN DILUTE AQUEOUS SOLUTIONS Geological Survey Water-Supply Paper 1827-D
- Spoljaric, N.; Crawford, W.A. (1978) GLAUCONITIC GREENSAND: A POSSIBLE FILTER OF HEAVY METAL CATIONS FROM POLLUTED WATERS Environmental Geology <u>2</u> (4) pp 215-221
- Toy, A.D.; Smith, T.D.; Pilbrow, J.R. (1973) ALUMINUM-27 NUCLEAR MAGNETIC RESONANCE IN AQUEOUS SOLUTIONS OF ITS CHELATES WITH HYDROXY CARBOXYLIC ACIDS Australian J. Chem. <u>26</u> pp 1889-1892.

REFERENCES

- Turner, R.C. (1969) THREE FORMS OF ALUMINUM IN AQUEOUS SYSTEMS DETERMINED BY 8-HYDROXYQUINO-LINOLATE EXTRACTION METHODS Can. J.Chem 47 pp 2521-2527
- Turner, R.C.; Ross, G.J. (1970) CONDITIONS IN SOLUTION DURING THE FORMATION OF GIBBSITE IN DILUTE ALUMINUM SALT SOLUTIONS. 4. EFFECT OF C1 CONCEN-TRATION AND TEMPERATURE AND A PROPOSED MECHANISM FOR GIBBSITE FORMATION Can. J. Chem 48 pp723
- Turner, R.C.; Wan Sulaiman (1971) KINETICS OF REACTIONS OF 8-QUINOLINOL AND ACETATE WITH HYDROXYALUMINUM SPECIES IN AQUEOUS SOLUTIONS 1. POLYNUCLEAR HYDROXYALUMINUM CATIONS Can. J. Chem. 49 pp 1684-1690
- Turner, R.C. (1971) KINETICS OF REACTIONS OF 8-QUINOLINOL AND ACETATE WITH HYDROXYALUMINUM SPECIES IN AQUEOUS SOLUTIONS 2. INITIAL SOLID PHASES Can. J. Chem. <u>49</u> pp1688
- Turner, R,C. (1975) THE EQUILIBRIUM CONSTANT FOR THE FORMATION OF Al₂(OH)₂⁴⁺ IN AQUEOUS SOLUTIONS Can. J. Chem. <u>53</u> pp 2811-2817

- Cotton, F.A.; Wilkinson, G. (1966) ADVANCED INORGANIC CHEMISTRY Interscience Publishers, N.Y.
- Deer, W.A.; Howie, R.A.; Zussman, J. (1975) AN INTRODUCTION TO THE ROCK-FORMING MINERALS Longman
- Hem, J.D. (1968) ALUMINUM SPECIES IN WATER <u>in</u> ADVANCES IN CHEMISTRY SERIES <u>73</u>: TRACE INORGANICS IN WATER American Chemical Society Washington, D.C.
- Hsu, P.H. (1968) INTERACTION BETWEEN ALUMINUM AND PHOSPHATE IN AQUEOUS SOLUTION in ibid.
- Levenspiel, 0. (1972) CHEMICAL REACTION ENGINEERING 2nd Ed. John Wiley and Sons Inc. New York, London, Sydney, Toronto
- Robie, R.A.; Hemingway, B.S.; Fisher, J.R. (1979) THERMODYNAMIC PROPERTIES OF MINERALS AND RELATED SUBSTANCES AT 298.15 K AND 1 BAR (10⁵ PASCALS) PRESSURE AND AT HIGHER TEMPERATURES. Geological Survey Bulletin 1452 U.S. Government Printing Office, Washington
- Sandell, E.B. COLORIMETRIC DETERMINATION OF TRACES OF METALS, 3rd Ed. Interscience Publishers (1959) New York
- Stumm, W.; Morgen, J. (1970) AQUATIC CHEMISTRY-AN INTRODUCTION EMPHASIZING CHEMICAL EQUILIBRIA IN NATURAL WATERS Wiley Interscience, New York, London, Sydney, Toronto