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The Direct Complexometric Titration of Thallium(III) Using Iron(III)-Sulfosalicylate Complex as Metal Indicator

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The iron(III)-sulfosalicylate complex has been used as the indicator for the direct complexometric determination of thallium(III). This indicator permits the rapid and accurate determination of both micro and macro quantities of thallium(III). The titrations are best carried out at about pH 2.6. Most of the divalent cations, such as calcium, strontium, barium, magnesium, manganese and mercury, and trivalent cations, such as chromium and aluminum, do not interfere in the determination.

Thallium(III) reacts with ethylenediaminetetraacetic acid (EDTA) to form a 1 : 1 complex. This reaction has been recently used as the basis for both the direct[1,2] and the indirect[3,4] titrimetric determination of thallium(III) using such metal indicators as xylenol orange, 1-(2-pyridylazo)-2-naphthol (PAN) and 4-(2-pyridylazo)resorcinol (PAR). In a previous communication[5] we reported on the use of familiar dyes, methylene blue and methyl violet, as metal indicators for the direct complexometric determination of thallium(III). Since colored-metal complexes were not used as indicators earlier in the titrimetric determination of thallium(III), a direct complexometric titration of it has been carried out using the iron(III)-sulfosalicylate complex as an indicator; the results obtained will be described in this communication. The use of sulfosalicylic acid for the indirect complexometric determination of thallium(III) has been previously reported.[6]

The determination of thallium(III) using the iron(III)-sulfosalicylate complex as an indicator is based on the facts that in spite of the greater stability of the iron(III)-EDTA complex[7] as compared with the thallium(III)-EDTA complex,[8] EDTA combines with free thallium(III) ions in preference to the iron(III) present as the sulfosalicylate complex, and that when all the thallium(III) ions have combined with EDTA, the violet color of the indicator is discharged due to the formation of the almost colorless iron(III)-EDTA complex, which is much more stable than the iron(III)-sulfosalicylate complex.

Experimental and Results

A 0.05 M solution of the disodium salt of EDTA was prepared by dissolving 18.615 g. of this salt in doubly-distilled water and by then making up the volume to a liter. The strength of the solution was checked by titrating it against calcium carbonate, using calcon as the metal indicator.

A stock solution of thallium(III) nitrate was prepared by dissolving thallium metal in nitric acid and by then oxidizing it to thallium(III)

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TABLE I. EFFECT OF HYDROGEN ION CONCENTRATION ON THE TITRATION OF THALLIUM(III)

Thallium(III) solution taken=30.66 mg.; EDTA solution=0.05 M
Volume of indicator used=0.5 ml.; EDTA used for blank=0.05 ml.

pH	1.5	2.0	2.3	2.6	2.8	3.0	3.2	3.5
Volume of EDTA used, ml.	2.80	2.90	3.00	3.00	3.00	3.00	2.80	2.65
Thallium(III) found, mg.	28.61	29.63	30.66	30.66	30.66	30.66	28.61	27.08

Note: 1 The volumes of EDTA given in Table I and the succeeding Tables II and III are corrected for blank.
2 The data recorded in Tables I, II and III represent the mean value of the multiple determination, standard deviation being within 0.5%.

with alkaline bromine. The thallium(III) hydroxide thus precipitated was washed well with water and dissolved in a minimum quantity of dilute nitric acid. The solution was then shaken with an excess of thallium(III) hydroxide in order to minimize the acidity of the solution. The thallium content of the solution was estimated by titrating it with a EDTA solution standardized as above, using xylenol orange as the metal indicator.

The iron(III)-sulfosalicylate complex indicator was prepared by mixing 10 ml. of a 0.05 M ferric alum solution and 30 ml. of 0.05 M sulfosalicylic acid, and by then making up the volume to 100 ml. Five-hundredths milliliters of this indicator was used throughout the experiment.

Buffer solutions with pH values in the 2.2—4.00 range were made by mixing requisite quantities of 0.01 M solutions of potassium hydrogen phthalate and hydrochloric acid.

The solutions of various metal ions used for interference studies were prepared by dissolving the requisite amounts of analytical-grade reagents in doubly-distilled water; they were standardized, where necessary, by the determination of their metal contents by usual methods.

The Effect of pH.—Determinations of thallium(III) were carried out at various pH values (adjusted with a pH meter using glass and calomel electrodes) in order to find out the optimum hydrogen ion concentrations for titration. The data recorded in Table I show that the indicator is pH-dependent and that it works well only in a limited pH range, from 2.3 to 3.0.

Titration Procedure.—A solution containing 10.22 to 91.98 mg. of thallium (III) was taken and diluted to about 20 ml. with doubly-distilled water; its pH was adjusted to about 2.6 by potentiometric titrations with dilute ammonium hydroxide; a requisite amount of a buffer solution was added to maintain the pH; 0.5 ml. of the iron(III)-sulfosalicylate complex indicator was added,

TABLE II. DETERMINATION OF THALLIUM(III) WITH EDTA USING IRON(III)-SULFOSALICYLATE COMPLEX INDICATOR AT pH 2.6

Volume of indicator used=0.5 ml.
EDTA used for blank=0.05 ml.

Th(III)* taken, mg.	Volume of EDTA used, ml.	Th(III)* found, mg.	Error %
10.22	1.00	10.22	—
20.44	2.00	22.44	—
30.66	3.00	30.66	—
40.88	4.00	40.88	—
51.10	5.00	51.10	—
61.32	6.00	61.32	—
71.54	7.05	72.05	+0.71
81.76	8.00	81.76	—
91.98	8.95	91.46	−0.57

* See Note 2 in Table I.

TABLE III. EFFECT OF FOREIGN IONS

Thallium(III) taken=40.88 mg.=4.00 ml. of 0.05 M thallium(III)
pH of the soln.=2.6; EDTA soln.=0.05 M

Foreign cation	Wt. of foreign cation, mg.	Volume of EDTA used, ml.	Th(III)* found, mg.
Ca^{2+}	40.00	4.00	40.88
Sr^{2+}	43.80	4.00	40.88
Ba^{2+}	34.31	4.00	40.88
Mg^{2+}	30.40	4.00	40.88
Zn^{2+}	32.68	5.55	56.12
Pb^{2+}	51.80	5.25	53.65
Cd^{2+}	41.90	5.10	52.12
Mn^{2+}	41.13	4.00	40.88
Hg^{2+}	38.90	4.00	40.88
Cu^{2+}	31.76	Interferes**	—
Ni^{2+}	44.01	Interferes**	—
Co^{2+}	43.32	Interferes**	—
Al^{3+}	33.70	4.00	40.88
Cr^{3+}	28.88	4.00	40.88
Bi^{3+}	46.55	Interferes	—
Ga^{3+}	34.86	Interferes**	—
In^{3+}	34.41	Interferes**	—
Ce^{3+}	35.30	Interferes**	—
Ce^{4+}	35.30	Interferes**	—

* See Note 2 in Table I.
** No sharp end point was obtained, therefore, the amount of EDTA used could not be recorded.

and the solution was titrated with a 0.05 M EDTA solution until the violet color of the solution was discharged. A blank titration with 0.5 ml. of the indicator was also carried out under similar conditions, and the necessary correction was made in the determinations. The blank correction amounted to 0.05 ml. of the 0.05 M EDTA solution. The results obtained are shown in Table II.

The Effect of Foreign Ions.—Since EDTA forms fairly stable complexes with large number of cations, many of them may be expected to interfere in the titrimetric determination of thallium(III). The determination of thallium(III) was carried out at pH 2.6 in the presence of almost equivalent amounts of many di- and tervalent cations; the results obtained are recorded in Table III. The divalent metal ions, such as calcium, strontium, barium, magnesium, manganese, and mercury, and the tervalent metal ions, such as chromium and aluminum, do not interfere, but gallium, indium, bismuth, cerium and most of the colored metal ions interfere in the determination of thallium(III).

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