DETERMINATION OF ALUMINUM:
FOUR ANALYTICAL METHODS

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ABSTRACT

Four procedures have been developed for determining the aluminum
concentration in basic matrices. Briefly, these are:

1. Atomic Absorption Spectroscopy (AAS), which was the routine method
    of analysis. Citrate was required to complex the aluminum and
    eliminate matrix effects. AAS was the least accurate of the four
    methods studied and was adversely affected by high aluminum
    concentrations.

2. The Fluoride Electrode Method was the most accurate and precise of
    the four methods. A Gran's[1] Plot determination was used to determine
    the end point and average standard recovery was 100 percent ±
    2 percent.

3. The Thermometric Titration Method was the fastest method for
    determining aluminum and could also determine hydroxide concentration
    at the same time. Standard recoveries were 100 percent ± 5 percent.

4. The pH Electrode Method also measures aluminum and hydroxide content
    simultaneously, but is less accurate and more time consuming than the
    thermal titration.

Samples were analyzed using all four methods and results were compared to
determine the strengths and weaknesses of each. On the basis of these
comparisons, conclusions were drawn concerning the application of each
method to our laboratory needs.

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INTRODUCTION

The determination of aluminum in basic solutions becomes increasingly more difficult as the Al becomes more concentrated. Nuclear waste solutions which are recycled through an evaporator become progressively more concentrated with aluminum (Al) and hydroxide (OH^-). At these high Al concentrations, atomic absorption spectroscopy no longer gives satisfactory results. The reason seems to be that Al undergoes some type of polymerization at concentrations above 1 $\underline{M}$. Raman spectroscopy confirms that there is some type of structural change (see Figure 1). Because of this problem, new methods were needed to obtain good analytical results.

Many methods and variations have been reported for aluminum determinations including the use of AAS[2], fluoride selective electrodes[3,4,5], thermometric titration[6,7], and pH electrodes.[8] These four methods seemed to be the best for analyzing solutions with high Al content. These techniques are based on procedures already reported, but include significant modification to make them applicable to samples analyzed at Hanford.

The work performed included determining general operating parameters, sample size, precision and accuracy, and interferences. The results were used to compare the methods and their applicability for nuclear waste determination.
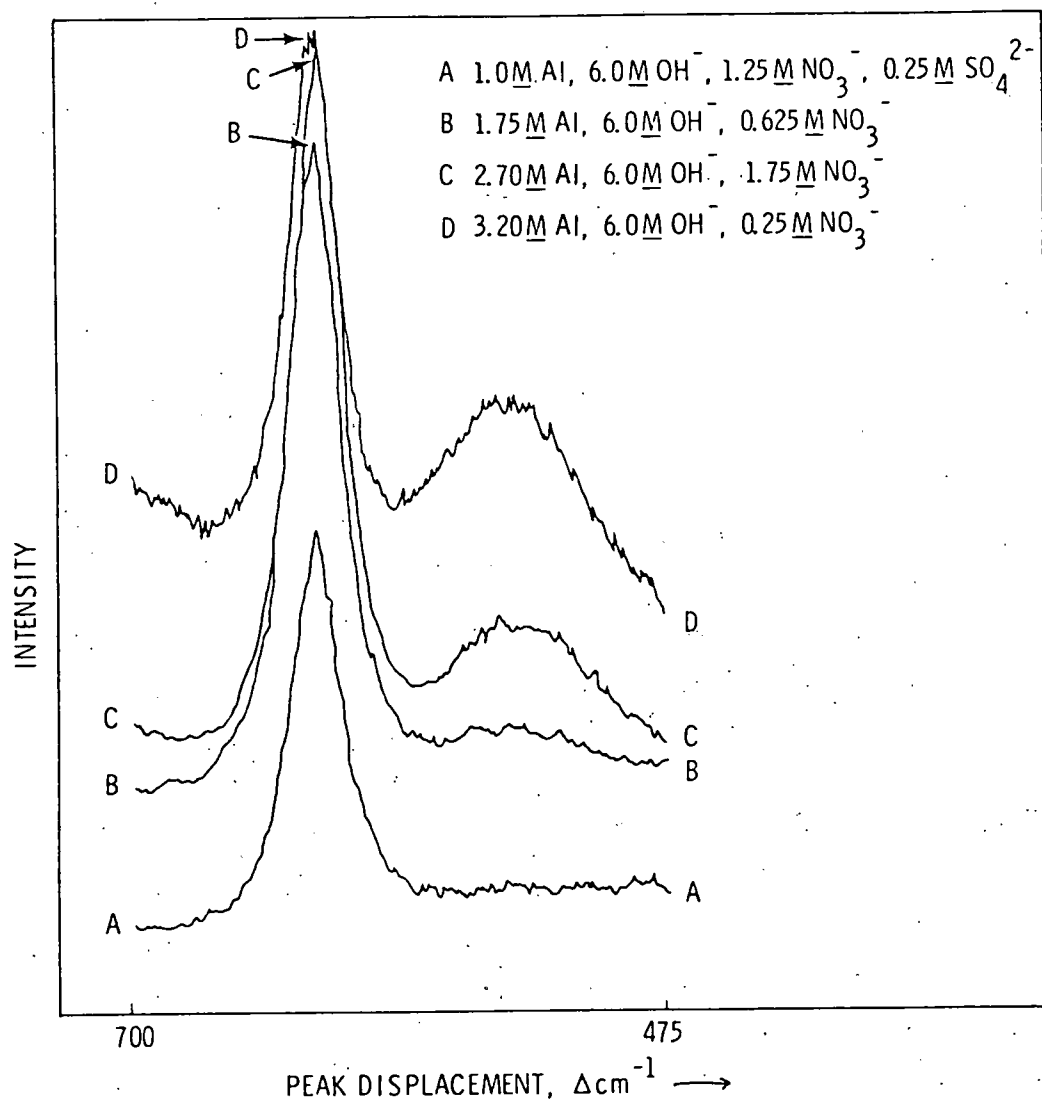
FIGURE 1

RAMAN SPECTRA OF SOLUTIONS CONTAINING Al

SUMMARY AND CONCLUSIONS

Four highly selective and reasonably accurate methods were developed
for determining aluminum (Al) concentration in nuclear waste solutions:
atomic absorption spectroscopy (AAS), thermometric titration, and a
fluoride electrode and a pH electrode method.

1. AAS: The sample and standards are prepared by adding sodium citrate
    to complex the Al. This method is fast and easy to run, but lacks
    precision and accuracy for solutions in which the Al concentration
    exceeds $1\underline{M}$. Also, the cost of obtaining an AAS unit suitable for
    handling radioactive samples can be prohibitive unless such a unit is
    already in operation.

2. Thermometric Titration: This method (based on work by Van Dalen[6])
    is most effective when the Al and OH^- concentrations are greater than
    $1\ \underline{M}$. Below this level, larger sample sizes are needed which poses a
    problem when dealing with radioactive samples. Thermometric
    titration is the fastest of the four methods (about five minutes per
    sample) and has the advantage of giving both and Al and OH^-
    concentrations. Results are reasonably accurate and more precise than
    AAS. There is also little interference from other metal ions due to
    precipitation in the basic solutions and the use of a complexant.

3. Fluoride Selective Electrode: This procedure is based on work done
    by E. W. Baumann at the Savannah River Laboratory[3], but has greater
    sensitivity than the other methods and is the most precise
    (± 2 percent). However, it is also slower than AAS or thermal
    titration. In highly basic matrices ($1.0\ \underline{M}$ to $3.5\ \underline{M}\ OH^-$) such as
    those of interest here, interfering ions precipitate out in the
    hydroxide form in most cases.

4. pH Electrode: This method was also developed by E. W. Baumann[8] and
    was inspired by the thermal titration described above. Oxalate is
    used as a complexing agent in this procedure for determining the
    concentration of Al and OH^-.

    Obtaining accurate end points is a time-consuming process and in
    some cases it is almost impossible. The results are also affected by
    differences in technique from one analyst to the next. Because of
    the time and difficulties involved with this method, it is probably
    most useful in verifying results from another method.

EXPERIMENTAL

REAGENTS

1. Atomic Absorption Spectroscopy

    ### Sodium Citrate (0.1 M)

    Dissolve 29.41 g of $Na_3C_6H_5O_7 \cdot 2H_2O$ in a one liter volumetric flask and dilute to volume with deionized water. Concentration limits are 0.090 to 0.110 $\underline{M}$.

    ### Aluminum Standard (10 g/l in HCl)

    Place 10 g aluminum wire in a 500 ml beaker and add 300 ml of 6 $\underline{M}$ HCl and stir slowly using a magnetic stirrer. When the wire has dissolved, quantitatively transfer the solution to a one liter volumetric flask. Bring to volume with 1 $\underline{M}$ HCl.

2. Thermometric Titration

    ### HCl Standard Solution (1.250 M)

    Dilute 0.104 liters of 12 $\underline{M}$ HCl to one liter, allow to cool and bring to volume. The concentration should be known to the nearest 0.0001 $\underline{M}$ prior to use.

    ### Sodium Tartrate (250 g/l)

    Dissolve 250 g of $Na_2C_4H_4O_6$ in a one liter volumetric flask and dilute to volume with deionized water. This solution is the complexant so concentration need not be known precisely.

    ### Potassium Fluoride (1.75 M)

    Dissolve 164.7 g of $KF \cdot 2H_2O$ in a one liter volumetric flask and bring to volume with deionized water. The concentration need not be known exactly.

3. Fluoride Selective Electrode Method

    ### pH 5 Acetate Buffer

    Add 270 g of $NaC_2H_3O_2 \cdot 3H_2O$ to a one liter volumetric flask. Then pipet in 60 ml of glacial acetic acid and bring to volume with deionized water.

3. Fluoride Selective Electrode Method (Continued)

       <u>Ethyl Alcohol (95%)</u>

       <u>Sodium Fluoride Standard (0.1000 M)</u>

Dry 5 g NaF for 3 hours at 120° C. Dissolve 4.199 g NaF in a one liter volumetric flask and dilute to volume with deionized water.

4. pH Electrode Method

       <u>Sodium Hydroxide Standard (0.1000 M)</u>

This solution is the titrant and should be standardized to four places (0.0001 $\underline{M}$) prior to use.

       <u>HCl Standard (0.1000 M)</u>

This is also used as a titrant and should be standardized to four places (0.0001 $\underline{M}$) prior to use.

       <u>Potassium Oxalate (1 M)</u>

Dissolve 184 g of $K_2C_2O_4 \cdot H_2O$ in a one liter volumetric flask and bring to volume with deionized water.

APPARATUS

1. Atomic Absorption Spectroscopy

       Varian Techtron AA-5 Atomic Absorption/Flame Emission Spectrophotometer.

2. Thermometric Titration

       A Sanda Thermo-Titrator with a radiometer automatic buret. Strip Chart Recorder

3. Fluoride Electrode Method

       Fluoride ion-selective electrode. Digital pH meter that can be read to the nearest 0.1 mV.

4. pH Electrode Method

A combination pH electrode.   Centrifuge.   Hot plate. A pH meter.   Vortex Mixer.

GENERAL PROCEDURE

1.   Atomic Absorption Spectroscopy

The 10 g/l aluminum standard is used to prepare standards ranging
in concentration from 1 μg/ml to 100 μg/ml. Sodium citrate is added
to each of these standards.

The sample is duluted to a concentration of 25 to 40 μg/ml to obtain
the best results. A second aliquot of the sample is diluted in the
same manner, with the addition of 25 μl of 10 g/l Al standard for a
10 ml dilution. Interference effects in a matrix are easily detected
by using a standard spike.

The calibration standards are run first and then the samples and
samples plus spike are run.

The absorbance data collected are used to calculate the aluminum
concentration in the sample solutions. The data points are analyzed
using the least squares method for absorbance verses concentration of
the calibration standards. Using this information, concentration in
μg/ml is determined for the sample and the sample plus spike.

The difference between the Al in the sample and the Al in the sample
plus spike is divided by the known Al in the spike. This number
times 100 represents the spike recovery. This value is very useful
for detecting matrix interference problems. To correct for
interference effects, the sample concentration is multiplied by 100
and divided by the spike recovery. This new concentration is the
"spike corrected" value.

2.   Thermometric Titration

Ten ml of sodium tartrate is placed in an insulated reaction vessel.
The sample (containing ∿0.5 millimoles of Al) is pipetted into the
tartrate solution and stirred for 20 to 30 seconds. Place the
thermistor and delivery tube from the automatic buret into the sample
solution, making sure that the tips are even and are submersed.
Start the strip chart recorder and the titration at the same time.
The buret automatically shuts off at the end point, and the number of
milliliters added are displayed on a counter on the buret. Turn off
the recorder, record the volume of titrant added, and add ∿ 20 ml of
1.75 $\underline{M}$ KF·2H$_2$0. Allow the solution to stir for 30 seconds, then
start the titration again. Record the second volume of HCl added
when the buret stops. When running this procedure, the Wheatstone
Bridge must be balanced prior to eace titration and the stir speed
and titration rates must be adjusted carefully. The accuracy is
affected significantly by titration rates and stir speeds which are
either too fast or too slow.

3.   Fluoride Ion-Selective Electrode Method

The sample size chosen should contain approximately 1 micromole of Al. Pipet this sample into a 100 ml polyethylene beaker and add one drop of methyl red indicator. If the sample turns yellow, add 1 $\underline{M}$ HCl dropwise until a red color appears. If the sample turns red, proceed to the next step. Add 1 ml of pH 5 acetate buffer and $\sim$ 19 ml of 95 percent ethanol. Place the beaker on a magnetic stirrer with a glass covered stir bar. Lower the electrode and observe the potential readings on the digital pH meter. Add 0.1 $\underline{M}$ NaF in 10 μl increments, noting the unstable potential readings from initial additions. Continue adding NaF until the reading stabilized within 15 to 20 seconds. Then make additions in 5 μl increments every 30 seconds. Record the potential 30 seconds after each addition and repeat 7 or 8 times.
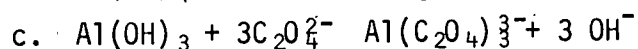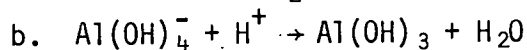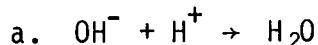
This data is plotted on Gran's Plot Paper without volume correction, since the volume change is insignificant. The end point is determined from the plot and is used to calculate the Al concentration.

4.   pH Electrode Method

Fifty μl of sample is pipetted into a 15 ml centrifuge tube containing 2 ml of deionized water. One ml of $BaCl_2$ is added to remove the carbonate (CO_3^{2-}) sulphate (SO_4^{3-}), and phosphate (PO_4^{3-}). Mix the solution on a Vortex mixer and if any precipitate is formed, centrifuge for three minutes.

Transfer the supernate quantitatively to a 25 ml polyethylene beaker. Titrate to pH 7 with 0.1000 $\underline{M}$ HCl and record the volume used. Add 1 ml of potassium·oxalate ($K_2C_2O_4$) and enough 0.1000 $\underline{M}$ HCl to bring the pH to between 5 and 6. Record the amount of HCl required to do this. Stir for one minute, then titrate again to pH 7 with 0.1000 $\underline{M}$ NaOH, recording the volume used. It is important not to go past pH 7 on the first part of the titration.

The equations involved in this procedure are:

a. $OH^- + H^+ \rightarrow H_2O$

b. $Al(OH)_4^- + H^+ \rightarrow Al(OH)_3 + H_2O$

c. $Al(OH)_3 + 3C_2O_4^{2-} \rightarrow Al(C_2O_4)_3^{3-} + 3 OH^-$

The volume of HCl required to reach pH 7 represents the total OH^- and Al concentration. The difference in the number of moles of NaOH needed to back-titrate to pH 7 and moles of HCl needed to bring the

pH from 7 to between 5 and 6 after oxalate addition is the total OH⁻
released for Al(OH)$_3$. Dividing this value by 3 gives the Al
concentration. The Al value is subtracted from the Al plus OH⁻ number
to obtain the free OH⁻ concentration.

RESULTS AND DISCUSSION

Solutions analyzed were from nuclear waste solutions containing high
aluminum (Al) concentrations ranging from 0.5 $\underline{M}$ to 3.5 $\underline{M}$. The methods
used for analysis were atomic absorption spetroscopy, thermometric
titration, a fluoride electrode method, and a pH electrode method. The
sample matrices typically included anions such as sulphate, phosphate,
carbonate, nitrate, and nitrite and cations such as sodium, potassium,
strontium, cesium, barium, calcium, manganese, iron, magnesium, zirconium,
and rubidium. Synthetic samples representing these matrices were prepared
for developmental work on these procedures.

Atomic absorption spectroscopy had been the normal method of analysis, but
results were very inaccurate for concentrations of aluminum greater than
1 $\underline{M}$. This problem demanded development of new procedures which will be
discussed here.

EVALUATION OF ATOMIC ABSORPTION METHOD

A known amount of standard Al solution was spiked into a sample to check
for matrix interference. The spike recovery obtained was then used to
correct the results for that particular analysis. Aluminum concentrations
below 1 $\underline{M}$ were all found to be quite accurate with a precision of
∿±10 percent when this technique was used. These numbers were adequate
for process control information. But as basic samples with increasing Al
concentrations were submitted, the percent recovery dropped and the results
became unreliable. The samples were being diluted in water, which lowered
the pH enough to cause precipitation of Al in the sample and spike. When
the dilution procedure was changed to dilution in 0.1 M NaOH and then 1 M
HCl there was an improvement in results. However, spike recoveries were
still low, causing the corrected values to be high when compared with
results from other methods (Table I). In most cases the uncorrected value
was better than the corrected one. This caused us to conclude that some
other problem was causing our Al analyses to be incorrect.

At concentrations above 1 $\underline{M}$, Al undergoes some type of polymerization.
Raman spectroscopy has confirmed this structural change (Figure 1). The
spectra in Figure 1 are for four solutions each containing Al, OH⁻, and
nitrate in varying concentrations. At concentrations above 1 $\underline{M}$ Al a new
peak at 535 cm⁻¹ develops, becoming more intense as the Al increases. A
peak at 690 cm⁻ also develops but it cannot be seen in these spectra
because of the nitrate peak at 710 cm⁻¹. The intensity of the aluminate
peak at 624 cm⁻¹ increases with concentration increases, but it does so
at a slower rate than the 535 and 690 cm⁻¹ peaks.

TABLE I

ALUMINUM CONCENTRATION IN EIGHT SYNTHETIC SAMPLES BY FOUR

INDEPENDENT METHODS

SAMPLE	AAS		THERMO-	F^-	pH
	UNCORRECTED	CORRECTED	TITRATOR	ELECTRODE	ELECTRODE
1	2.01 M	2.56 M	2.21 M	2.24 M	2.26 M
2	1.27	1.65	1.16	1.20	1.25
3	1.35	1.61	1.47	1.47	1.42
4	1.92	2.70	2.32	2.20	2.25
5	2.10	2.62	2.30	2.40	2.42
6	1.81	2.35	1.79	1.84	1.75
7	1.66	1.82	1.72	1.57	1.67
8	1.79	2.56	2.16	1.90	1.93

The addition of complexing agents such as fluoride (F^-) and ethylenediaminetetracetate (EDTA) has been shown to increase the sensitivity of Al analysis.[1]   The complexing agents should also convert all the Al to the same form and given more accurate values.   Tables II and III show that spike corrected concentrations agree better with other methods when a complexant is used.   However, the fluoride results were still unacceptable and the EDTA standards would not remain stable longer than a day or two (see Table IV).   The low solubility of the complexes formed was another problem encountered, particularily with the EDTA.

Sodium citrate was also examined for use as a complexant.   The solubility for these complexes was higher than for EDTA and the calibration standards remained stable for at least three weeks.   The citrate results were significantly better than those from the other complexing agents (Table V).

EVALUATION OF THERMOMETRIC TITRATION

The thermo-titrator operates on the principle that each reaction has a particular heat of reaction associated with it.   By measuring these heats of reaction, it is possible to determine the end point of a titration.

Samples high in Al content are added to a sodium tartrate solution to complex the Al.   However, this displaces 1 OH^- from the aluminate ($Al(OH)_4^-$), increasing the initial OH^- concentration.   This total OH^- content is titrated automatically with an auto-buret.   A first derivative plot of the potential change produced by the heat change in the reaction vessel is plotted on a strip chart recorder.   Figure 2 shows both the
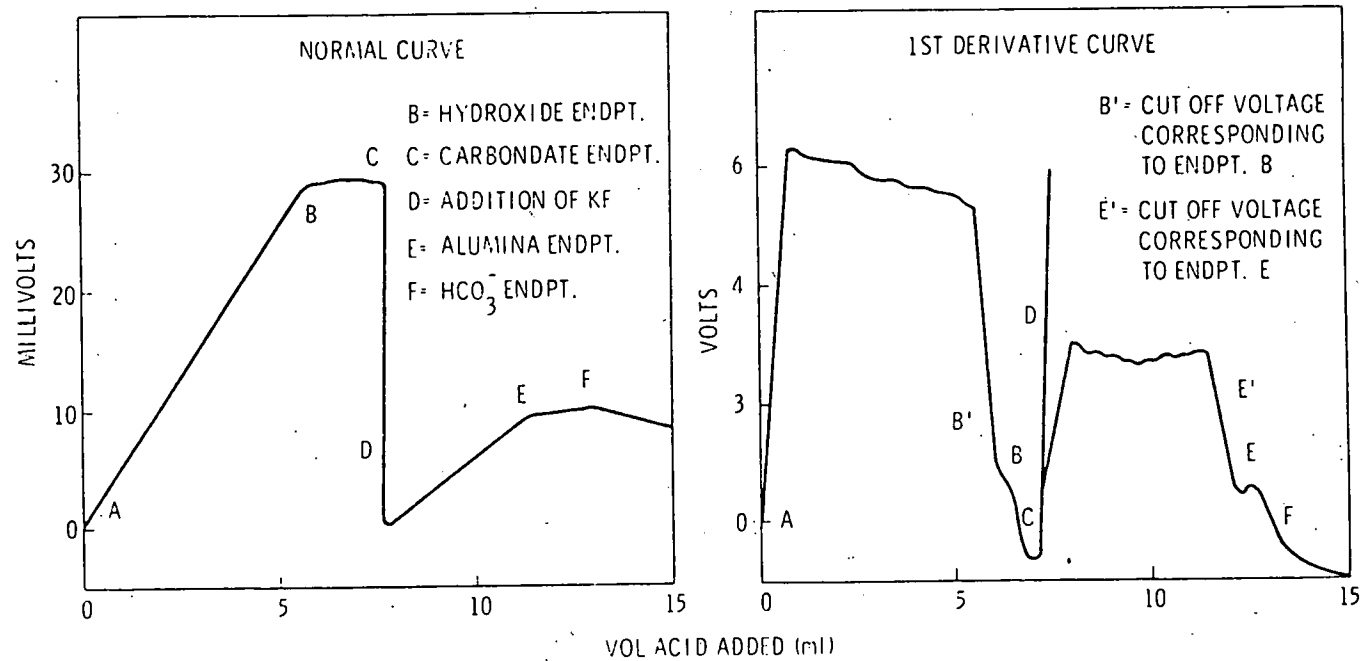
FIGURE 2

NORMAL AND FIRST DERIVATIVE CURVES FOR THE TITRATION OF A SOLUTION CONTAINING OH^-, $Al(OH)_4^-$, AND CO_3^{2-}

TABLE II

COMPARISON OF AAS RESULTS FOR Al CONCENTRATION WITH AND WITHOUT FLUORIDE AS A COMPLEXANT

SAMPLE	WITHOUT F^-		WITH F^-	
	UNCORRECTED	CORRECTED	UNCORRECTED	CORRECTED
1	2.01 M	2.56 M	1.83 M	2.41 M
2	1.27	1.65	1.08	1.35
3	1.35	1.61	1.24	1.46
4	1.92	2.70	2.00	2.52
5	2.10	2.62	2.21	2.51
6	1.81	2.35	1.54	1.90
7	1.66	1.82	1.30	1.76
8	1.79	2.56	1.72	2.10

TABLE III

COMPARISON OF AAS RESULTS FOR Al CONCENTRATION WITH AND WITHOUT EDTA AS A COMPLEXANT

SAMPLE	WITHOUT EDTA		WITH EDTA	
	UNCORRECTED	CORRECTED	UNCORRECTED	CORRECTED
1	2.01 M	2.56 M	2.25 M	3.41 M
2	1.27	1.65	0.92	1.01
3	1.35	1.61	1.29	1.47
4	1.92	2.70	2.05	2.41
5	2.10	2.62	2.08	2.24
6	1.81	2.35	1.68	1.89
7	1.66	1.82	1.58	1.72
8	1.79	2.56	1.81	2.13

TABLE IV

EFFECT OF TIME ON THE CONCENTRATION OF 40 µg/ml Al STANDARDS COMPLEXED WITH EDTA

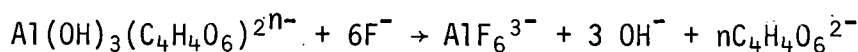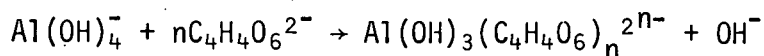| AGE OF STANDARD (DAYS)	APPARENT Al CONCENTRATION (µg/ml)
0	41
1	39
3	38
7	35
14	32
21	30

TABLE V

AAS RESULTS FOR Al CONCENTRATION WITH AND WITHOUT CITRATE AS A COMPLEXANT. CITRATE VALUES ARE SPIKE CORRECTED

SAMPLES	WITHOUT CITRATE		WITH CITRATE		
	UNCORRECTED	CORRECTED	FRESH	1 WEEK OLD	3 WEEKS OLD
1	2.01 M	2.56 M	2.25 M	2.22 M	2.64 M
2	1.27	1.65	1.09	1.11	1.19
3	1.35	1.61	1.51	1.79	1.44
4	1.92	2.70	2.18	2.24	2.29
5	2.10	2.62	2.19	2.32	2.21
6	1.81	2.35	1.79	1.92	1.86
7	1.66	1.82	1.87	1.81	1.90
8	1.79	2.56	1.85	2.14	2.02

regular output and the first derivative plot for a complete titration of a system containing carbonate (CO_3^{2-}) in addition to $Al(OH)_4^-$ and OH^-. The system is designed so that when the potential for the first derivative drops below two millivolts the titration is automatically halted.

After the first titration is completed, KF is added to complex the Al completely, freeing the remaining OH^-. The entire procedure requires about five minutes. The two complexant reactions are:

$$Al(OH)_4^- + nC_4H_4O_6^{2-} \rightarrow Al(OH)_3(C_4H_4O_6)_n^{2n-} + OH^-$$

$$Al(OH)_3(C_4H_4O_6)^{2n-} + 6F^- \rightarrow AlF_6^{3-} + 3\ OH^- + nC_4H_4O_6^{2-}$$

The 3 OH^- released are titrated using the same procedure. The number of millimoles (mmoles) of acid added in the second titration is divided by three to obtain the number of millimoles of Al.

The total hydroxide found in the first titration minus the Al concentration equals the initial OH^- concentration. Table VI lists results for a series of synthetic samples. Table VII shows the effect of decreasing either the OH^- or the $Al(OH)^-$ content.

TABLE VI

RESULTS OF Al ANALYSIS USING THE THERMO-TITRATOR

KNOWN Al CONCENTRATION	DETERMINED Al CONCENTRATION
0.120 M	0.119
0.195	0.189
0.200	0.209
0.200	0.199
3.23	3.33

TABLE VII

THE EFFECT OF CHANGING THE OH^- AND Al CONTENT FOR THE THERMO-TITRATOR

mmoles OH^-	KNOWN mmoles Al	DETERMINED mmoles Al
2.50	0.500	0.500
2.50	0.300	0.301
2.50	0.200	0.199
2.50	0.100	---
2.00	0.400	0.412
1.50	0.300	0.294
1.00	0.200	0.194
0.50	0.100	---

Normally, the limiting factor for this method is the amount of Al present. If less than two millimoles of Al in the sample the results are erroneously high. The amount of OH⁻ can be quite low as long as the Al limitation is observed.

EVALUATION OF FLUORIDE ELECTRODE METHOD

The fluoride electrode procedure is based upon the use of sodium fluoride (NaF) as the titrant. Figure 3 shows a typical titration curve. Potential readings taken before the end point are extremely unstable, causing the determination to be very time consuming if one waits for a stable reading. The end point can be more quickly and accurately determined by adding an excess of NaF, then making small incremental additions, recording the potential after each addition. Table VIII compares the two methods of titrating to the end point and using Gran's Plot Paper to determine this value. There is little difference in the precision or accuracy.

TABLE VIII

COMPARISON OF TITRATING TO THE END POINT VERSUS USE OF GRAN'S PLOT FOR THE FLUORIDE ELECTRODE

KNOWN Al CONCENTRATION	END POINT DETERMINATION	GRAN'S PLOT DETERMINATION
0.200 M	0.193 M	0.195 M
0.400	0.395	0.394
0.020	0.0196	0.0198
0.0010	0.00101	0.00098
1.000	0.996	0.999

Another problem arises in titrating to the end point. The pH of the buffer solution becomes critical in this method, but does not affect the Gran's plot method. Table IX shows the difference between methods for variance of the buffer pH.

TABLE IX

EFFECT OF CHANGING THE BUFFER FOR Al DETERMINATION USING THE FLUORIDE ELECTRODE

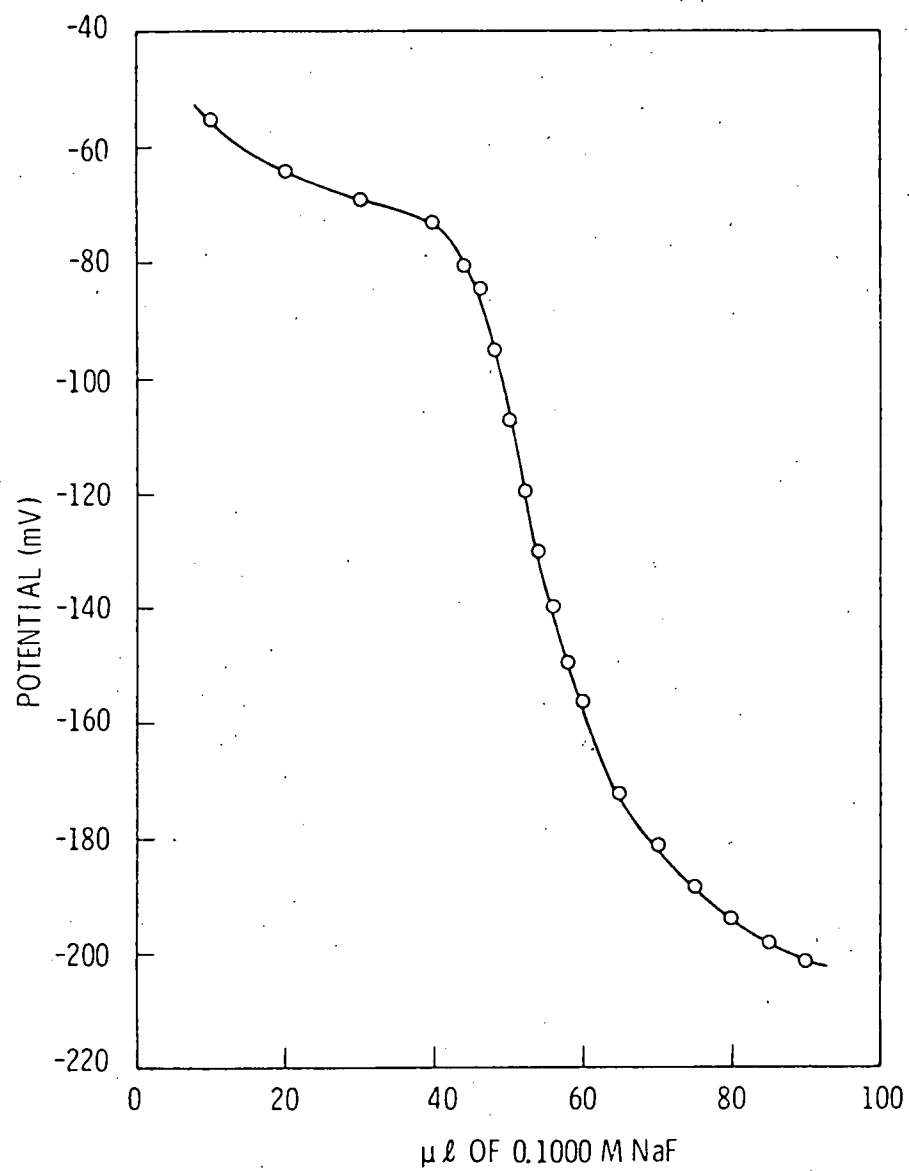| pH OF BUFFER	KNOWN Al CONCENTRATION	END POINT DETERMINATION	GRAN'S PLOT DETERMINATION
3.65	0.0374 M	0.0391 M	0.0369 M
4.32	0.0374	0.0363	0.0370
4.82	0.0374	0.0339	0.0368
5.00	0.0374	0.0367	0.0372
5.50	0.0374	0.0355	0.0362

FIGURE 3

TYPICAL TITRATION CURVE FOR THE TITRATION OF ALUMINUM
WITH FLUORIDE

Either methanol or ethanol can be used without affecting the results, but ethanol is safer to work with and was used for this reason.

Results from a number of standards and samples indicate that the method is extremely sensitive and that is is probably the most versatile of the methods examined.

EVALUATION OF pH ELECTRODE METHOD

The acid-base titration curve for $Al(OH)_4^-$ and OH^- contains two distinct breaks (see Figure 4). The added acid reacts almost entirely with the free OH^- up to the first break. As the OH^- content decreases, the $Al(OH)_4^-$ begins to effectively compete for the acid, converting the $Al(OH)_4^-$ to $Al(OH)_3$ until the second break occurs. Using the first break alone to determine OH^- concentrations does not give accurate values (see Table X).

TABLE X

OH^- CONCENTRATION USING THE FIRST TITRATION BREAK

Al CONCENTRATION	ACTUAL OH^- CONCENTRATION	DETERMINED OH^- CONCENTRATION
0.100 M	0.135 M	0.141 M
0.106	0.450	0.462
0.252	0.750	0.795
0.361	1.004	1.101
0.502	1.620	1.740
0.711	2.011	2.105

Originally an attempt was made to determine the Al concentration from the difference between the two breaks. In most cases, this difference was small compared to the amount of acid required to reach the first break. Consequently, a small error in the OH^- determination produced a large error in the Al concentration.

To circumvent this problem, the total OH^- plus Al concentration is determined by titrating to the second break. Oxalate ($C_2O_4^{2-}$) is added to complex the Al and release the OH^-. This reaction is slow, making it necessary to add a known amount of acid to drive the reaction to completion. This acid is added until the solution remains at a constant pH between 5 and 6. At this point the sample is titrated to pH 7 with
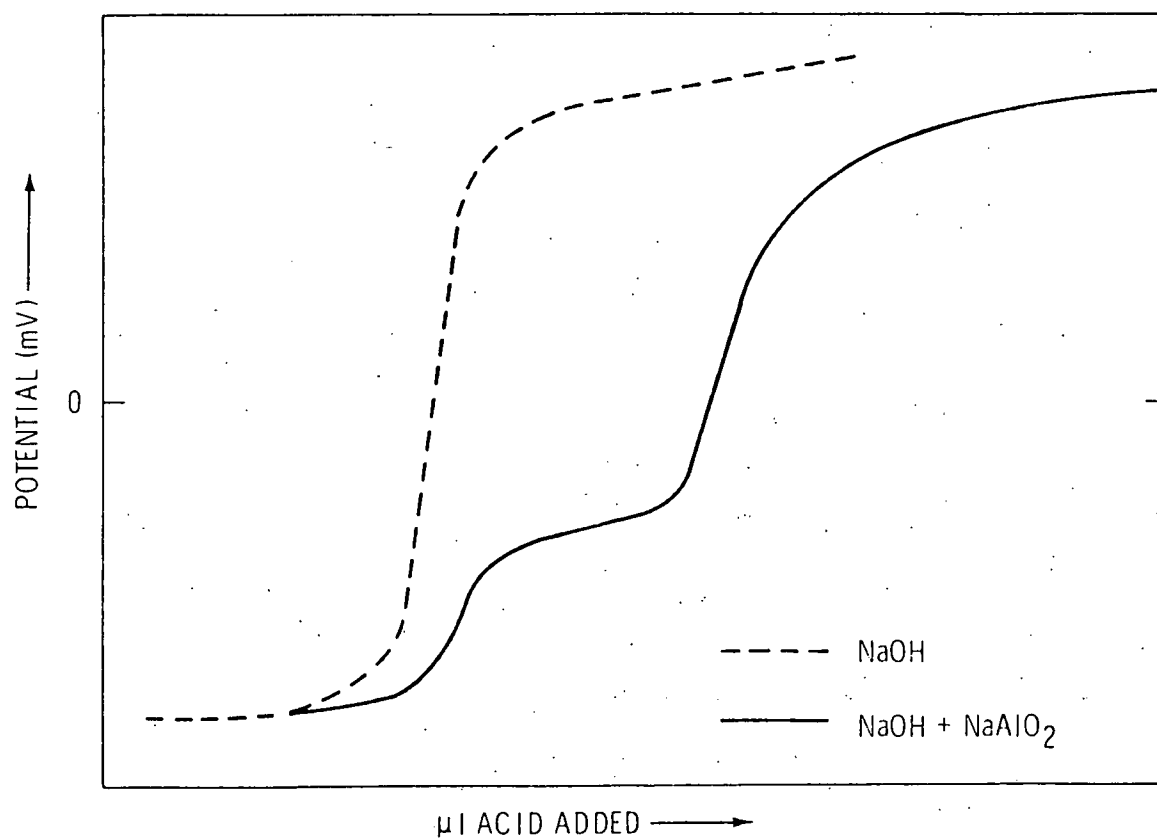
FIGURE 4

TITRATION CURVES FOR BASIC SOLUTIONS WITH AND WITHOUT $Al(OH)_4^-$

0.1000 M NaOH. Table XI lists results obtained with this procedure. Although the results are good, the procedure is time consuming and easily biased by differences in technique.

TABLE XI

DETERMINATION OF Al USING THE pH ELECTRODE

ACTUAL Al CONCENTRATION	DETERMINED Al CONCENTRATION
0.091 M	0.087M
0.151	0.153
0.202	0.199
0.400	0.410
0.499	0.491
0.751	0.748
1.011	1.078

An automatic differential titrator may be used to obtain these results more quickly. Final work with this technique has not been carried out yet but the preliminary data indicates the feasibility of such a system. A procedure similar to this has already been developed.[9] By using a first derivative output, two peaks will be observed as the titration proceeds. This is shown in Figure 5. The peaks are located at the same places as the breaks in the titration curves. The titration continues to just past the second peak where it is halted long enough to add the $C_2O_4^{2-}$ and then acid is added until the pH remains between 5 and 6. The solution is back-titrated with base until a peak appears in the first derivative output. The same calculations are used here as were used with the manual method.

INTERFERING ION STUDIES

The effect of various ions were examined for each procedure using synthetic samples. The results of these studies are given in Table XII.

The results for the AAS do not show interference effects since all values are spike corrected. Spike correction is used to negate interference effects, but we have seen that the results are not always reliable.

TABLE XII

EFFECTS OF VARIOUS IONS UPON EACH METHOD

| ION	ACTUAL Al CONCENTRATION	DETERMINED Al CONCENTRATION (M)			
		AAS WITH CITRATE	THERMO-TITRATOR	F^- ELECTRODE	pH ELECTRODE
$0.2M\ NO_3^-$	0.200 M	0.210 M	0.202 M	0.201 M	0.206 M
$0.2M\ NO_2^-$	0.200	0.216	0.201	0.200	0.199
$0.2M\ PO_4^{-3}$	0.200	0.205	0.197	0.197	0.189
$0.2M\ SO_4^{-2}$	0.200	0.189	0.200	0.195	0.192
$0.2M\ CO_3^{-2}$	0.200	0.201	0.203	0.195	0.211
$0.2M\ Na^+$	0.200	0.190	0.192	0.201	0.215
$0.2M\ K^+$	0.200	0.192	0.195	0.204	0.189
$0.2M\ Sr^{+2}$	0.200	0.206	0.205	0.191	0.189
$0.2M\ Cs^+$	0.200	0.201	0.206	0.200	0.201
$0.2M\ Ba^{+2}$	0.200	0.195	0.191	0.201	0.212
$0.2M\ Ca^{+2}$	0.200	0.204	0.200	0.190	0.207
$0.2M\ Mn^{+2}$	0.200	0.191	0.430	0.189	0.193
$0.2M\ Fe^{+3}$	0.200	0.183	0.210	0.211	0.202
$0.2M\ Mg^{+2}$	0.200	0.211	0.195	0.205	0.187
$0.2M\ Zr^{+4}$	0.200	0.191	0.420	----	0.193
$0.2M\ Rb^+$	0.200	0.205	----	0.195	0.208
$0.2M\ Cd^{+2}$	0.200	0.201	0.208	0.199	0.195
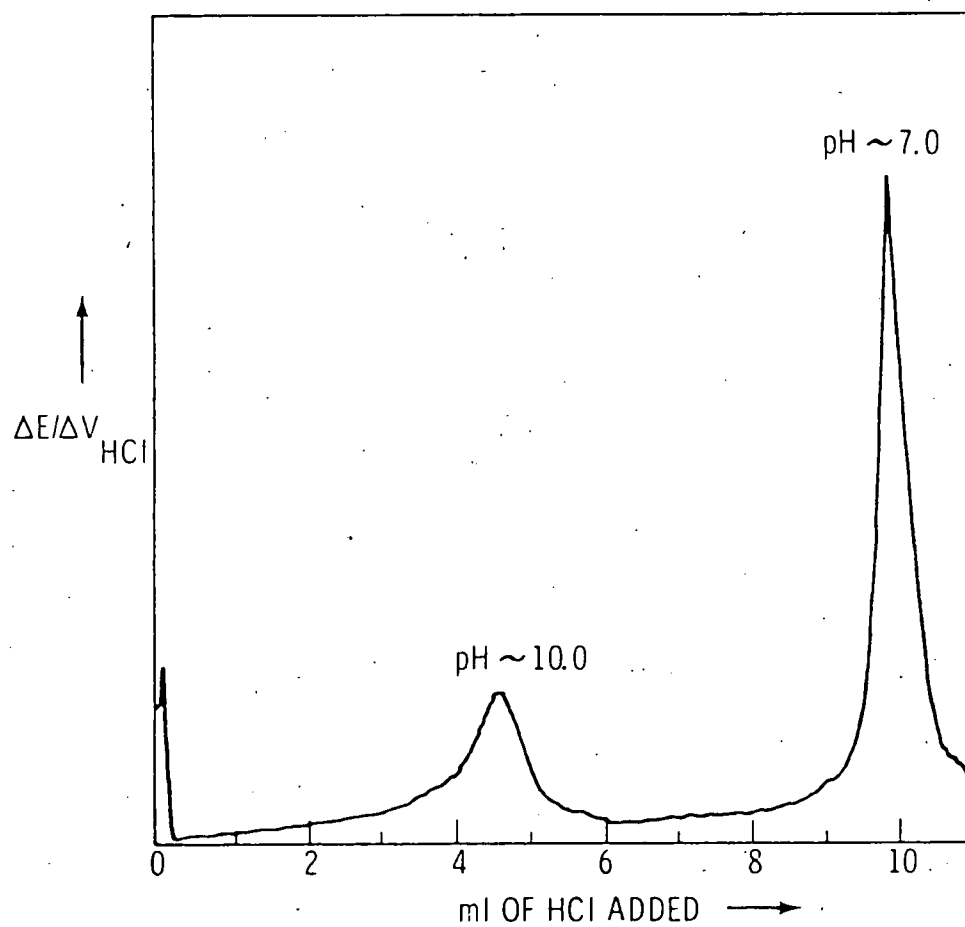
FIGURE 5

TWO PEAKS OBSERVED IN DIFFERENTIAL TITRATION OF OH^- AND $Al(OH)_4^-$

Most metal ions will interfere with Al determinations using the fluoride
electrode. But with the addition of base, most metals precipitate out
in the hydroxide form. The samples we analyzed were basic, so no serious
problems arose. Addition of OH^- to acidic samples prior to running the
procedure has the same effect.

The pH electrode method had the fewest interference problems. For this
reason, this method can be used as a check for the other methods.

The thermometric titration method was also relatively free from
interference, except for manganese and zirconium. Any precipitate should
be removed prior to analysis.

PRECISION AND ACCURACY

Table XIII is a comparison of accuracy and precision for each method.
Each number was determined from a series of 10 sample analyses. These
samples represented a cross-section of the types of samples we were
handing.

TABLE XIII

ACCURACY AND PRECISION AT THE 95% CONFIDENCE LEVEL

SAMPLE	AAS	THERMO-TITRATOR	F^- ELECTRODE	pH ELECTRODE
1 1.89M NaOH 0.191M Al	101.1 ± 10.9%	99.9 ± 4.1%	98.9 ± 2.1%	97.8 ± 6.5%
2 2.80M OH^- 0.20M SrCl$_2$ 0.20M Al	100.9 ± 11.3%	104.1 ± 6.7%	99.6 ± 1.9%	98.3 ± 7.2%
3 1.01M OH^- 0.20M Al	99.7 ± 10.1%	99.8 ± 4.6%	99.3 ± 2.3%	101.3 ± 7.6%

The three synthetic samples used are described in Table XIII. This list
shows that all four methods give results close to the actual aluminum
concentration. Precision is the major difference between procedures.

Precision for AAS results were around ±11 percent at the 95 percent
confidence level. The fluoride electrode was ~±2 percent at the
95 percent C. L., and the thermal titration and pH electrode methods
were ±4.6 percent and ±7.6 percent respectively.

APPLICATIONS

Each method examined has different merits depending upon desired results and the type of matrix. Speed and accuracy vary with every method as the concentration and ionic character change.

AAS is the best method for samples containing less than 1 $\underline{M}$ aluminum if poor precision can be tolerated. Ease of operation, speed, and the use of citrate to complex the Al and improve results makes this method a useful one.

The thermo-titrator is most effective with samples with high Al content. This method is very easy and rapid to run. Low Al concentrations cause problems since larger sample sizes are needed, thus increasing the radiation from radioactive samples. Exposure limits become a factor for consideration.

The fluoride titration method is useful with any concentration of Al. This fact makes it a valuable check and backup procedure. The potential problem of interfering metal ions is reduced considerably for highly basic nuclear waste material.

A pH electrode and simple pH meter are generally available in most laboratories, making Al determination possible where it is not being done on a routine basis. For repetitive analysis, this procedure is too time-consuming and another should be used.

ACKNOWLEDGMENT

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