DP-1632

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Savannah River Laboratory
Aiken, SC 29808

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

Printed in the United States of America

Available from

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy A04; Microfiche A01

725569

DP-1632
Distribution Category: UC-4

DETERMINATION OF FREE ACID BY STANDARD ADDITION METHOD IN POTASSIUM THIOCYANATE

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Approval Date: June 1982

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ABSTRACT

The free acid content of solutions containing hydrolyzable ions has been determined potentiometrically by a standard addition method. Two increments of acid are added to the sample in 1M potassium thiocyanate solution. The sample concentration is calculated by solution of three simultaneous Nernst equations.

The method has been demonstrated for solutions containing Al^{3+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Th^{4+}, or UO_2^{2+} with a metal-to-acid ratio of <2.5. The method is suitable for determination of 10 μmoles acid in 10 mL total volume. The accuracy can be judged from the agreement of the "Nernst" slopes found in the presence and absence of hydrolyzable ions. The relative standard deviation is <2.5 percent.

The report includes a survey of experiments with thermometric, pH, and Gran plot titrations in a variety of complexants, from which the method was evolved. Also included is a literature survey of sixty references, a discussion of the basic measurements, and a complete analytical procedure.

CONTENTS

DETERMINATION OF FREE ACID BY STANDARD ADDITION METHOD IN POTASSIUM THIOCYANATE

INTRODUCTION

Accurate determination of free acid (e.g., nitric acid in the presence of hydrolyzable ions such as Al^{3+} or UO_2^{2+}) is essential to successful reprocessing operations at the Savannah River Plant (SRP). The correct acidity must be established for the solvent extraction, ion exchange, and precipitation operations to separate and purify the actinide products. Also, free acid content must be known for neutralization or destruction of nitric acid in waste solutions from these operations.

Present analytical methods have not always been adequate to meet the needs of changing process conditions. Resulting solutions have sometimes contained metals or metal concentrations that were inadequately complexed and hence caused difficulty in free acid determinations. This work evaluates methods of free acid determination with the ultimate objective of developing a single free acid method generally applicable to SRP solutions.

SUMMARY

Free acid was successfully determined in solutions of nitric acid and the nitrates of aluminum, chromium(III), iron(III), mercury(II), nickel(II), thorium, and uranium(VI), at metal-to-acid ratios <2.5. The simple procedure is suitable for automation and microprocessor control.

The method consists of two additions of known increments of acid into a solution containing the sample aliquot (10 μmoles free acid) in 10 mL 1M potassium thiocyanate. The potential is determined in the initial solution, and after each addition, with a glass electrode and pH meter.

The sample concentration is calculated by solution of three simultaneous Nernst equations. Two programs for this iterative computation were written: one for the PDP-15 computer and another for a Hewlett-Packard 67 (or 97) programmable calculator. The accuracy of the result is verified by a slope that approximates the theoretical Nernst value. The relative standard deviation is <2.5%.

This report includes a survey of experiments with thermometric, pH, and Gran Plot titrations in a variety of complexants, from which this particular system and technique evolved. The appendix includes a literature survey of sixty references, a discussion of the basic measurements, and a complete analytical procedure.

DISCUSSION

Background

In mixtures of a strong acid, such as HNO_3, and salts of hydrolyzable metal ions, such as $Al(NO_3)_3$ or $UO_2(NO_3)_2$, analytical determination of the strong acid content ("free acid") is complicated by the acid contributed to the system by the hydrolysis of the metal ions:

$$M^{n+} + mH_2O \rightleftharpoons M(OH)_m^{(n-m)+} + mH^+ \qquad (1)$$

Hydrolysis increases when free acid concentration is diminished, which occurs on dilution or neutralization. Thus, hydrolysis leads to high values of free acid unless experimental conditions are imposed during the analysis that repress or eliminate the hydrolytic contribution.

The problem of free acid determination has been a continuing one throughout the nuclear processing industry and elsewhere. Many approaches have been tried, as shown in the literature survey of Appendix A.

The general solution to the problem of free acid determination has been to add a reagent that will complex the metal ions so they do not hydrolyze. Complexants, such as fluoride, have been used with varying degrees of success with neutralization titrations.

An alternative approach is to add a complexant and only partially neutralize the solution. This avoids regions of low acidity where hydrolysis is enhanced. This approach is based on the Gran Plot titration method,[1] (see Appendix B), where known increments of base are added. The complexant chosen depends on the composition of the solution titrated.

The method we developed proceeds one step further into the effort of inhibiting hydrolysis, by increasing the acidity during the analysis. Known increments of standard acid (instead of base) are added, and potassium thiocyanate is used as complexant. In the resulting acidic system, the single moderately strong complexant will suffice for all SRP solutions. Although calculations can be made by Gran Plot, a better approach is mathematical solution of simultaneous equations.

SURVEY EXPERIMENTS

Initial experiments were made to survey several complexants and techniques for the hydrolyzable ions Al^{3+}, Cr^{3+}, Fe^{3+}, Th^{4+}, and UO_2^{2+}. The traditional complexants tried, which are listed in Table 1, include three solutions currently used at SRP. One technique investigated was titration with standard base, in the presence of complexant. The titration was followed thermometrically and potentiometrically (pH). Thermometric monitoring was evaluated because it has been used successfully for nuclear processing solutions by other investigators.[2,3,4] The other technique consisted of development of Gran Plots through addition of standard acid to the metal ion in the complexing solution. Applicability of the Gran Plot technique could thus be assessed.

Thermometric/pH Titrations -- Conditions for the thermometric/pH titrations are listed in Table 2. The titrations were performed with a Sanda Thermo Titrator, DVR Model (Sanda, Inc., Philadelphia, PA). Temperature and pH, detected by thermistor and glass electrode, respectively, were recorded concurrently on strip charts.

The thermometric and pH titration curves are given in Figures 1 through 6. The dotted line indicates the theoretical equivalence point. These figures are presented for information and reference and are not discussed in detail. The effectiveness of each complexant and mode of detection can be judged from the correspondence of the curves to the theoretical end point and to one another.

The effect of the fluoride concentration on complexation of iron is shown in Figures 1 and 6. The concentration of complexed fluoride used for SRP Gran Plots was insufficient to complex the iron added. At the higher fluoride concentration recommended by Oak Ridge National Laboratory (ORNL) for thermometric titrations,[2] the iron is satisfactorily complexed.

The usefulness of thermometry for free acid determination in highly radioactive process solutions appears to be limited, even with a suitable complexing system. The amount of heat generated must be great enough so that it can be accurately measured. As shown in Table 3, thermometric titrations generally require millimoles of acid, >15 mL in the titration system, and a titrant concentration >1N, to avoid dilution effects. The quantity of acid required is too large for many solutions of interest at SRP, where samples are limited to <100 μL because of radioactivity or availability.

Gran Plot Titrations -- Gran Plot experiments were conducted by adding increments of standard acid into metal nitrate solutions in selected complexants, according to the experimental conditions given in Table 4. The pH was determined with a Beckman or Orion combination glass electrode. Experiments with fluoride complexant are not included because stable pH readings were not obtained.

Gran Plot titrations are discussed in Appendix B. A plot of $(V_o + v_n)10^{-pH}$ versus the volume of acid added (v_n) ideally produces a straight line. The intercept on the volume axis corresponds to the volume of titrant equivalent to the initial acid content. In the Gran Plot curves (Figures 7 through 12) intercepts of the linear extrapolations should fall near zero on the abscissa. Linearity indicates the complexant is suitable for Gran Plot determinations.

The effectiveness of respective complexants is demonstrated by comparing Figures 8 through 12 with Gran Plots made with water alone (Figure 7). The effectiveness of acidification in suppressing hydrolysis is evident in some instances, where the curve becomes linear after several incremental additions of acid. General feasibility of the method of standard acid additions with thiocyanate complexant is evident from Figure 9.

STANDARD ADDITION METHOD

Basic Principles

The rationale for choosing a method of standard addition of acid is to minimize hydrolysis by performing the analysis in an acidic medium. The pH range required for each metal of interest can be calculated from the hydrolysis constants given in Table 5. These constants represent the first hydrolysis step, given by the equation

$$M^{n+} + H_2O \rightleftarrows M(OH)^{(n-1)+} + H^+ \tag{2}$$

with the constant defined by

$$K_h = \frac{[M(OH)^{(n-1)+}][H^+]}{[M^{n+}]} \tag{3}$$

Thus, the pH at which 50% of the metal is hydrolyzed corresponds to the pK_h of the metal. At a pH about one unit lower, less than 10% of the ion is hydrolyzed.

With the exception of iron, all ions considered in this work have an acceptably low hydrolysis by pH 2. The hydrolysis constant of Pu(IV) is included in Table 5 to indicate that Pu(IV), if present in more than the trace concentrations of the SRP solutions of interest, would constitute a major interference.

Use of a complexant as the titration medium provides an additional control over the hydrolysis of the ions. Potassium thiocyanate was chosen because it is the salt of a strong acid and a strong base and hence exhibits no buffering action. Thiocyanate is a moderately strong complexant for many metal ions; the stability constants for the metal thiocyanates are included in Table 5. The effectiveness of thiocyanate is evident in Figure 9, where the Gran Plot for the ions tested was almost linear.

General Procedure

The detailed experimental procedure, written to stand alone independent of this report, is given in Appendix C. A sample aliquot containing about 0.01 meq free acid is added to 10 mL of 1M KSCN solution. The H^+concentration in the resulting solution is about 10^{-3}M. The pH (~3) is at the high end of the pH range at which hydrolysis is slight. Subsequent additions of acid will inhibit hydrolysis further.

The potential of the initial stirred solution is measured with a pH glass electrode and a pH meter in the millivolt mode. An increment of standard acid is then added to change the potential by about 20 mV, and the stable potential is recorded. This step is repeated.

The experimental data, consisting of three potential readings and the volumes of electrolyte, sample, and increments of acid are used to establish three simultaneous Nernst equations. These equations are solved to determine the initial concentration. Details are given in Appendix C. Because the mathematical solution must be obtained by iteration, a computer-based program is used. Two computational programs were used:[9] one is the ADDFIT program[10] adapted for the Digital Equipment Corporation PDP 15 computer; the other is a program written for the Hewlett-Packard 67 or 97 programmable calculator.

Demonstration of Method

Mixtures of 1M HNO_3 and 1M solutions of $Al(NO_3)_3$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Hg(NO_3)_2$, $Ni(NO_3)_2$, $Th(NO_3)_4$, or $UO_2(NO_3)_2$ were used to develop and demonstrate the method. The free acid content of each metal nitrate solution was estimated independently by the following procedure:

(1) The molarity of the metal ion M^{n+} was determined by EDTA titration,[11] except for UO_2^{2+}, which was determined by a modified Davies-Gray titration.[12]

(2) The total acid equivalents displaced by an aliquot from a column of hydrogen-form Dowex® 50 (Dow Chemical Company) ion exchange resin was determined by titration with standard base.

(3) The difference (in equivalents) between (2) and (1) was found; this corresponds to the normality of free acid in the metal nitrate solution.

This difference method, though not highly accurate, indicated that the metal nitrates contained little free acid.

Standard addition experiments, performed by adding acid to the thiocyanate-metal nitrate solutions (similar to Figure 9), generally confirmed the low free acid content. However, for certain nitrates, the calculated slope (see Appendix B) was abnormally high, as shown in Table 6. These high slopes indicated that hydrolytic interference was significant. When acid was added to suppress hydrolysis prior to the free acid determination, the slopes approached the Nernst value, and the calculated free acid content of the salt solution became low and more or less constant.

These experiments demonstrated that chromium and thorium, in particular, require a minimum initial acidity. The free acid method appears to be generally applicable at acid/metal ratio >0.4.

Detailed analyses of 1-1 metal-to-acid mixtures were made. Table 7 compares determinations by two different analysts at different times and with different solutions and electrodes. The average relative standard deviation for the two sets was 2.5%.

In Table 8, these results are also compared with the free acid determined by the difference method and by the conventional pH titration in 3% potassium fluoride. Agreement is satisfactory, except for solutions containing chromium and mercury, where the potassium fluoride method gives high results. Included in this table are determinations of free acid in "simulated dissolver solutions" -- the worst case for high concentrations of uranium and aluminum in SRP systems. The standard addition method gives results 3 to 6% higher than the potassium fluoride method in this instance.

Quality of KSCN Reagent

The quality of reagent-grade potassium thiocyanate varies widely. Impurities in reagent KSCN can affect the accuracy of the standard addition determination.

Because the determination is carried out in dilute unbuffered acid solution, traces of acidic or basic impurities directly affect the acid content found. As seen in Table 9, a basic impurity (bicarbonate?) was common to most reagent chemicals, all of which met ACS reagent specifications. In Figure 13, titration curves for solutions of these reagents all have a break between pH 4 and 5.

Some ACS reagent-grade KSCN also contained an impurity that caused precipitate formation in solutions containing thorium or uranium, with accompanying high free acid values. From the infrared absorption spectrum of the uranium precipitate, the impurity was identified as a uranyl phosphate. The precipitate was not sufficiently crystalline for identification by X-ray diffraction.

The phosphorus content of the solid reagents, determined by inductively coupled plasma-emission spectroscopy, varied from 40 to 750 ppm. Although recrystallization is reported to produce high-purity KSCN,[13] the phosphorus was not completely removed by a single recrystallization from water.

The effect of phosphate on determination of free acid in Simulated Dissolver Solution 1 (1M H^+, 1.5M UO_2^{2+}, 1M Al^{3+}) is shown in Table 10. The free acid content was determined with KSCN solutions containing 0.07 to 7.9 ppm phosphorus. Phosphorus concentrations as high as 0.5 ppm did not affect the apparent free acid content. In some experiments, the thiocyanate was acidified prior to addition of the sample in an attempt to control the precipitation reaction. The acid addition seemed to stabilize the potential readings during the experiment, but had little effect on the free acid values obtained.

TABLE 1

Complexing Solutions Surveyed

Name	Composition	Reference	Comment
"Complexed Fluoride"	Saturated NaF (~1M) plus 0.01M NaI	SRP usage	Gran Plot
"Complexed Oxalate"	Saturated $K_2C_2O_4$ (~1.8M) plus 0.01M NaI	SRP usage	Gran Plot
Thiocyanate	8.5% KSCN	SRP usage	Gran Plot; sometimes mixed 1:1 with complexed oxalate
Ferrocyanide	12.5 g KNO_3, 12.5 g $K_4Fe(CN)_6$ in 250 mL	5	
Calcium EDTA	0.1M Na_2H_2EDTA, 0.24M $Ca(NO_3)_2$ adjusted to pH 5.0	6	
Potassium Fluoride	5M KF	2	
Potassium Iodate	0.3M KIO_3	4	

TABLE 2

Conditions for Thermometric/pH Titrations

15 mL solution

500 µL 2M HNO_3 (1 millimole)

1000 µL 1M Metal Nitrate (1 millimole)

Titrant: 1M NaOH (1.5 mL total added from automatic titrator)

TABLE 3

Thermometric Titrations

Source* of Data	mmoles H^+ Determined	Total Volume, mL	Electrolyte	Ions Masked
ORNL[2]	0.2-4	25	20 mL 4.5M NaF	Th^{4+}, UO_2^{2+}
AGNS[4]	0.2-2 (plus 2.5 mmole H^+)	<35	25 mL 5M KF	7-60 mg Pu(IV)
AGNS[4]	0.5-1.5	<35	30 mL 0.45M $K_2C_2O_4$	8-100 mg UO_2^{2+}
Germany[3]	2-15	100	10/20 mL 5M KF	10 mmole Th^{4+} 1 mmole Al^{3+} fission products
SRL experiments	1	15	~2M $K_2C_2O_4$ (NaI) 1M NaF (NaI) 5M KF 8.5% KSCN CaEDTA $K_4Fe(CN)_6$	1 mmole UO_2^{2+}, Al^{3+}, or Fe^{3+}

---

* ORNL - Oak Ridge National Laboratory

AGNS - Allied General Nuclear Services

TABLE 4

Conditions for Gran Plot Experiments

5.0 mL Solution

+100 μL 1M Metal Nitrate Solution (100 μmoles)

+10 10-μL Additions of 1M HNO_3 (100 μmoles total)

TABLE 5

Hydrolysis Constants and Thiocyanate Stability Constants

Metal Ion	First Hydrolysis Constant;[7] log K_h	Stability Constant of Thiocyanate Complex;[8] log K_1
Al^{3+}	-5.0	-
Cr^{3+}	-4.0	1.87
Fe^{3+}	-2.2	1.99
Hg^{2+}	-3.4	$K_{So} = 10^{-19.8}$*
Ni^{2+}	-9.9	1.18
Th^{4+}	-3.2	1.08
$UO_2{}^{2+}$	-5.8	0.76
Pu^{4+}	-0.5	-
$PuO_2{}^{2+}$	-5.6	-
Rare Earths^{3+}	-8 to -10	0.2-0.8

---

* K_{So} is solubility product constant.

TABLE 6

Free Acid Determinations in Metal Nitrate Solutions by Standard Addition Method

Metal	Acid/Metal Ratio	Calculated Free Acid in 1M Metal Solution, M	Slope, mV/decade of H^+ Concentration*
Al^{3+}	0	0.03	60
	0.1	0.03	60
	0.4	0.01	62
Cr^{3+}	0 0	0.16	75
	0.1	0.09	63
	0.2	0.09	64
	0.4	0.08	60
Fe^{3+}	0	0.06	67
	0.1	0.04	61
	0.2	0.04	61
	0.4	0.02	61
Th^{4+}	0	0.18	81
	0.1	0.07	62
	0.2	0.04	59
	0.4	0.03	60
UO_2^{2+}	0	0.06	70
	0.1	0.01	55
	0.2	0.03	57
	0.4	0.01	61

---

* See Appendix B.

TABLE 7

Two Sets of Free Acid Determinations of 1-1 Metal-Acid Mixtures

	Analyst 1				Analyst 2			
Metal	Average Free Acid, M	Standard Deviation	Average Slope	Number of Determinations	Average Free Acid, M	Standard Deviation	Average Slope	Number of Determinations
H^+ Only	0.492	0.0094	58.6	3	0.493	0.016	59.1	2
Al^{3+}	0.488	0.0007	58.7	3	0.502	0.026	59.1	2
Cr^{3+}	0.517	0.0107	59.2	3	0.533	0.015	59.8	2
Fe^{3+}	0.492	0.0138	58.7	3	0.523	0	60.6	2
Hg^{2+}	0.520	0.0079	58.9	3	0.524	0.019	58.9	2
Ni^{2+}	0.500	0.0007	58.9	2	0.505	0.005	59.7	2
Th^{4+}	0.527	0.0041	58.6	2	0.550	0.020	60.0	2
$UO_2{}^{2+}$	0.511	0.0050	59.7	2	0.478	0.018	58.3	2
Pooled Standard Deviation		0.008				0.017		

TABLE 8

Free Acid Content of 1-1 Metal-Acid Mixtures by Three Methods

Metal	Standard Addition Analyst 1	 Analyst 2	KF Method	Metal Detn. and Ion Exchange
H^+ Only	0.492	0.493	0.494	0.500
Al^{3+}	0.488	0.502	0.493	0.503
Cr^{3+}	0.517	0.533	1.49	0.522
Fe^{3+}	0.492	0.523	0.502	0.518
Hg^{2+}	0.520	0.524	1.25	0.532
Ni^{2+}	0.500	0.505	0.509	0.526
Th^{4+}	0.527	0.550	0.492	0.551
UO_2^{2+}	0.511	0.478	0.498	0.507
Simulated Dissolver Solution 1 (1M H^+, 1.5M UO_2^{2+}, 2M Al^{3+})		1.09	1.03	
Simulated Dissolver Solution 2 (1M H^+, .008M UO_2^{2+}, 2M Al^{3+})		1.06	1.02	

TABLE 9

Recovery of Acid Spike from Different KSCN Solutions (without pH adjustment)

No.	Vendor	Lot No.	pH of 1M Solution	% Recovery of 10 μmole Acid Spike
1	Fisher	701203	8.8	40
2	Fisher	794979	7.5	64
3	Baker	327751	5.4	99
4	Baker	812081	7.4	65
5	Baker	814088	5.9	53
6	Fisher recrystallized	701203	6.7	97
7	Fisher recrystallized and fused	701203	6.4	96

TABLE 10

Effect of Phosphorus Impurity in Solutions Containing Uranium*

	Free Acid Concentration, M**			
ppm P in Solution →	0.07	0.50	0.76	7.9
µL 0.1M HNO_3 Added				
0	0.240	0.242(1)	0.293	0.85(1)
40-50	0.235	0.249(1)	0.258(1)	-
100	0.233	0.242	0.271(3)	0.79(1)
150	-	-	0.259	-

---

* 10 mL 1M KSCN + acid indicated + 25 λ of 1.5 dilution of simulated dissolver solution 1 (1M H^+, 1.5M UO_2^{2+}, 1M Al^{3+})

** Duplicate determinations except as noted in parentheses.

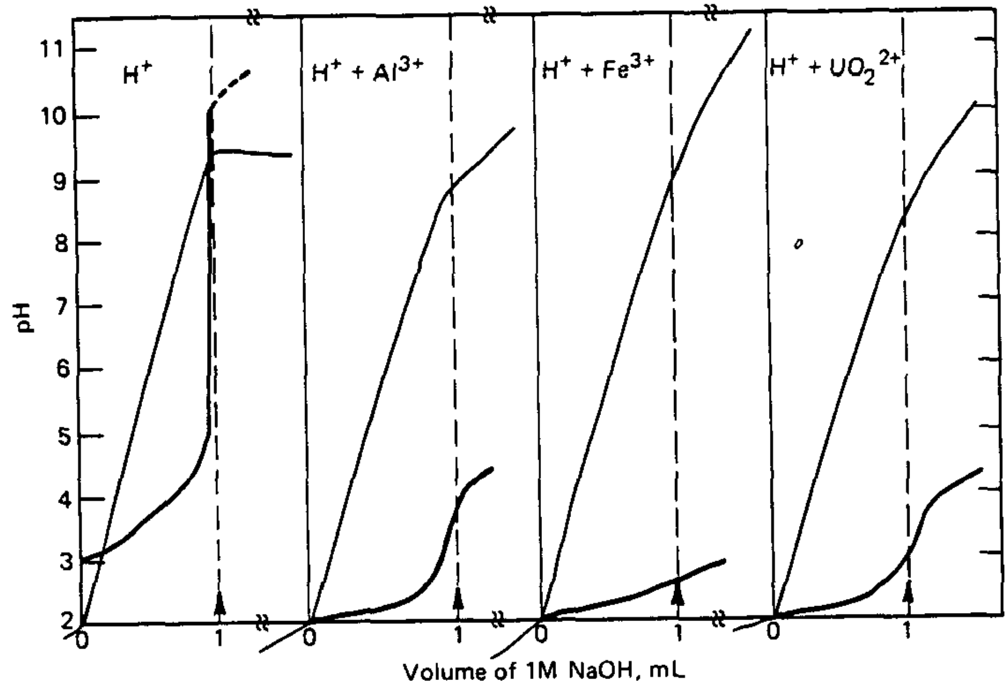

FIGURE 1. Thermometric/pH Titrations in Complexed Fluoride

Thermometric ———

pH ━━━

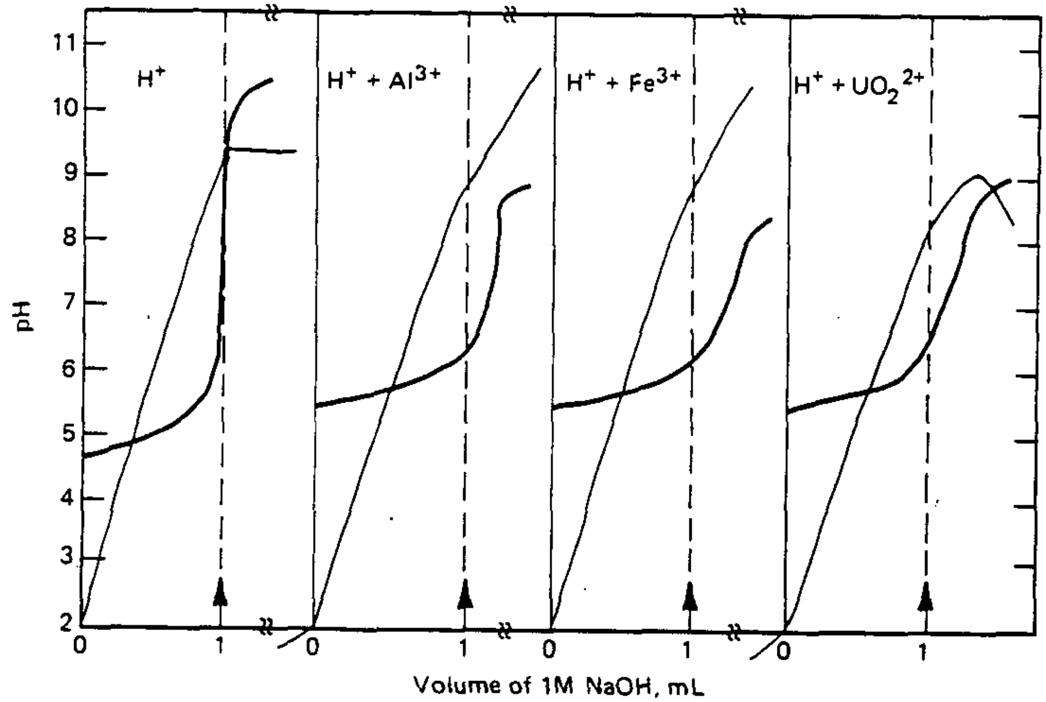

FIGURE 2. Thermometric/pH Titrations in Complexed Oxalate

Thermometric ———

pH ━━━

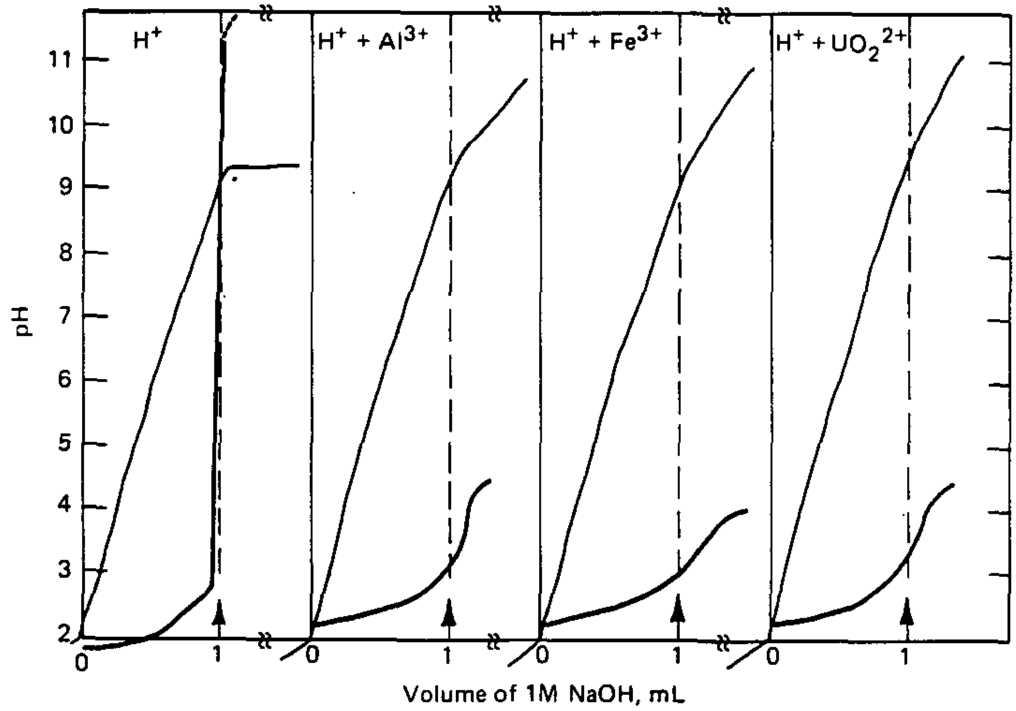

FIGURE 3. Thermometric/pH Titrations in Thiocyanate

Thermometric ———

pH ▬▬▬

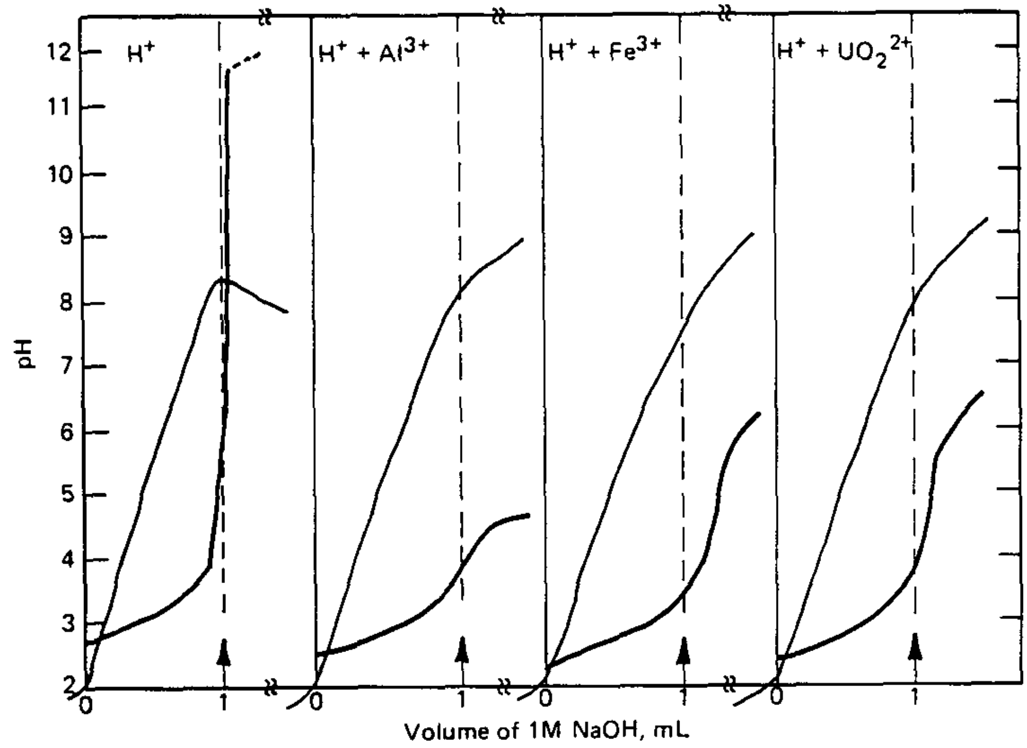

FIGURE 4. Thermometric/pH Titrations in Ferrocyanide

Thermometric ——

pH ▬▬

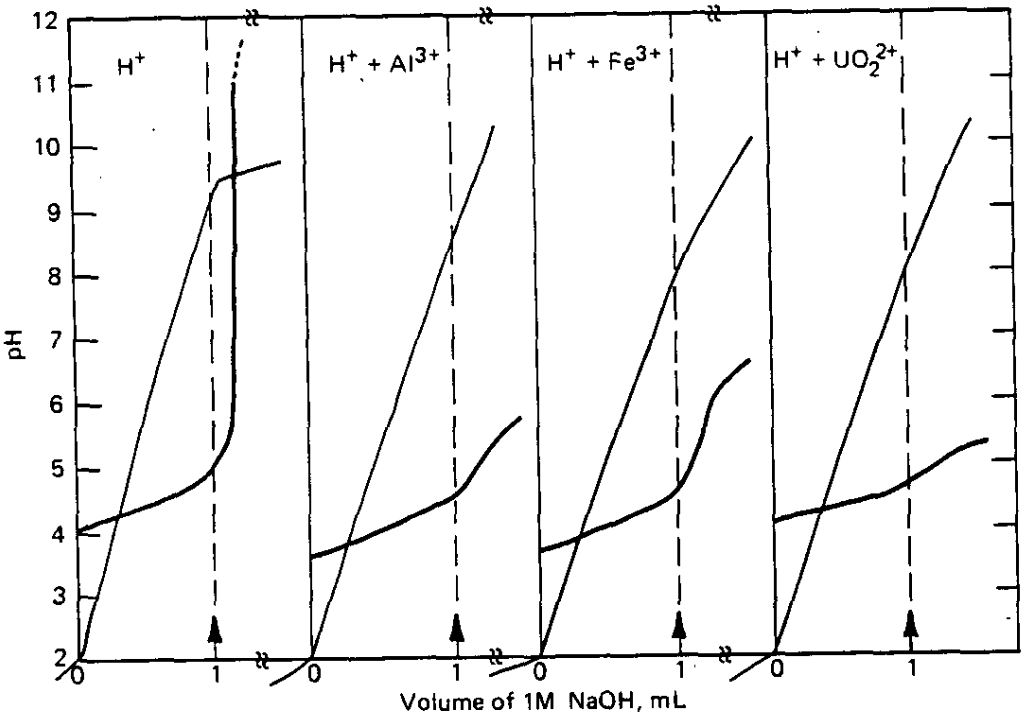

FIGURE 5. Thermometric/pH Titrations in Calcium EDTA

Thermometric ———

pH ━━━

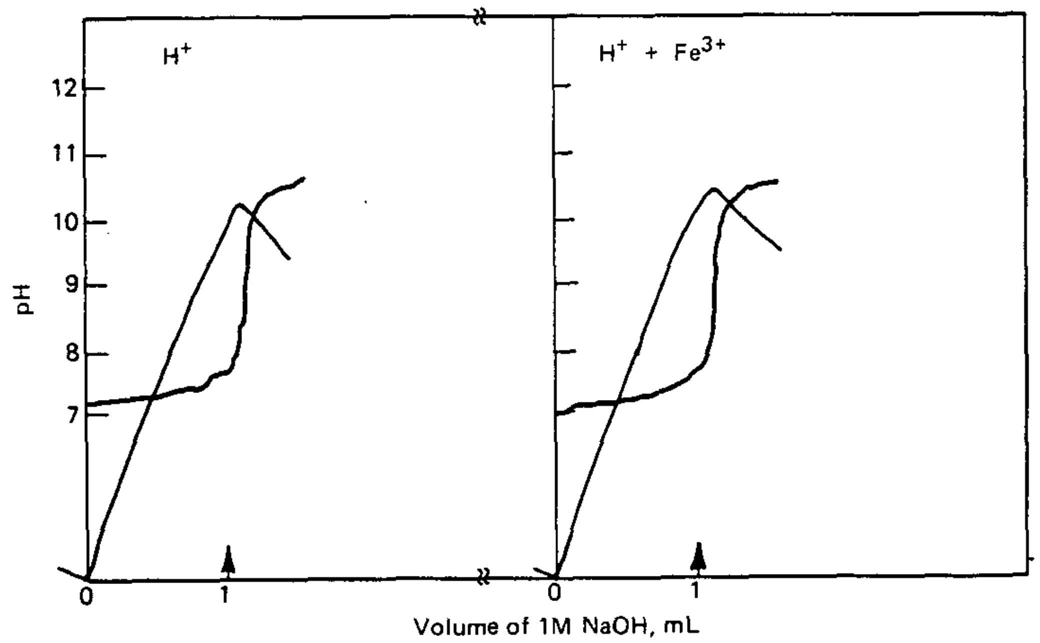

FIGURE 6. Thermometric/pH Titrations in 5M Potassium Fluoride

Thermometric ———

pH ━━━

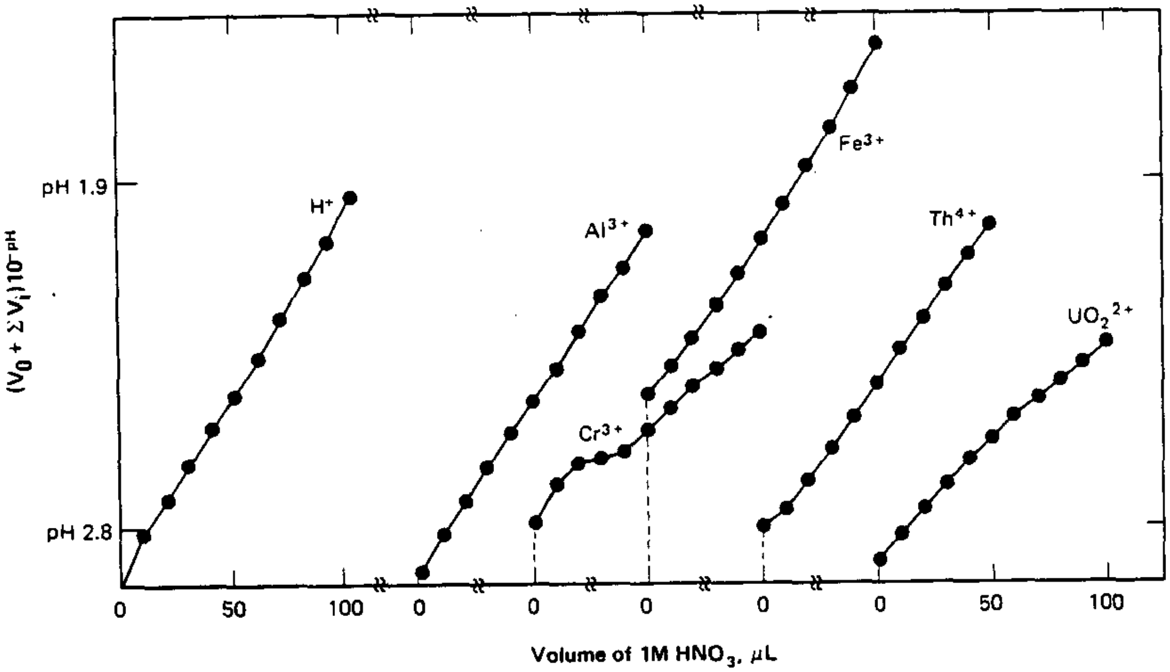

FIGURE 7. Gran Plot Titration in Water Only

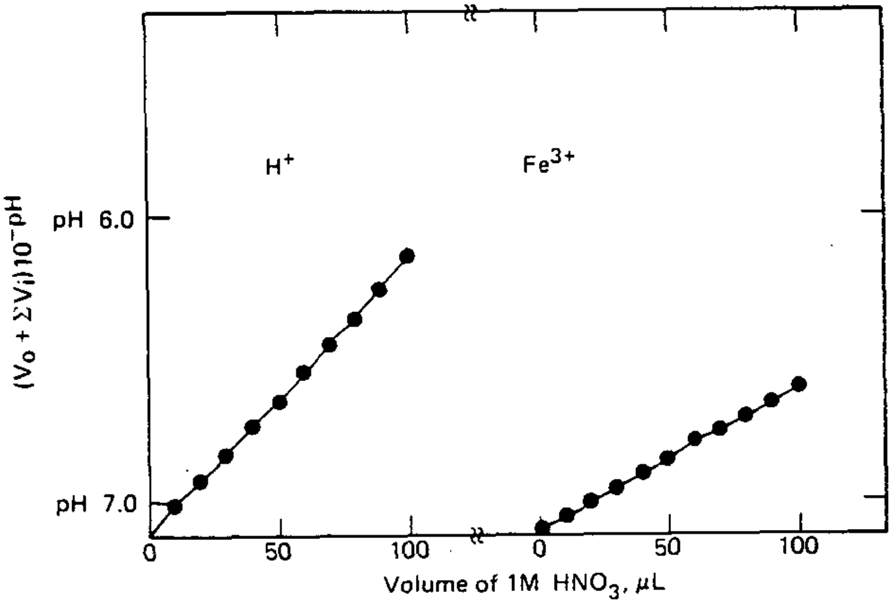

FIGURE 8. Gran Plot Titration in Complexed Oxalate

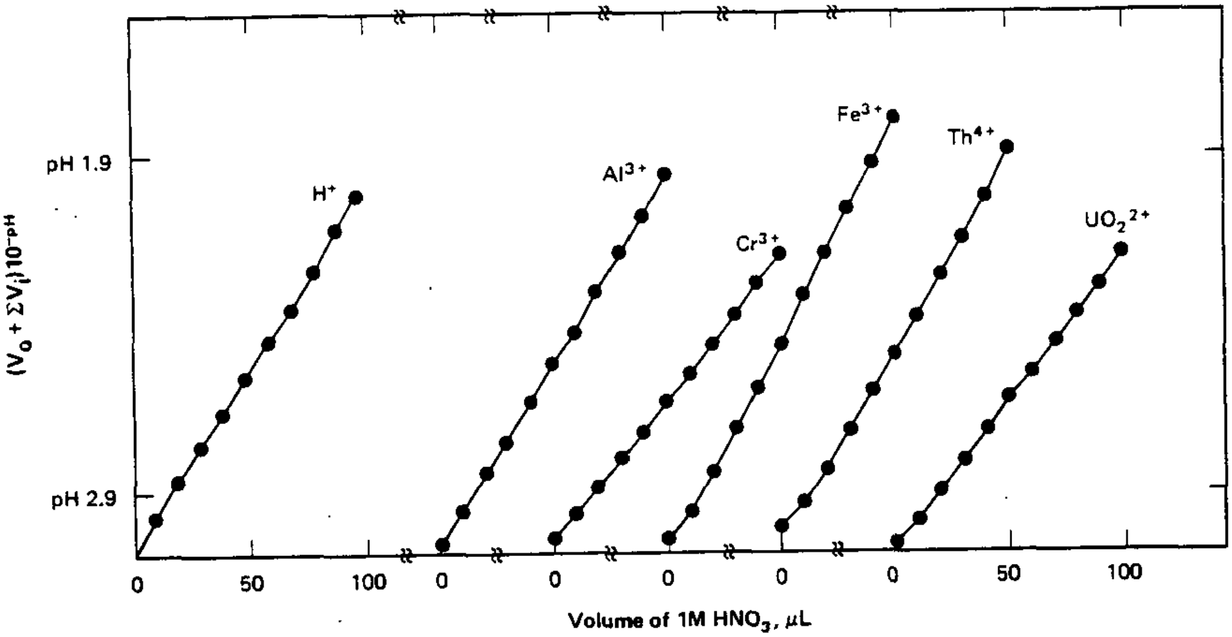

FIGURE 9. Gran Plot Titration in Thiocyanate

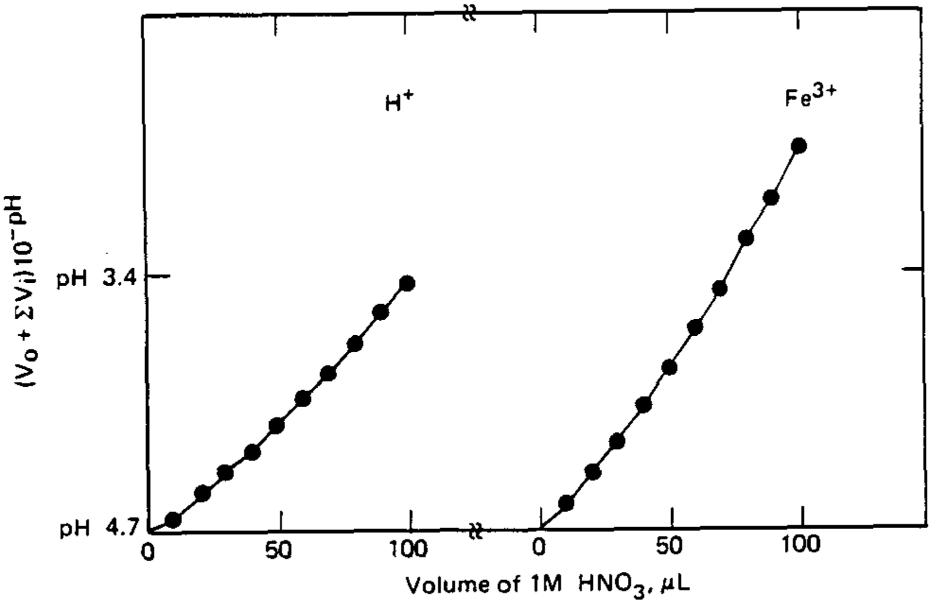

FIGURE 10. Gran Plot Titration in Ferrocyanide

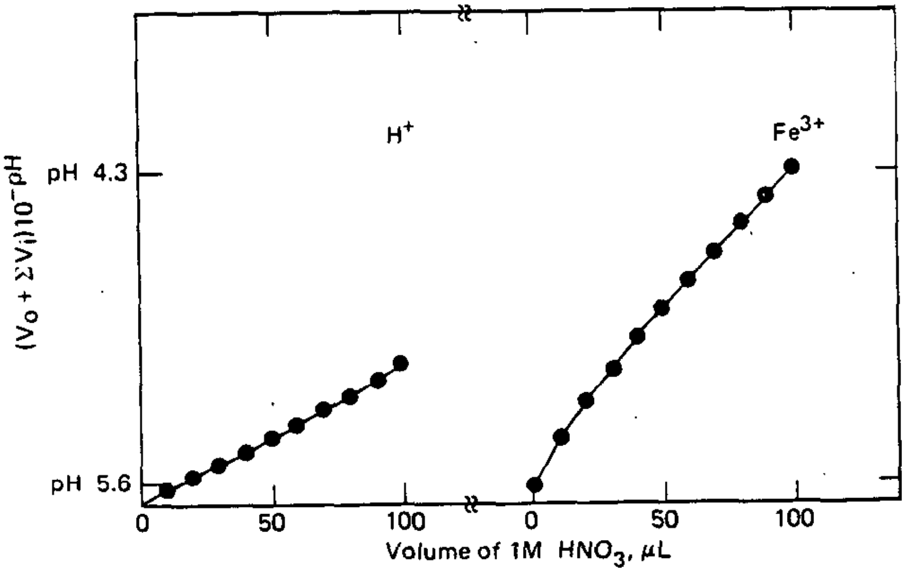

FIGURE 11. Gran Plot Titration in Calcium EDTA

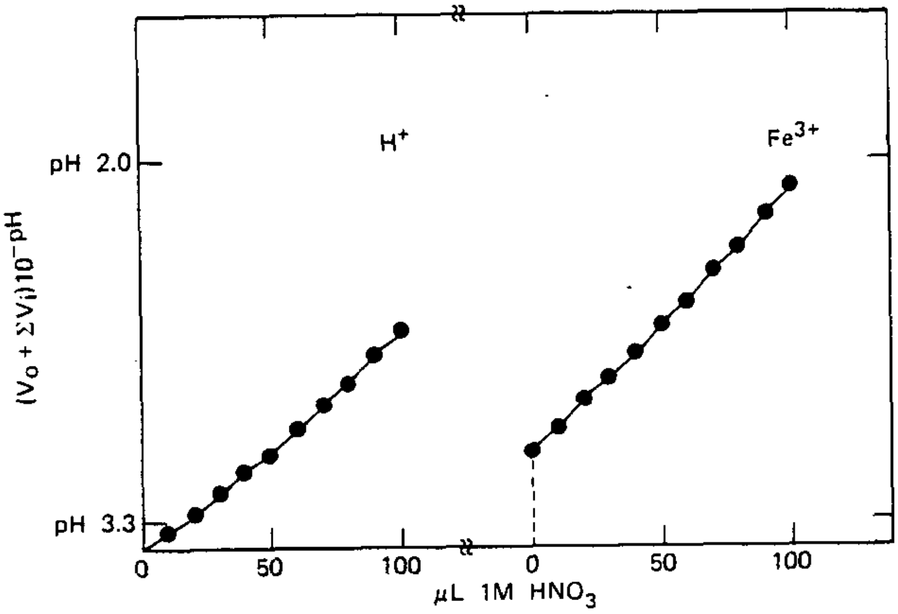

FIGURE 12. Gran Plot Titration in Potassium Iodate

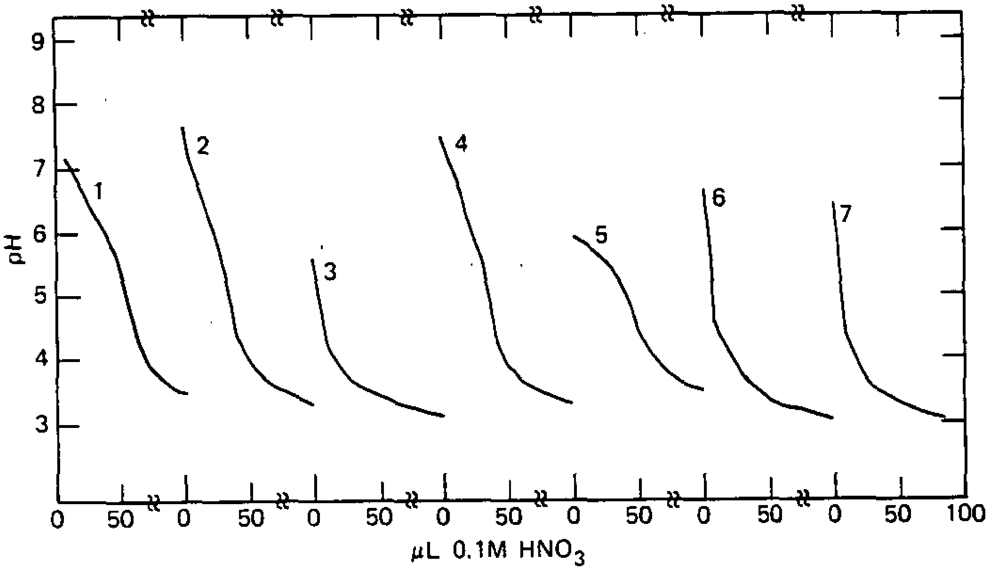

FIGURE 13. Titration Curves of 1M Potassium Thiocyanate Solutions (see Table 9 for identification)

APPENDIX A

LITERATURE SEARCH

This section contains a search of the literature through Nuclear Science Abstracts and Energy Data Base files and other sources. Publications are listed in Table 1A in alphabetical order by first author. Tables 2A and 3A categorize the references by modes of determination and masking method.

TABLE 1A

Free Acid Bibliography

1. Sten Ahrland, New Methods for the Determination of Free Acid in the Presence of Large Amounts of Uranyl Salt. Acta Chem. Scand 14, 2035-45 (1960). NSA 15, 8684
2. F. J. Armson et al., An Investigation into the Determination of Trace Quantities (0.3-0.5%) of Free Nitric Acid in Uranyl Nitrate Hexahydrate and Uranyl Nitrate Liquors, SCS-R-4 (1949).
3. M. Barrachina and M. A. Villar, Determination of Free Acid of Iron Chloride Solutions. An. Real. Soc. Espan. Fis. Quim., Ser. B63 (1), 107-10 (1967). (Spanish) CA 6, 101308z
4. V. K. Bhargava, et al., Rapid Spectrophotometric Method for Free Acid Determination in Uranyl Nitrate and Chloride Solutions. Anal. Chim. Acta 53(1), 210-13 (1971). CA 74, 134650y
5. John A. Bishop and Sherwood Summ, Determination of Free Acid in Ferric Solutions. Chemist Analyst 43, 96-7 (1954). CA 49, 780e
6. W. J. Blaedel and J. J. Panos, Titration of Nitric Acid in Solutions of Aluminum Nitrate, Anal. Chem. 22, 910 (1950).
7. F. G. Bodewig, Enthalpimetric Titration of Free Acid in Simulated Nuclear Fuel Solutions Containing Thorium and Other Hydrolyzable Ions, Anal. Chem. 46, 454 (1974).
8. Glenn L. Booman, et al. Determination of Free Acid in the Presence of Hydrolyzable Ions, Anal. Chem. 30, 284 (1958). IDO-14387 (1956); NSA 11, 1428.
9. D. T. Bostick, Evaluation of Refractometry for Free Acid Analysis in Aqueous Purex Systems. ORNL/TM-6775 (May 1979).
10. Josef Cepelak, et al. Determination of Uranyl Nitrate in the Presence of Nitric Acid by Acidimetric Titration. Chem. Listy 52, 547 (1958). CA 53, 1987h.
11. R. E. Connick. Note on the Determination of Nitric Acid in Uranyl Nitrate Solutions, MDDC-1245. NSA A1-692.
12. Frantisek Cuta, et al. Potentiometric and Conductometric Titration of Free Acids and of Acids Liberated from Ni Salts by Hydrolysis at High Temperatures. Chem. Listy 48, 1341-5 (1954). CA 49, 780y

13. N. Cvjeticanin, et al. Analytical Control of the Nuclear Fuel Reprocessing Process. Tehnika (Belgrade) 18, 1997-2004 (1963). (Serbo-Croatian) NSA 18, 41585

14. J. W. Dahlby, G. R. Waterbury, and C. F. Metz. Investigation of Two Methods for Measuring Free Acid in Plutonium Solutions. LA-3876 (1967).

15. Nicole Damien and Philippe Cauchetier. Determination of Free Acid in Concentrated Aqueous Solutions of Plutonium, Anal. Chim. Acta 41, 483-495 (1968). (French)

16. Z. I. Dizdar and L. D. Obrenovic. Determination of Free Acid in Uranium(VI) Solutions by Means of Cation Exchangers. Anal. Chim. Acta 21, 560 (1959).

17. Theodor Eder. Methods for Determining the Free Acid in Aluminum Sulfate. Z. Anal. Chem. 119, 399 (1940). CA 35,52

18. Theodor Eder. Determination of the Free Acid in Aluminum Sulfate when Iron and Ammonium Salts are Present. Z. Anal. Chem. 119, 409 (1940). CA 35,52

19. S. Emura and S. Okasaki, Potentiometric Titration of Free Acid, Uranium(IV), (VI), and Hydrazine-Monohydrate in Uranous Nitrate Solutions with Alkali. Bunseki Kagaku 18, 976-80 (August 1969). (Japanese)

20. T. Erben, L. Gehem, and E. Vervecken, Simultaneous Quantitative Determination of Free Acid and Uranium(VI) in Aqueous and Organic Samples by Differential Potentiographic Titration in Non-Aqueous Medium. NP-13271 (1962). NSA 18, 1504

21. R. H. Gaddy and R. S. Dorsett, Determination of Free Acid by Automated Ion-Exchange Colorimetry. Anal. Chem. 40, 429-32 (1968).

22. K. Y. Gallagher and C. M. Johnson. A Search for an In-Line Nitric Acid Analyzer. USDOE Report RFP-2986 (1980).

23. R. P. Graham, Determination of Acid in the Presence of Aluminum, Anal. Chem. 18, 472 (1946).

24. J. M. Guillen Glaban, Simultaneous Potentiometric Determination of Free Acid and Aluminum in Irradiated Moderated Thermal Reactor Fuels, An. Real Soc. Espan. Fis. Quim. (Madrid), Ser. B, 64, 931-6 (1968) (Spanish) CA 70, 83287t

25. M. E. Jones, et al. Determination of Free Acid in Solutions of Aluminum and Thorium and Uranyl Nitrates. KAPL-1497 (1956). NSA 10, 3908

26. Andre Kergreis, Free Acidity Determinations in Aqueous Solutions, Comm. Energie At. (France) CEA R-2982 (1966) (French). CA 66, 25853f

27. Hisashi Kubota and D. A. Costanzo, "Reactions in Concentrated Lithium Chloride Solution. Determination of Free Acid and Hydrolyzable Cation." Anal. Chem. 36, 2454 (1964).

28. J. L. Marley and D. A. Costanzo, The Determination of Free Acid in the Presence of Uranium and Thorium by Thermometric Titration. ORNL/TM-7456 (in press).

29. Oscar Menis, High Frequency Titration as Applied to the Determination of Thorium, Uranium, Sulfate, and Free Acid. CF-59-5-72 (1959). NSA 15, 8663

30. Oscar Menis, et al. Determination of Free Acid in Solutions of Uranyl Sulfate. ORNL-2178 (1956). NSA 11, 929

31. F. J. Miller and P. F. Thomason, Thermometric Titration of Acids in the Presence of Hydrolyzable Ions. Anal. Chem. 31, 1498 (1959). NSA 13, 19863

32. H. H. P. Moeken and W. A. H. Van Neste, A Rapid Empirical Method for the Simultaneous Determination of Free Acid and Stainless Steel in Sulphate Solutions, NP-16884 (1967).

33. H. H. P. Moeken and W. A. H. Van Neste, Determination of Free Acid, Iron, and Uranium in Nitrate Solutions, NP-16883 (1967).

34. Robert Lee Moore and H. R. Schmidt, Determination of Free Acid in Solutions Containing Uranyl Nitrate, Aluminum Nitrate, and Sodium Dichromate. HW-14603 (1957). NSA 11, 8292.

35. G. A. Moshkareva, et al., Determination of Free Acid in Aluminum Sulfate, Sb. Tr. Ural. Nauch.-Issled. Khim. Inst. 26, 76-9 (1971) (Russian). CA 78, 23535c

36. Kenji Motojima and Kimie Izawa, "Potentiometric Titration of Free Acid and Uranium in Uranium(VI) Solutions with Alkali." Anal. Chem. 36, 733 (1964).

37. A. S. Newton, et al. Rapid Determination of Nitric Acid and Thorium in Thorium Nitrate Solutions, CC-3241 (1945 - decl. 1955). *NSA 10*, 3431

38. P. Pakalns. "Potentiometric Titration of Free Acid in Salt Solutions After Addition of Potassium Oxalate as a Complexing Agent." *Anal. Chim. Acta 127*, 263 (1981).

39. A. K. Parlour, Determination of Free Acid in UNH Solutions. Problem Assignment No. 208-X2A. CC-1432 (1955) *NSA 10*, 2285

40. L. P. Pepkowitz, et al., Determination of Free Acid in the Presence of Hydrolyzable Ions, *Anal. Chem. 24*, 1956 (1952).

41. J. L. Pflug and F. J. Miner, Determination of Free Acid in Plutonium Solutions, *Anal. Chim. Acta 23*, 362-7 (1960). *NSA 15*, 161

42. E. A. Polyak, Determination of Free Acid and Iron(III). USSR Patent 224,135 (1968). *CA 70*, 64083g

43. R. C. Propst, Conductometric Acidimetry in the Presence of Hydrolyzable Ions, DP-76 (1955).

44. J. A. Ryan, et al., Determination of Free Acidity in Solutions Containing Uranyl and Other Hydrolyzable Ions. SCS-R-378 (1955). *NSA 14*, 9481

45. J. R. Sanderson, Determination of Free Acidity in Aqueous Solutions of Uranyl Nitrate Using an Extraction Procedure, Part I. SCS-R-146 (1950). *NSA 14*, 10451

46. D. J. Savage, Problems in the Determination of Acidity in Nitric Acid Solutions of Plutonium Nitrate. *Proc. Soc. Anal. Chem. 11* (10), 266-8 (1974). *CA 83*, 37154t

47. H. Schmieder and E. Kuhn. Determination of Free Acid in Plutonium, Uranium, and Thorium Solutions. AEC-TR-7141, translated from *Talanta 16*:691-700 (1969).

48. M. M. Senyavin and A. M. Sorochan, Determination of Free Acid in the Presence of Different Salts. Trudy Komissii...Anal. Khim. 7, 246-71 (1956) (Russian); *CA 50*, 15344f. Translated into French from Russian, CEA-tr-R-1078 (1956). *NSA 15*, 12802T

49. Maynard E. Smith, Determination of Free Acid in Plutonium Solutions, LA 1864 (1955). *NSA 9*, 4110

50. J. E. Strain, In-Line Free Acid Monitor for Nuclear Fuel Reprocessing. ORNL/TM-6800 (May 1979).

51. J. A. Suarez and Gonzalez Del Rey, Determination of Free Acid in Solutions with Hydrolyzable Cations, Coloq. Hisp.-Fr. Trat. Combust. Irradiados Quim. Plutonio, 2nd 1969 (Pub. 1971), 301-24 (Spanish). CA 80, 90854k

52. M. Talas, Acid Determination in Uranyl Salt Solutions in the Presence of Some Hydrolyzable Compounds, UJV-1006/64 (1964). NSA 15, 307

53. D. Thiele and W. Baehr, Determination of Free Acid in Plutonium(IV) Solutions, EURFNR-756; translation of KFK-1133 (German) (1970).

54. D. Thiele and W. Baehr, Acidimetric Determination of the Free Acid and the Uranium in Nitric Acid Solutions in the Presence of Plutonium(IV). KFK 503 (1966) (German).

55. D. Thiele and W. Baehr, Acid in Concentrated Nitric Acid Solutions of Plutonium(IV), KFK-499 (1966) (German).

56. Magdalena Tomasevic, Application of EDTA for Determination of Free Acid in Solution of Hydrolyzable Salts of Complex Composition. Hem. Ind. 27(9), 399-402 (1973). (Serbo-Croatian). CA 80, 152474x

57. H. Tsuji and Yu Yokoyama, Application of Differentiation Circuits to Potentiometric Titration. II. Determination of Free Acid and Uranium in Nitric Acid Solution Containing Uranium. Bunseki Kagaku 17, 939-44 (August 1968) (Japanese)

58. H. Vogg, Potentiometric Titration of Free Acid and Plutonium in Nitric Acid Plutonium Solutions, EUR-3692 or EURFNR-418, Translation of KFK-622.

59. T. L. Williams, L. G. Jordan, L. L. Ouzts, and G. A. Huff, The Determination of Free Acid in Plutonium Solutions by Thermometric Titration. AGNS 35900-2.4-82 (1980).

60. M. Zamek, Stepwise Thermometric Titration of Free Acid and Uranyl with Single Reagent, Collect. Czech. Chem. Comm. 41(12), 3754-7 (December 1976) (German).

61. No Author, The Determination of Low Nitric Acid Concentration in Uranyl Nitrate Hexahydrate. SCS-M-104 (1948). NSA 13, 16778

62. No Author, The Determination of Free Acid in Uranyl Nitrate Solution. SCS-M-129 (1950). NSA 13, 16779

TABLE 2A

Modes of Detection/Determination

	Reference Nos.
Refractometry	9,22,37
Conductivity	22,31,40,43,50
Thermometry	7,8,28,59,60
pH/Potentiometry	1,2,4,10,11,12,16,22,23,24,25,26,27,28,31,35,38,44,46,47,48,51,52,54,56,57,61,62
Differential Potentiometry	19,20,30
pH/Indicator	3,6,18,35,42
Graphical	15
Colorimetry	5,21,48
High-Frequency Titration	29

TABLE 3A

Masking Methods

	Reference Nos.
Ion Exchange	3,16,21,26
Fluoride	3,18,28,30,34,35,42,46,48,59
EDTA	15,42,56
Oxalate	6,8,35,38,44,48,51,59,62
Citrate	3,5,22,41
Peroxide	10,11,37
Iodate	22,49
Cyanoferrate(II)	39
Sulfate	1,37
Cyanide	48,52
Chloride	27,48
Thiocyanate	52 (in dimethylformamide)

APPENDIX B

BASIC RELATIONSHIPS AND CALCULATIONS

pH Measurement

The glass electrode measures the activity of free hydrogen ion in solution. The potential of the cell, which also includes a reference electrode, is given by the Nernst equation, written for present use as

$$E = E_0 + S \log c$$

where E is the measured potential; E_0 is the constant term that includes all constant contributions to the cell potential, including the activity coefficient which is stabilized by use of constant ionic strength; S is the response of the electrode, ideally the Nernst slope (2.303 RT/nF) of 59 mV per decade of concentration; c is the hydrogen ion concentration in the solution.

The hydrogen ion concentration, c, is related to the measured pH by the definition

$$pH = -\log c$$

Thus $(E - E_0)/S = -pH$

and $c = 10^{-pH} = 10^{(E-E_0)/S}$

Gran Plot Method[1]

In the Gran Plot method, increments of standard acid or base are added, and the hydrogen ion concentration (as pH or E) is measured after each addition. The data are placed in a linear relationship in which the intercept corresponds to the acid concentration of the original solution.

Derivation of the equation is the same for acid or base addition, except for the sign v_n. The equivalents of the acid in the original solution can be expressed in terms of the titrant volume and concentration, C:

$$(c)(V) = (v_e)(C)$$

With each successive increment of acid or base added to the solution, the relationship becomes:

$$c_n\ (V + v_n) = (v_e \pm v_n)C$$

Where the sign in the right-hand term is positive when acid is added and negative when base is added. C is the normality of acid or base added.

Equation can be rearranged to a linear form

$$\pm\ v_n = (1/C)\ [c_n(V + v_n)] - v_e$$

The value of v_e corresponds to the intercept of a linear extrapolation.

The value of c_n can be expressed in terms of either the measured pH or potential, giving

$$c_n = 10^{-pH} = 10^{(E-E_o)/S}$$

A value for the slope S is required for the calculation. Unless special procedures are adopted, the value of 59 mV/decade of concentration is generally assumed. With the pH response of a pH meter, the Nernst slope is imposed at the set temperature; later model pH meters input a % theoretical slope derived from calibration between two standard buffer solutions.

When the potential E in millivolts is used, a slope value must be assigned. The slope can be estimated experimentally through a preliminary determination with acid and the background electrolyte or by the technique of known dilution of the solution during the analysis.

Mathematical Fitting[9]

Another approach to interpretation of the data is to solve simultaneous Nernst equations for the three unknown values: E_o, S, and c_o. Symbols are defined in Table 1B.

$$E_1 = E_o + S \log c_o$$

$$E_2 = E_o + S \log \frac{c_oV_o + c_2v_2}{V_o + v_2}$$

$$E_3 = E_o + S \log \frac{c_oV_o + c_2v_2 + c_3v_3}{V_o + v_2 + v_3}$$

TABLE 1B

Definition of Symbols

Measured quantities:

E_1 = potential of thiocyanate solution plus sample aliquot, mV

E_2 = potential after addition of v_2 mL of standard acid, mV

E_3 = potential after addition of v_3 mL of standard acid, mV

c_2 and c_3 = concentrations of standard acid
(usually $c_2 = c_3$), M

V = volume of potassium thiocyanate (usually 10 mL), mL

v_1 = volume of sample, mL

V_o = $(V + v_1)$, mL

v_2 = volume of first acid addition, mL

v_3 = volume of second acid addition, mL

Calculated quantities:

c_o = initial concentration in solution measured, M

E_o = constant term, mV

S = slope; usually ~59 mV/decade

c_1 = concentration in sample, M
$(c_oV_o)/v_1$

These equations must be solved by iteration. Two methods used in this work were the ADDFIT program[10] which can handle many data sets, but requires a computer such as the PDP 15; and a program developed for the Hewlett-Packard Model 67 calculator by W. H. Fellner [Du Pont Engineering Service Division, Wilmington, DE, personal communication (1981)]. The Fellner program is limited to three data points and enables at-desk calculations. Three properly chosen data points (with the change in potential of about 20 mV at each acid addition) are sufficient for an accurate and precise free acid determination.

A mathematical fit of the data will always be obtained, but the experimenter must establish that the calculated slope is physically reasonable, as discussed earlier.

APPENDIX C

PROCEDURE FOR DETERMINATION OF FREE ACID BY THE STANDARD ADDITION METHOD

Principle and Limitations

Scope

This method can determine free acid in the presence of Al^{3+}, Cr^{3+}, Fe^{3+}, Hg^{2+}, Ni^{2+}, Th^{4+}, or UO_2^{2+} at metal/acid concentration ratios <2.5. The concentration of free acid in the measured solution should be about 10^{-3}M.

Basis

In mixtures of a strong acid, such as HNO_3, and salts of hydrolyzable metal ions, such as $Al(NO_3)_3$ or $UO_2(NO_3)_2$, analytical determination of the strong acid content ("free acid") is complicated by the acid contributed to the system by the hydrolysis of the metal ions:

$$M^{n+} + mH_2O \rightleftarrows M(OH)^{(n-m)+} + mH^+ \qquad (1)$$

Hydrolysis leads to high values of free acid unless experimental conditions are imposed during the analysis that repress or eliminate the hydrolytic contribution.

The acid contribution from hydrolysis of the metal ions is minimized in two ways: (1) through use of the complexant thiocyanate as titration medium and (2) through an acid environment that is maintained throughout the determination.

Additions of standard acid are made into 1M potassium thiocyanate that contains the sample aliquot. The pH (as mV) is measured with a combination glass electrode in the initial solution and after each of two acid additions.

The concentration of free acid is calculated from three sets of data points and three simultaneous equations. The data points consist of the measured potentials and the corresponding standard acid additions. The three equations, solved by iteration, are:

$$E_1 = E_o + S \log c_o \qquad (2)$$

$$E_2 = E_o + S \log \frac{c_o V_o + c_2 v_2}{V_o + v_2} \qquad (3)$$

$$E_3 = E_o + S \log \frac{c_o V_o + c_2 v_2 + c_3 v_3}{V_o + v_2 + v_3} \qquad (4)$$

The symbols are defined in Table 1C. Iterative solutions have been programmed for Hewlett-Packard calculators, Model 67 or 97 [W. H. Fellner, Du Pont Engineering Service Division, Wilmington, DE, personal communication (1981)] and for the PDP 15 computer.[9]

A mathematical solution will always be obtained, but it is necessary to confirm that the fit is physically reasonable. The calculated slope should be similar to that found (~59) in the absence of hydrolyzable ions. If hydrolytic acid is significant, the slope will be too large. This has been observed with higher concentrations of Cr^{3+}. A predose of standard acid is made in this case, to produce a more acidic medium, prior to initiation of the standard addition procedure.

Interferences

Ions that hydrolyze at pH <2 may interfere.

Precision and Accuracy

When pure potassium thiocyanate (see Reagents and Standards) is used and the calculated slope falls in the Nernstian range, there is no known bias. The relative standard deviation is less than 2.5%.

Experimental Procedure

Apparatus

pH meter
Combination glass electrode (Beckman #39501 or Orion #91-05)
Vials (1" x 3")
Stirring bar (5/16" x 3/4")
Magnetic stirrer
Manostat Digipet® (Manostat Corporation) buret, 1 mL
Miscellaneous micropipets (Cole-Parmer)
10-mL pipet, or equivalent

Reagents and Standards

Potassium thiocyanate, KSCN, 1M. Dissolve 97.2 grams KSCN in one liter deionized water. Adjust pH to 5.0 with nitric acid.

NOTE: Some ACS Reagent-grade KSCN contains phosphate that interferes in solutions that contain uranium or thorium. For such solutions, KSCN that contains <60 ppm P is required. (Obtained by custom synthesis from Kings Mountain Specialties, Inc., Kings Mountain, NC.)

Nitric acid, HNO_3, 0.1xxx<u>M</u> standardized.

Procedure

NOTE: The procedure should be performed first with an aliquot of standard acid to verify the experimental conditions (e.g., KSCN quality and electrode behavior) through recovery of the spike and the appropriate electrode slope (~59).

Step	Comment
1. Pipet 10 mL KSCN into a vial with stirring bar.	1. This volume should be accurately measured. This is V.
2. Add sample aliquot.	2. The measured volume of sample should contain about 0.01 millimole of free acid. This is v_1.
3. Place the electrode in the stirred solution; record the potential in mV.	3. Allow potential to stabilize, e.g., 5 minutes. This is E_1.
4. Add enough acid from the Digipet® to change the potential by ~20 mV. Record the stable potential reading and the volume added.	4. These are E_2 and v_2. Stable readings should be attained in 1-2 minutes.
5. Repeat step 4.	5. This is E_3. The volume of acid added in step 5 only is v_3.

Example:

V = 10 mL
v_1 = 0.1 mL

Input:

$c_2 = c_3$ = 0.1000M
V_o = 10.1 mL
v_2 = 0.130 mL
v_3 = 0.290 mL

E_1 = 227.4
E_2 = 248.7
E_3 = 269.0

Output:

$c_o = 9.699 \times 10^{-4}$M
E_o = 405.06
S = 58.96
$c_1 = (9.699 \times 10^{-4})(10.1)/0.1000 = 0.980$M

TABLE 1C

Definition of Symbols

Measured quantities:

E_1 = potential of thiocyanate solution plus sample aliquot, mV

E_2 = potential after addition of v_2 mL of standard acid, mV

E_3 = potential after addition of v_3 mL of standard acid, mV

c_2 and c_3 = concentrations of standard acid (usually $c_2 = c_3$), M

V = volume of potassium thiocyanate (usually 10 mL), mL

v_1 = volume of sample, mL

$V_o = (V + v_1)$, mL

v_2 = volume of first acid addition, mL

v_3 = volume of second acid addition, mL

Calculated quantities:

c_o = initial concentration in solution measured, M

E_o = constant term, mV

S = slope; nominally ~59 mV/decade

c_1 = concentration in sample, M
$= (c_oV_o)/v_1$

REFERENCES

1. F. J. C. Rossotti and H. Rossotti. "Potentiometric Titrations Using Gran Plots." J. Chem. Ed. 42, 375-8 (1965).

2. J. L. Marley and D. A. Costanzo. The Determination of Free Acid in the Presence of Uranium and Thorium by Thermometric Titration. ORNL/TM-7456 (in press).

3. J. F. Bodewig. "Enthalpimetric Titration of Free Acid in Simulated Nuclear Fuel Solutions Containing Thorium and Other Hydrolyzable Ions." Anal. Chem. 46, 454 (1974).

4. T. L. Williams et al. Determination of Free Acid in Plutonium Solutions by Thermometric Titration. AGNS 35900-2.4-82 (July 1980).

5. A. K. Parlour. Determination of Free Acid in UNH Solutions. Problem Assignment No. 208-X2A. CC-1432 (1955).

6. M. Tomasevic. "Application of EDTA for Determination of Free Acid in Solution of Hydrolyzable Ions of Complex Composition." Hem. Ind. 27(9), 399-402 (1973).

7. C. F. Baes and R. E. Mesmer. The Hydrolysis of Cations. New York, NY, Wiley (1976.)

8. Stability Constants and Stability Constants Supplement No. 1. Special Publications 17 and 25. London, The Chemical Society (1964 and 1971).

9. E. W. Baumann. Determination of Free Acid by Standard Addition Method in Potassium Thiocyanate. Du Pont — SRL Internal Report DPST-81-407, E. I. du Pont de Nemours & CO., Savannah River Laboratory, Aiken, SC (1981).

10. M. J. D. Brand and G. A. Rechnitz. "Computer Approach to Ion-Selective Electrode Potentiometry by Standard Addition Methods." Anal. Chem. 42, 1172-7 (1970).

11. L. Meites, Ed. Handbook of Analytical Chemistry, First Edition. New York, NY, McGraw-Hill (1963).

12. W. Davies and W. Gray. "A Rapid and Specific Titrimetric Method for the Precise Determination of Uranium Using Iron(II) Sulphate as Reductant." Talanta 11, 1203 (1964).

13. I. M. Kolthoff, E. B. Sandell, E. J. Meehan and S. Bruckenstein. Quantitative Chemical Analysis, Fourth Edition, p. 796. London, The Macmillan Company (1969).