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University of California

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663 Los Alamos, New Mexico 87545

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Peter Kiefer

SELECTIVE TWO-STEP TITRATION OF THORIUM BY SULFATE DISPLACEMENT OF THE DIETHYLENETRIAMINEPENTAACETIC ACID COMPLEX

by

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ABSTRACT

Thorium and other metals are complexed with excess diethylenetriaminepentaacetic acid (DTPA) at pH 1.4, the excess DTPA is titrated with Bi(III) to a xylenol orange end point, sulfate is added to complex Th(IV), and the displaced DTPA again is titrated with Bi(III). Of 61 metal ions and nonmetal anions tested, only Ga(III), Sc(III), tungstate, citrate, oxalate, and thiosulfate interfere seriously. Lesser interferences are In(III), Zr(IV), V(IV), and permanganate. The standard deviation is 2 μg for 56 to 840 μg Th.

I. INTRODUCTION

A selective titrimetric method for determining submilligram levels of thorium was required for eventual use in an automated instrument of the type described by Marsh et al.[1] Our previous method, involving titration of the Th(IV)-xylenol orange complex with DTPA in a 0.05*M* HBr medium,[2] is not selective and requires prior separation of thorium for analyzing many nuclear materials.

To attain a more selective method, we evaluated concepts from several recently published methods. Cetyltrimethylammonium bromide (CTAB) is incorporated in a spectrophotometric method involving the Th(IV)-xylenol orange complex in order to make measurements at lower pH, where diverse ion interferences are less.[3] We found that the Th(IV)-xylenol orange-CTAB complex is not titrated with DTPA at the recommended pH. The use of semixylenol orange as a more selective chromogenic agent for thorium[4] was considered, but we could not locate a reliable commercial source of the pure compound. Methods in which the bromophenol blue or bromochlorophenol blue complexes of Th(IV) are titrated with aspartic acid[5] failed to give distinct end points.

The method we developed is based on the selective displacement of the organic complexant of a Th(IV) complex with sulfate followed by titration of the displaced complexant. In two such methods for milligram levels of thorium,[6,7] more ethylenediaminetetraacetic acid (EDTA) is added than is required to complex Th(IV) and other ions at pH 2, the excess EDTA is titrated with Bi(III) to a xylenol orange end point, sulfate is added at pH 1, and the displaced EDTA is again titrated with Bi(III). Our modifications include substitution of DTPA for EDTA, use of a single pH of 1.4 for the entire method, and extension to submilligram levels of thorium. Improved selectivity is shown by the tolerances measured for 61 metal ions and nonmetal anions.

II. EXPERIMENTAL

A. Selection of Complexant and pH Level

The substitution of DTPA, whose stability constant with Th(IV) is 10^4 greater than that of EDTA,[8] permits complex formation at a lower pH to gain selectivity. A single pH for both Bi(III) titrations provides ease of operation, especially with an eventual automated analyzer. It also provides greater tolerances for diverse ions because their complexation is equal for the initial and final titrations of excess complexant and sulfate-displaced complexant.

The effect of pH on the titration of 560 μg Th is given in Table I. We selected a pH value of 1.40 ± 0.05, toward the lower end of the range of quantitative measurement, for routine use.

B. Diverse Ion Tolerances

Tables II and III summarize the tolerances of 45 metal ions and 16 nonmetal anions. The ions were added individually to 1.99 μmol (462 μg) Th and titrated. The highest molar ratio tested for all ions was 100, except 1000 for fluoride. If a result was significantly different at the 95% confidence level relative to thorium alone, testing was continued with lower molar ratios until there was no significant difference.

TABLE I

EFFECT OF pH ON TITRATION ACCURACY

pH	Th Result[a] (μg)	pH	Th Result[a] (μg)
1.10	583	1.35	559
1.15	588	1.40	561
1.20	581	1.45	561
1.25	579	1.50	561
1.30	563	1.55	566

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[a] 95% confidence limits are 556 to 564 μg Th.

We tested special treatments (given in Sec. III) designed to provide increased tolerances for individual diverse ions. Obtained tolerances and relevant footnotes are given in Tables II and III. Addition of ascorbic acid has positive and negative aspects because it reduces Ce(IV), Fe(III), and V(V) to oxidation states having greater tolerances, but it reduces gold, palladium, and selenium to colloids that adversely affect end-point discrimination. It also forms a red complex with U(VI) that interferes in the end-point measurement. Thiourea reduces Cu(II), a serious interference, to more tolerable Cu(I). Hydrogen peroxide reduces permanganate to less interfering Mn(II). The titrant Bi(III) obviously is not a direct interference, but its presence requires additional DTPA solution, resulting in loss of end-point distinction caused by the increased volume. Special treatments to increase tolerances of certain nonmetal anions include fuming with perchloric acid to volatilize fluoride, masking of phosphate with Mg(II), and masking of sulfate with Ba(II).

C. Reliability

The reference solution was prepared using thorium metal that had been characterized for metallic impurities by emission spectrography and for major nonmetallic impurities by chemical analyses. The indicated purity was 99.7 ± 0.2%. Its assay value was established by direct DTPA titration at pH 2 using xylenol orange as the indicator.[9,10] At this pH, the titration of the detected metal impurities was insignificant. The concentration of the DTPA solution had been established relative to zinc metal, NBS SRM 683, and 99.99% copper metal with no difference. These calibrations are described in Sec. III.

Table IV summarizes the results of titrating six portions of the thorium reference solution at each of five levels from 56 to 840 μg Th by the recommended procedure. Bias is insignificant and the standard deviation is a relatively constant 2 μg over this range corresponding to 3.5% at the low limit of 56 μg, and 0.3% at the upper limit of 840 μg.

TABLE II

METAL ION TOLERANCES

Metal Ion	Tolerance Level[a]	Metal Ion	Tolerance Level[a]	Metal Ion	Tolerance Level[a]	Metal Ion	Tolerance Level[a]
Ag(I)	2	Cr(VI)	5	Mn(VII)	0.5 [h]	Sc(III)	g
Al(III)	50	Cu(II)	5 [f]	Mo(VI)	1	Se(IV)	10 [b]
As(III)	5	Er(III)	100	Na(I)	100	Sn(IV)	1
Au(III)	2 [b]	Fe(III)	25 [d]	Ni(II)	10	Te(IV)	10
Ba(II)	50	Ga(III)	g	Pb(II)	10	Tl(III)	3
Be(II)	10	Hg(II)	50	Pd(II)	5 [b]	U(VI)	40 [i]
Bi(III)	2 [c]	In(III)	0.5	Pt(IV)	10	V(V)	0.1 [d]
Ca(II)	100	La(III)	100	Re(IV)	1	W(VI)	g
Cd(II)	100	Lu(III)	25 [e]	Rh(III)	10	Y(III)	50 [e]
Ce(IV)	50 [d,e]	Mg(II)	100	Ru(III)	1	Zn(II)	100
Co(II)	10	Mn(II)	10	Sb(III)	10	Zr(IV)	0.5
Cr(III)	5						

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[a] The highest molar ratio tested without interference. Molar ratio relative to 1.99 µmol (462 µg) Th.

[b] In absence of ascorbic acid, which produces a precipitate, probably colloids of gold, palladium, and selenium.

[c] Used as titrant. Forms Bi(III)-DTPA complex at pH 1.4 that is not displaced by sulfate. Presence requires larger quantity of DTPA solution. Increase in volume causes indistinct end point.

[d] Tolerance level with ascorbic acid present.

[e] Probably tolerant to higher ratio. Compound used had thorium impurity.

[f] Tolerance level with thiourea present.

[g] Interferes essentially quantitatively.

[h] With hydrogen peroxide present.

[i] Tolerance level decreases to molar ratio of 10 in presence of ascorbic acid.

TABLE III

NONMETAL ANION TOLERANCES

Anion	Tolerance Level[a]	Anion	Tolerance Level[a]	Anion	Tolerance Level[a]	Anion	Tolerance Level[a]
Acetate	25	Chloride	100	Nitrate	100	Sulfate[b]	1 [e]
Bromide	100	Fluoride[b]	1000 [c]	Oxalate	b	Thiocyanate	100
Bromate	10	Iodide	100	Phosphate[b]	5 [d]	Thiosulfate	b
Citrate	b	Iodate	10	Silicate	100	Tartrate	25

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[a] The highest molar ratio tested without interference. Molar ratio relative to 1.99 µmol (462 µg) Th.

[b] Interferes essentially quantitatively.

[c] Tolerance level after fuming sample with HNO_3 and $HClO_4$ to dryness.

[d] Tolerance level with Mg(II) masking.

[e] Tolerance level with Ba(II) masking.

TABLE IV

RELIABILITY OF RECOMMENDED PROCEDURE

Thorium Taken (µg)	Thorium Titrated[a] (µg)	Thorium Titrated[a] (%)	Standard Deviation (µg)	Standard Deviation (%)
56.0	54.9	98.0	1.9	3.5
112.0	112.9	100.8	1.9	1.7
280	282	100.7	2.4	0.9
560	560	100.0	1.2	0.2
840	840	100.0	2.3	0.3
			2.0[b]	

[a] Average of six titrations.

[b] Pooled standard deviation.

III. RECOMMENDED PROCEDURE

A. Apparatus

1. Buret, 5-mℓ, 0.01-mℓ divisions. A light focused on the solution, with subdued room lighting, provides more acute discernment of the end-point color change.
2. Magnetic stirrer, Teflon-coated bars.
3. pH meter.

B. Reagents

Analytical reagent grade chemicals, except as noted, and distilled water are used. Reagents that do not require special preparation are not listed.

1. **DTPA Solution, 1m*M*.** Dissolve 0.392 g of DTPA (Aldrich Chemical Company) in water, dilute to 995 mℓ, adjust the pH to 1.4 with 15.6*M* HNO_3, and dilute to 1 ℓ with 0.1*M* HNO_3.

2. **Bismuth Nitrate Solution, 1.000m*M*.** Dissolve 0.2090 g of 99.9+% bismuth metal in 6 mℓ of 5*M* HNO_3 with gentle heat, dilute to 995 mℓ with 0.01*M* HNO_3, adjust the pH to 1.4 with about 2 mℓ of 1.6*M* HNO_3, and dilute to 1 ℓ with 0.01*M* HNO_3.

3. **Copper Nitrate Reference Solution, 5m*M*.** Using 99.99% copper metal that is surface-cleaned with HNO_3, prepare an accurate 5m*M* solution in about 0.05*M* HNO_3.

4. **Zinc Chloride Reference Solution, 5m*M*.** Using 99.9+% zinc metal, such as NBS SRM 683, surface-cleaned with HCl, prepare an accurate 5m*M* solution in about 0.05*M* HCl.

5. **Buffer Solution.** Dissolve 4.6 g of maleic acid in water, dilute to about 90 mℓ, adjust the pH to 1.4 with HNO_3, and dilute to 100 mℓ with 0.1*M* HNO_3.

6. **Buffer-Ascorbic Acid Solution.** Dissolve 4.6 g of maleic acid and 8.4 g of ascorbic acid in about 90 mℓ of water, adjust the pH to 1.4 with HNO_3, and dilute to 100 mℓ with 0.1*M* HNO_3.

7. **Xylenol Orange Solution, 0.5%.** Dissolve 0.125 g of xylenol orange in a mixture of 20 mℓ of water and 5 mℓ of absolute ethanol.

8. **Ammonium Sulfate Solution, 3*M*.** Dissolve 39.6 g of anhydrous ammonium sulfate in water, add 7 mℓ of 15.6*M* HNO_3, dilute to about 90 mℓ, adjust the pH to 0.65 with HNO_3, and dilute to 100 mℓ with 0.1*M* HNO_3.

9. **Potassium Tetroxalate Solution, 0.1*M*.** Dissolve 18 g $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ in 1 ℓ of water. This solution is recommended by the NBS for pH meter calibration at pH 1.5.[11]

10. **Hydrogen Peroxide Solution, 3%.** Freshly prepare by diluting 30% solution with water.

11. **Thiourea Crystals.**

C. Calibration of DTPA Solution.

Titrate the DTPA solution with six 4- to 5-mmol portions of each of the copper and zinc reference solutions. For copper, use 1-(2-Pyridylazo)-2-naphthol(PAN) indicator, pH 5.5 with hexamethylenetetramine buffer, and 60°C. For zinc, use xylenol orange indicator, pH 5.7 with pyridine buffer, and ambient temperature.

D. Sample Analysis

Special Treatments for Samples Containing Certain Impurities

Fluoride. Add 1 mℓ of $15.6M$ HNO_3 and 1 mℓ of $6M$ $HClO_4$ to the sample aliquot, heat to dryness, and dissolve the residue in up to 5 mℓ of $1M$ HNO_3.

Sulfate. Before adding the buffer solution, step 1, add 2 mmol of Ba(II) per mmol of sulfate. The tolerance for sulfate then is an equal molar ratio relative to thorium.

Phosphate. Before adding the buffer solution, step 1, add 2 mmol of Mg(II) per mmol of phosphate. The tolerance for phosphate then is a molar ratio of 5 relative to thorium.

Copper. Before adding the buffer solution, step 1, add thiourea crystals until blue Cu(II) just reduces to colorless Cu(I).

Permanganate. Before adding the buffer solution, step 1, add 3% H_2O_2 until purple Mn(VII) reduces to pink Mn(II).

Calibration of pH Meter. Calibrate the pH meter frequently at pH 1.5 with the $0.1M$ potassium tetroxalate solution.

1. Add 1 mℓ of buffer solution or buffer-ascorbic acid solution to a sample aliquot of 5 mℓ or less containing 56 to 840 µg Th.
   - Use the buffer solution for samples containing greater than a 10-molar ratio of uranium relative to thorium or when any gold, palladium, or selenium is present.
   - Use the buffer-ascorbic acid solution for samples containing Ce(IV), Fe(III), and V(V).

2. Add 5 mℓ of 1mM DTPA solution and adjust the pH to 1.4 with NaOH and HNO_3.
   - From this step on, maintain the pH at 1.4 ± 0.05.

3. Add 0.1 mℓ of xylenol orange solution.
   - Yellow indicates complete formation of the Th(IV)-DTPA complex.
   - Red indicates more than 5 mmol of Th or Th and one or more diverse metals (bismuth, zirconium, gallium, scandium, or tungsten). The last three are serious interferences. The tolerances for bismuth and zirconium relative to Th are 2 and 0.5, respectively. Additional quantities of DTPA can be added as long as the tolerance limits are not exceeded. Also, a smaller sample aliquot may be analyzed.

4. Titrate with the 1mM bismuth nitrate solution to the yellow-to-red end point.

5. Add 0.5 mℓ of $3M$ ammonium sulfate solution.
   - A cloudy suspension indicates Ag(I), Ba(II), or Hg(I). Tolerances are given in Table II.

6. Refill the buret and titrate with the 1mM bismuth nitrate solution to the yellow-to-red end point and record the volume of titrant as V.

7. Calculate the concentration of thorium by

$$C = \frac{(232.04)\,(mM)\,(V)}{(S)}$$

where

C = thorium concentration, µg/mℓ or µg/g

mM = millimolarity of bismuth nitrate solution

V = volume, mℓ, of bismuth nitrate solution used for final titration

S = sample aliquot, mℓ or g

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