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ABSTRACT

A method is described for determination of free acid in solutions containing the hydrolyzable ions Al(III), Cr(III), Fe(III), Hg(II), Ni(II), Th(IV), and U(VI). Standard additions of acid are made into a solution of 1M KSCN containing about 0.001M H^+. The concentration of the sample is calculated either by solving three simultaneous Nernst equations, by the Gran plot procedure, or by means of a microprocessor pH meter. Molar concentrations of metal ion up to 2.5 times that of the acid can be tolerated. The relative standard deviation is ±2%. The method has been applied to analysis of nuclear processing solutions that contain Pu(III), in addition to the ions listed above.

BRIEF

A method is described for determination of free acid in solutions containing the hydrolyzable ions Al(III), Cr(III), Fe(III), Hg(II), Ni(II), Th(IV), and U(VI), with a relative standard deviation of ±2%.

INTRODUCTION

Accurate determination of free nitric acid (i.e., acid concentration in the presence of hydrolyzable ions) has been a continuing problem throughout the nuclear industry and elsewhere. At the Savannah River Plant (SRP), determination of free acid is necessary for successful processing of nuclear fuel by the Purex and other processes. The correct acidity must be established for solvent extraction, ion exchange, and precipitation operations that separate and purify the actinide products. Free acid content must also be determined prior to neutralization or destruction of nitric acid in waste solutions from these operations.

Dilution or neutralization of acid samples, an inherent part of most analytical procedures, will add to the apparent acidity by enhancing hydrolysis. The acid concentration found will be biased high unless experimental conditions are used that repress or eliminate the hydrolytic contribution to the acidity.

A survey of methods for free acid determination was made (1). The solution to the problem has generally been to add a reagent that will complex the metal ions. Complexants such as fluoride have been used with varying degrees of success with neutralization titrations. An alternative approach that has been used at SRP is partial neutralization and calculation of the end point by the Gran Plot method (2). Test solutions with low acidity, where hydrolysis is enhanced, are thus avoided. Even this method is not always adequate.

The method described here proceeds one step further in the effort to prevent or reduce hydrolysis. Standard additions of acid (instead of base) are made. The complexant is potassium thiocyanate which, being the salt of a strong acid and strong base, does not affect the acid content of the analytical system.

THEORY

Hydrolysis constants (3) and thiocyanate stability constants (4) for the metals investigated are given in Table 1. From the equation for the first hydrolysis step

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

it is apparent that increasing the acidity or decreasing the free metal ion concentration (e.g., by complexation) will reduce hydrolysis by driving the equilibrium to the left.

From the corresponding hydrolysis constant,

$$K_h = \{[M(OH)^{(n-1)+}][H^+]\}/[M^{n+}] \tag{2}$$

it is seen that the pH at which half the metal ion is hydrolyzed corresponds to the pK_h. At a pH about one unit lower, where only about 10% of the metal is hydrolyzed, a moderate complexant like thiocyanate can in most cases provide sufficient supplemental inhibition of hydrolysis.

Except for iron, the ions considered in this work are only slightly hydrolyzed at or below pH 2. In nuclear material processing applications, significant hydrolytic contributions would be expected from Pu(IV) but not from Pu(III), which is similar to the trivalent lanthanides.

EXPERIMENTAL SECTION

Apparatus. Measurements of the pH or the potential in mV were made with Orion or Beckman combination pH electrodes and conventional pH meters. The Orion Research Microprocessor Ionalyzer Model 901 (Orion Research Incorporated) in the KA/1 known addition mode was also used. Reagent additions were made with micropipets, a 1-mL Manostat Digipet® (Manostat Corporation) or the SMI UniPump Model 200 (Scientific Manufacturing Industries, Inc.).

Reagents. Reagent-grade chemicals and distilled or deionized water were used throughout. Standard 0.1XXXM HNO_3 was prepared by standard methods. 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 prepared. Concentration of each metal was determined by EDTA titration (5), with the exception of uranium, which was determined by Davies-Gray titration (6).

The 1M potassium thiocyanate solution was treated to remove trace phosphate impurity. Approximately 0.5 g $ZrO_2(NO_3)_2 \cdot 2H_2O$ was added per liter of solution. Some solutions turned pink. After the solution was stirred 30 minutes or more, the pH was adjusted to 5. The solution became colorless and a precipitate formed. After the precipitate settled out, the solution was filtered through a Whatman #41 filter paper or equivalent. The pH was again adjusted to 5. The quality of the thiocyanate reagent was verified by performing the standard addition procedure with standard nitric acid.

Procedure. The test solution consisted of a measured volume of potassium thiocyanate to which sample was added to give an acid concentration of about .001M (e.g., 10 mL thiocyanate plus .01 millimole sample). The electrode was placed in the stirred solution and the steady mV or pH reading (after about two minutes) was recorded. Then 100 µL of standard HNO_3 was added, and the stable reading was recorded (two minutes). These additions and readings were repeated as required, depending on the calculation method used.

The response of the electrode (slope) was determined either with standard buffer solutions or from known dilutions of nitric acid in the potassium thiocyanate solution. This experimental slope was used in subsequent calculations.

Three different methods of calculation were used. In one method, three mV readings (initial plus those from two acid additions) were used to calculate the initial concentration c, the slope S, and the constant E_0 by solution of three simultaneous Nernst equations with a modified ADDFIT program (7) or another program developed for this purpose (1). In the second method, a Gran plot was made of four pH readings. In the third, an Orion microprocessor pH meter, in the known addition mode, calculated the acid concentration from a single acid addition and an experimentally determined slope.

RESULTS AND DISCUSSION

Gran Plot Titrations

The effectiveness of thiocyanate as complexant was demonstrated by a series of Gran plot titrations. A solution of 0.1M nitric acid was added in 10-μL increments to 5 mL of water or of 1M KSCN that contained 100 μmoles of aluminum, chromium(III), iron (III), thorium, or uranyl nitrate.

The experimental data are presented in Figures 1 and 2 as Gran plots. The ordinate is the total volume of the solution (initial volume V_0 plus the increments v_i) times the corresponding acid concentration (i.e., 10^{-pH}). The pH range is also indicated on the ordinate. The abscissa is the volume of acid added. With no acid in the initial solution, from free acid or hydrolysis, the plot should be a straight line that extrapolates to zero on the abscissa.

In the aqueous solutions (Figure 1), a significant amount of hydrolysis is apparent, particularly for iron, chromium, and thorium. In the thiocyanate solution (Figure 2), the lines approach linearity with the intercept at zero. For iron and thorium it is apparent that a certain minimum free acid is still required before hydrolysis is suppressed.

Analysis of Metal Nitrate-Nitric Acid Mixtures

The method was developed and demonstrated through analysis of 1-1 mixtures of nitric acid and solution of aluminum, chromium(III), iron(III), mercury(II), nickel(II), thorium or uranyl nitrate. Preparation of a free acid "standard" containing hydrolyzable metal ion salts is difficult because the salts themselves may be either acid-rich (i.e., contain free acid) or acid-deficient.

The free acid content of each metal nitrate solution was estimated as the difference between (a) the total equivalents of acid released from acid-form cation exchange resin by an aliquot of the metal nitrate solution and (b) the analytically determined total metal concentration:

$$\text{Free Acid} = (\text{equivalents of } H^+ \text{ from resin}) - (n \times \text{Molarity of } M^{n+}) \quad (3)$$

Although the accuracy of the free acid value obtained was poor because of the nature of the calculation, we found the metal nitrate reagents were neither significantly acid-rich nor acid-deficient.

Detailed analyses were made of 1-1 nitric acid-metal nitrate mixtures. Table 2 compares free acid content of nitric acid alone and in the mixtures, determined three ways: by the non-routine difference method described above; by neutralization titration in 3% potassium fluoride solution, a routine method used in our laboratory; and by the simple method described in this paper. With stoichiometric metal nitrates and adequate complexation, the acid content of all mixtures should be the same.

The results from the three methods mostly agree within ±5%. The notable exceptions are the chromium and mercury solutions, where fluoride complexation was apparently insufficient to prevent hydrolysis.

Table 3 compares analyses of mixtures performed with this method at different times with different nitric acid standards, with different electrodes and by different analysts. The pooled relative standard deviation for the two sets was ±2.5%.

The maximum metal/acid ratio has not been systematically determined for each metal ion. We find that molar ratios up to 2.5 can be tolerated for each ion. The worst case in our process samples, where H:U:Al is 1:1.5:2, has been satisfactorily analyzed.

Methods of Calculation

Hydrogen ion concentrations were determined with the glass electrode. The response of the electrode is given by the Nernst equation:

$$E = E_o + S \log c \tag{4}$$

where E is the measured potential in millivolts; S is the response of the electrode, nominally 59 mV per decade of concentration at 25°C; c is the concentration of the hydrogen ion in the test solution; and E_o is the sum of all constant contributions to the potential, including the potential of the reference electrode, the liquid junction potential, and the activity coefficient of the hydrogen ion, assumed constant in this constant ionic strength solution.

We have used three methods of calculation: solution of simultaneous Nernst equations, Gran plots, and the single standard addition. We find in some instances that solution of the simultaneous equations results in unrealistic slopes and inaccurate concentration values. The Gran plot with several data points is preferred where additional samples are difficult to obtain or prepare, because imprecise acid additions or mV readings will be averaged out. The single addition technique is useful for rapid determinations.

Analysis of Standards and Process Samples

This method has been adopted for analysis of samples from the Purex and other nuclear processing operations at SRP, replacing a Gran Plot neutralization procedure with fluoride or oxalate complexant. The relative precision has improved from ±10% to ±2%, even in solutions that have historically been difficult to analyze. The accuracy of the determination for some samples has also been improved.

Quality of KSCN Reagent

Because the determination is carried out in dilute unbuffered solutions of acid, acidic or basic impurities directly affect the result. Therefore, the potassium thiocyanate was neutralized before use.

Another, unexpected problem occurred because of the presence of phosphate in almost all the ACS reagent-grade potassium thiocyanate we tested. Phosphate caused precipitate formation with sample solutions that contained thorium or uranium, and free acid values that were too high. The uranium precipitate was identified as a uranyl phosphate from the infrared absorption spectrum. The precipitate was not sufficiently crystalline for further characterization by X-ray diffraction. Identification of the precipitate as $(UO_2)_3(PO_4)_2 \cdot 8H_2O$ would be consistent with the solubility product (log $K_s = -49$) recently reported by Markovic and Pavkovic (8) in solutions of similar pH.

The phosphorus content of solid potassium thiocyanate reagent, determined by inductively coupled plasma-emission spectroscopy, varied from 40 to 750 ppm. Although recrystallization is reported to produce high purity potassium thiocyanate (9), a single recrystallization from water was not sufficient to purify the reagent for our application. The treatment with zirconyl nitrate described in the experimental section removed essentially all the phosphorus from the potassium thiocyanate solutions.

Automation

The simplicity of the experimental procedure makes the method suitable for automation in an integrated system. We are currently automating the analysis for laboratory use and on-line analysis of process streams.

REFERENCES

1. Baumann, E. W. Aiken, S.C., June 1982, U. S. Department of Energy Report DP-1632.
2. Rossotti, F. J. C; Rossotti, H. J. Chem. Ed. **1965**,42,375-8.
3. Baes, C. F.; Mesmer, R. E. "The Hydrolysis of Cations"; Wiley: New York, 1976.
4. Sillen, L. G; Martell, A. E. "Stability Constants" and "Stability Constants Supplement No. 1"; The Chemical Society: London, 1964 and 1971.
5. Meites, L., Ed. "Handbook of Analytical Chemistry"; McGraw-Hill:New York, 1963.
6. Davies, W.; Gray, W. Talanta **1964**,11,1203.
7. Brand, M. J. D.; Rechnitz, G. A. Anal. Chem. **1970**,42,1172-7.
8. Markovic, M.; Pavkovic, N. Inorg. Chem. **1983**, 22,978-82.
9. Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. "Quantitative Chemical Analysis", 4th ed.; Macmillan:London, 1969.

CREDIT

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LIST OF FIGURES

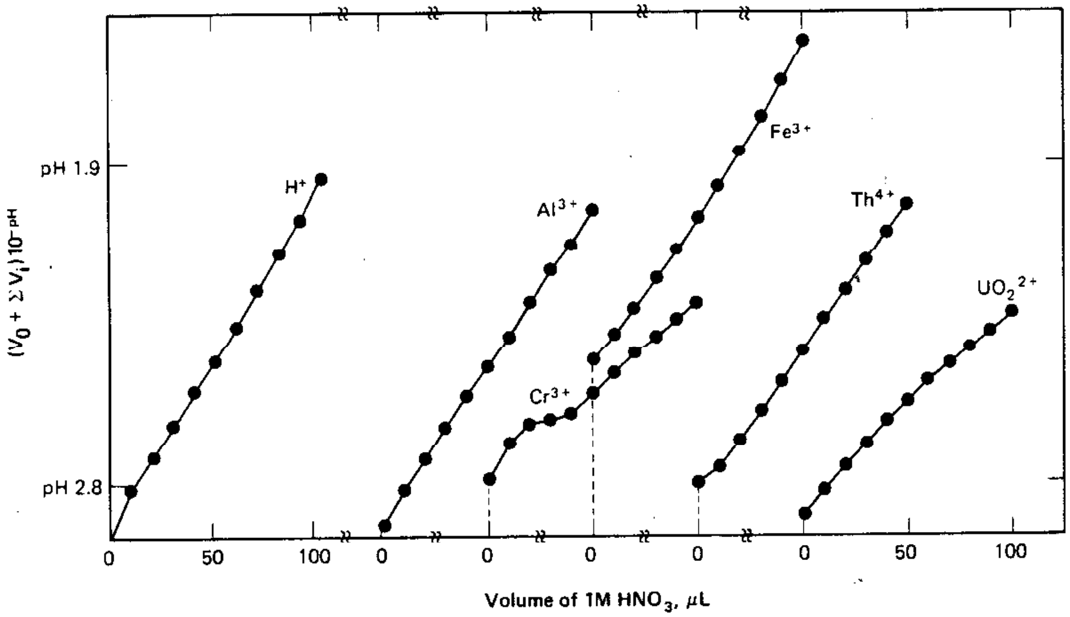

FIGURE 1. Gran Plot Titration in Water

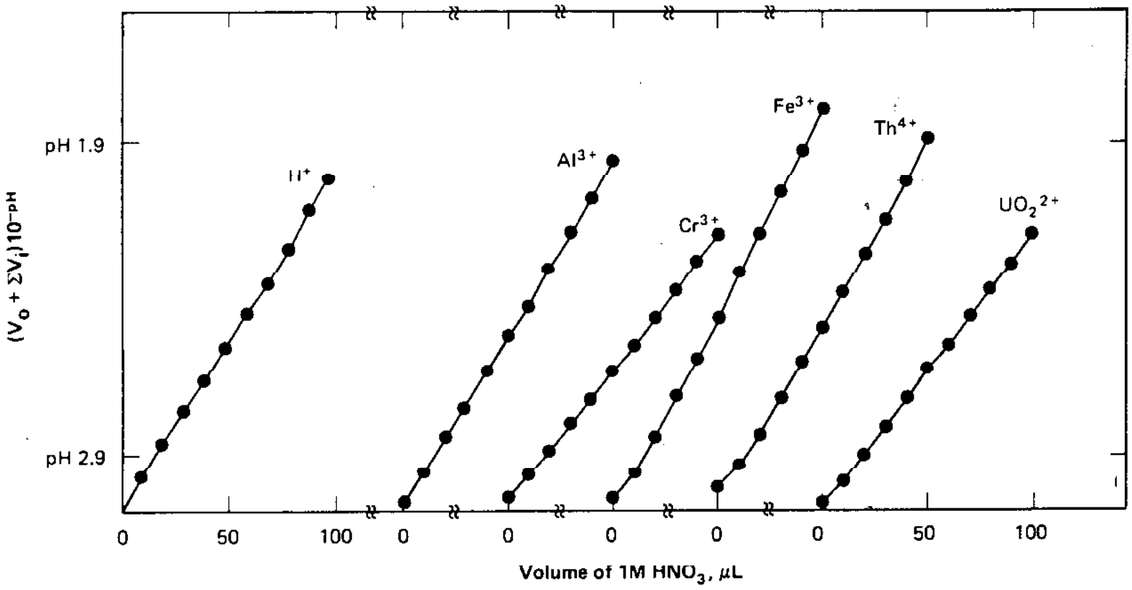

FIGURE 2. Gran Plot Titration in 1M Potassium Thiocyanate

TABLE 1

Hydrolysis Constants and Thiocyanate Stability Constants

Metal Ion	First Hydrolysis Constant(3) log K_h	Stability Constant of Thiocyanate Complex(4) 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 to 0.8

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* K_{so} is solubility product constant.

TABLE 2

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

Metal	Ion Exchange and Metal Concentration	Titration in KF	Standard Addition Analyst 1	Standard Addition Analyst 2
H^+ Only	0.500	0.494	0.492	0.493
Al^{3+}	0.503	0.493	0.488	0.502
Cr^{3+}	0.522	1.49	0.517	0.533
Fe^{3+}	0.518	0.502	0.492	0.523
Hg^{2+}	0.532	1.25	0.520	0.524
Ni^{2+}	0.526	0.509	0.500	0.505
Th^{4+}	0.551	0.492	0.527	0.550
UO_2^{2+}	0.507	0.498	0.511	0.478

TABLE 3

Two Sets of Free Acid Determination of 1-1 Metal-Acid Mixture*

	Analyst 1				Analyst 2			
Metal	Average Free Acid, M	Deviation	Average Slope	Number of Determinations	Average Free Acid, M	Standard Deviation	Average Slope	Number of Determination
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		

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* Calculated by solution of three simultaneous equations.