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**VOLUMETRIC DETERMINATION OF HYDROXIDE,
ALUMINATE, AND CARBONATE IN ALKALINE
SOLUTIONS OF NUCLEAR WASTE**

E. W. BAUMANN

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**VOLUMETRIC DETERMINATION OF HYDROXIDE,
ALUMINATE, AND CARBONATE IN ALKALINE
SOLUTIONS OF NUCLEAR WASTE**

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ABSTRACT

An integrated procedure was developed for determining OH^- , $\text{Al}(\text{OH})_4^-$, and CO_3^{2-} in alkaline nuclear waste. The free alkali, the hydroxide released when $\text{Al}(\text{OH})_3$ is complexed with oxalate, and the precipitated BaCO_3 were determined by acidimetric titration. With a 50- μl sample, the relative standard deviations were 1 to 2% for non-radioactive test solutions and 2 to 5% for radioactive process solutions.

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VOLUMETRIC DETERMINATION OF HYDROXIDE, ALUMINATE, AND CARBONATE IN ALKALINE SOLUTIONS OF NUCLEAR WASTE

INTRODUCTION

Alkaline nuclear waste solutions from the Savannah River Plant (SRP), which are principally by-products from uranium and plutonium recovery, contain the alkaline components NaOH, NaAl(OH)_4 , and Na_2CO_3 . Determination of the concentration of these components, among others, is required for characterization of this highly radioactive waste and for evaluation of processes for waste management.

In a survey of SRP stored wastes,¹ the hydroxide concentration was calculated from pH determined in salt solutions² at $\text{pH} \geq 14$; the aluminate and carbonate were determined by laser-Raman spectrometry.³ Poor cation-anion material balance obtained in this and other work was blamed in part on the recognized imprecision of the hydroxide determination. Use of two different methods to determine these interdependent species also may have contributed to the poor material balance.

A better method was needed for supporting the continuing waste management studies. Sequential titration appeared feasible and attractive. The procedure developed combines precipitation and complexation to separate the components into titratable segments. All three analyses can be performed on a single, small (50 μl) sample of waste, which minimizes personnel exposure.

REVIEW OF METHODS

Determination of the combination of hydroxide, aluminate, and carbonate in solution has been of continuing interest for process control in the aluminum industry. A variety of titrimetric methods have been suggested, based on selective titration of each alkaline component.⁴⁻⁸

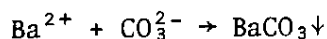
The free hydroxide has been titrated to an empirical pH value or to the visible precipitation of Al(OH)_3 . Aluminum has been determined through the acid or base released on complexation or by precipitation as the fluoroaluminate. Carbonate has been separated by precipitation as barium carbonate and titrated with acid. End points have been detected by visual observation of the onset of Al(OH)_3 precipitation, by acid-base indicators, by pH measurement, and by thermometry.

The method described in this report is an adaptation of a procedure that employs oxalate as complexing agent.⁸ The end points are detected at pH 7 with a pH meter.

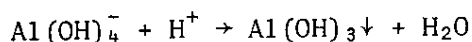
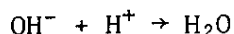
GENERAL PROCEDURE*

The procedure consists of three acid-base titrations, each to pH 7: the first determines molarity of OH⁻ plus Al(OH)₄⁻; the second determines three times the Al(OH)₄⁻ molarity; and the third determines two times the CO₃²⁻ molarity.

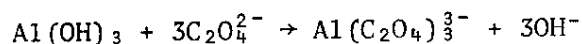
After carbonate is separated by addition of barium chloride



the hydroxide and aluminate, which remain in solution, are neutralized by titration with acid.

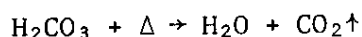
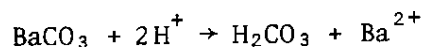


The aluminum in the freshly formed Al(OH)₃ is then complexed, with release of 3OH⁻, by addition of excess potassium oxalate:⁸



The reaction is forced to completion by addition of excess standard HCl, which is subsequently back-titrated with standard NaOH.

The barium carbonate precipitate is dissolved in a known quantity of excess standard acid. The solution is heated to expel CO₂.



The excess acid is titrated with NaOH.

TITRATION CURVES

Titration curves for neutralization of hydroxide and aluminate in the presence and absence of carbonate are shown in Figure 1. The presence of carbonate affects the pH and the shape of the

* A detailed experimental procedure is given in the Appendix.

curve at the equivalence point. In the absence of carbonate, the inflection point in the curve at pH ~ 7 is well-defined. Although precipitation of $\text{Al}(\text{OH})_3$ is reported to be complete between pH 6 and 7,⁹ the slope of this curve is sufficiently steep that little error is introduced by consistent designation of the end point at pH 7.

The curves also show that precipitation of $\text{Al}(\text{OH})_3$ commences at pH ~ 9.5 , and that dissolution of the $\text{Al}(\text{OH})_3$ is complete at pH ~ 4.5 . Although the shape of the titration curves will indicate the presence of aluminum, the breaks are not sharp enough and the pH values are not consistent enough for quantitative determination of aluminum from titration curves.

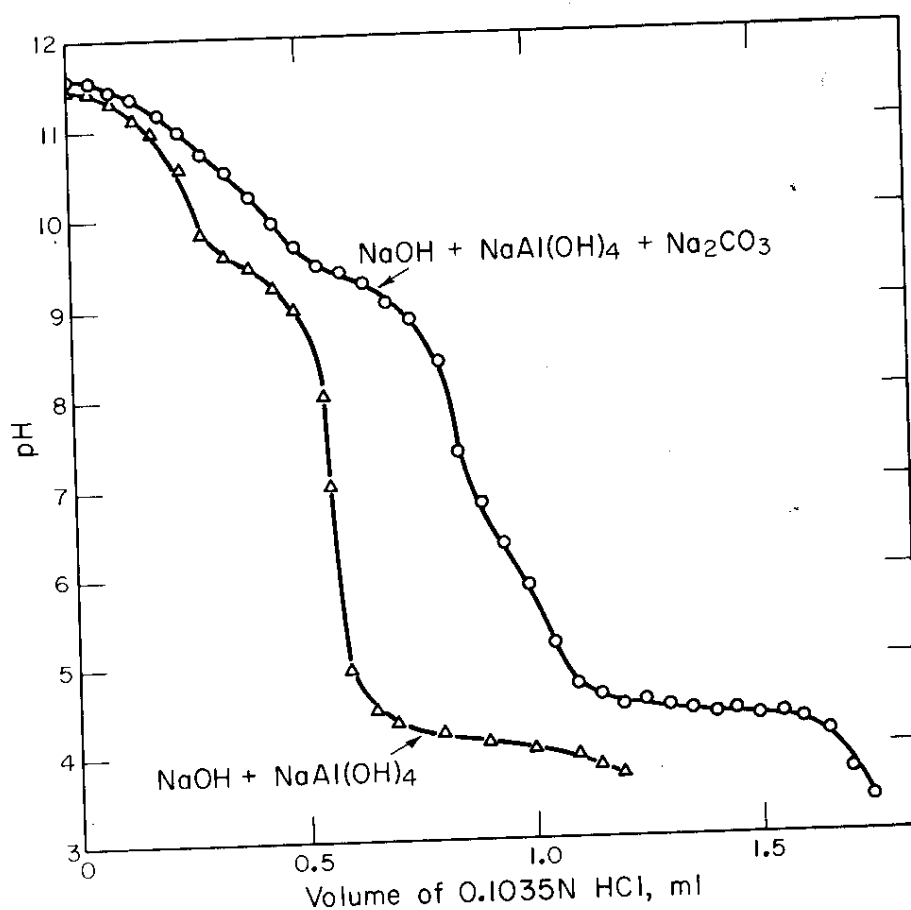


FIG. 1 TITRATION CURVES OF SODIUM ALUMINATE SOLUTIONS

ACCURACY AND PRECISION

Solutions in Table 1 were prepared to nominal (but not primary standard) concentrations by dissolving weighed amounts of solid reagents. Little bias is indicated for the hydroxide and carbonate determinations. For both solutions, however, the aluminate concentration was biased 6% low. The results may reflect a low assay for the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ reagent, which was used in preparation of these solutions. An independent determination of aluminum by EDTA titration (shown in parentheses in Table 1) gave aluminum values that agreed with those obtained by the titration method within experimental error.

A standard solution was later prepared by dissolving high-purity aluminum in sodium hydroxide. The aluminum concentration determined by the titration method showed no bias and agreed with that found by EDTA titration.

TABLE 1
ANALYSIS OF PREPARED SOLUTIONS

	OH^-	$\text{Al}(\text{OH})_4^-$	CO_3^{2-}
<i>NaOH + Al(NO₃)₃ + Na₂CO₃</i>			
Nominal, M	0.0412	0.0333	0.0333
Found, M ^a	0.0425	0.0315	0.0337
		(0.0319) ^d	
RSD, % ^b	1.4	2.2	2.4
Bias from Nominal, %	+3	-6	+1
<i>Simulated High-Level Waste Supernate^c</i>			
Nominal, M	0.75	0.50	0.30
Found, M ^a	0.734	0.466	0.310
		(0.477) ^d	
RSD, % ^b	1.4	0.4	1.3
Bias from Nominal, %	-2	-6	+3

a. Average of ≥ 5 determinations, 2 experimenters.

b. Relative standard deviation.

c. 0.5M $\text{NaAl}(\text{OH})_4$, 0.75M NaOH , 2.2M NaNO_3 , 1.1M NaNO_2 , 0.3M Na_2SO_4 , 0.3M Na_2CO_3 .

d. Al^{3+} determined by EDTA titration.

Results of duplicate analyses of a series of high-level waste solutions, determined on 50- μ l samples, are given in Table 2. The relative standard deviation of 2 to 5% for this series indicates the range of precision to be expected in analyses of high-level waste samples. Remote pipetting and handling of the radioactive samples may explain the loss in precision between these solutions and the nonradioactive solutions in Table 1.

TABLE 2
ANALYSIS OF HIGH-LEVEL WASTE SOLUTIONS

Sample	Concentration of Constituent, M					
	OH^-		$\text{Al}(\text{OH})_4^-$		CO_3^{2-}	
1	1.254	1.184	0.295	0.305	0.200	0.200
2	0.412	0.422	0.356	0.350	0.152	0.171
3	7.595	7.580	0.550	0.560	0.137	0.124
4	6.884	6.720	0.466	0.514	0.088	0.090
5	2.505	2.587	0.198	0.181	0.127	0.128
6	1.680	1.631	0.101	0.105	0.081	0.085
7	1.656	1.648	0.112	0.103	0.104	-
RSD, α %	1.7		5.0		5.1	

α . Relative standard deviation.

INTERFERENCES

Sulfate does not interfere with the analysis. Barium sulfate precipitates along with the carbonate, but it does not dissolve in the excess acid added.

Phosphate interferes in the carbonate determination by the procedure described, where the titration end point is designated as pH 7.* Barium phosphate precipitates with the barium carbonate and subsequently dissolves in the acid added. Because the phosphate does not decompose on heating, the resulting phosphoric acid makes part of the excess acid inaccessible to titration and also shifts the end point. Differential methods can be used to make a phosphate correction.

* T. J. Hanson, Atlantic Richfield Hanford Company, personal communication (1974).

APPENDIX: EXPERIMENTAL PROCEDURE

Apparatus

Expanded Scale pH Meter
Vortex Mixer
Hot Plate
Centrifuge
Magnetic Stirrer
Combination Glass Electrode, such as Beckman 39501
15-ml Conical Centrifuge Tubes, with Cap
Micropipet, such as *Digipet*,** 1 ml
*Teflon** stirring Bars, 10mm x 3mm
10 ml Beakers
Micropipets and Transfer Pipets, as required

Reagents

0.1N HCl, standardized
0.1N NaOH, standardized
0.5M barium chloride (104 g BaCl₂/ℓ)
1M potassium oxalate (184 g K₂C₂O₄·H₂O/ℓ)
Buffer solution, pH 7

Procedure

1. With the glass electrode in pH 7 buffer, adjust the pH meter to read 7.0 on both the standard and expanded scales.
2. Pipet 50 μl (or other appropriate volume) of sample into a centrifuge tube that contains about 2 ml of H₂O.
3. Add ∼1 ml 0.5M BaCl₂.
4. Mix on Vortex mixer.
5. Centrifuge to separate precipitate.

NOTE: Keep sample in closed centrifuge tube until immediately before the titration (Step 6). This solution is subject to change in composition by absorption of CO₂ from the air, with precipitation of BaCO₃; a precipitate in the solution to be titrated is unacceptable.

6. Quantitatively transfer supernate to 10-ml beaker; rinse tube carefully with ∼1 ml of H₂O, taking care not to disturb the precipitate. Add rinse to solution in beaker. (If precipitate is disturbed, centrifuge again before removing supernate.) Replace cap on tube and reserve the precipitate for carbonate determination.

* Registered tradename of Du Pont.

** Registered tradename of Manostat Corp., NY.

7. Proceed at once to titrate the solution for OH^- and $\text{Al}(\text{OH})_4^-$, as follows:
 - a. Titrate with 0.1N HCl to pH 7. (Make final adjustment of pH with meter on expanded scale.) Record volume required; call this A.
 - b. Add 1 ml of $\text{K}_2\text{C}_2\text{O}_4$,* and then add an excess of 0.1M HCl from the refilled buret, so that the pH is permanently at 5-6. Record the volume of HCl added to the solution; call this B.
 - c. Allow the solution to stir \sim 1 min. Then titrate with standard 0.1N NaOH to pH 7 (on expanded scale). Record volume of NaOH; call this C.
8. Determine CO_3^{2-} content of precipitate from Step 6 as follows:
 - a. Add \sim 1 ml of H_2O and 1000 μl of HCl to the precipitate and agitate to dislodge precipitate. Total volume should be 2 to 3 ml. Mix on Vortex mixer.
 - b. Loosen cap of centrifuge tube and place tube in boiling water for 10 min. Mix again on Vortex mixer to expel CO_2 . (If sulfate is present, all of the precipitate will not dissolve.)
 - c. Quantitatively transfer solution (with rinse) to 10 ml beaker and titrate to pH 7 (on expanded scale) with 0.1 N NaOH. Record volume required; call this D.

Calculations

$V = \text{ml of sample}$

Titration of OH^- and $\text{Al}(\text{OH})_4^-$

A = ml of HCl to first end point, Step 7.a.

B = ml of HCl added in Step 7.b.

C = ml of NaOH added in Step 7.c.

Titration of CO_3^{2-}

D = ml of NaOH added in Step 8.c.

* The Ba^{2+} remaining in solution from the carbonate precipitation step precipitates as BaC_2O_4 ; this does not interfere in the determination, but it consumes oxalate so that the amount of oxalate added must be greater than Ba^{2+} to ensure that sufficient oxalate is available to complex the aluminum.

1. Molarity of $\text{OH}^- + \text{Al}(\text{OH})_4^- = \frac{(\text{A}) (\text{N of HCl})}{V}$
2. Molarity of $\text{Al}(\text{OH})_4^- = \frac{(\text{B}) (\text{N of HCl}) - (\text{C}) (\text{N of NaOH})}{3 \cdot V}$
3. Molarity of $\text{OH}^- = [(1) - (2)]$
4. Molarity of $\text{CO}_3^{2-} = \frac{(1.000) (\text{N of HCl}) - (\text{D}) (\text{N of NaOH})}{2 \cdot V}$

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