The Spectrophotometric Determination of Thallium(III) with Xylenol Orange[1]

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Thallium(III) has been determined spectrophotometrically by extracting the thallium(III)-complexes of *p*-phenetidine,[2] *p*-aminophenol,[3] rhodamine B,[4,5] brilliant green,[6] methylviolet[7] and bis(dimethylaminophenyl)-antipyrylcarbinol[8] into a suitable organic solvent. In the present paper, a very sensitive reagent, xylenol orange, which forms a water-soluble complex with thallium(III), is used for the spectrophotometric determination of trace amounts of thallium.

Experimental

Reagents and Apparatus.—*Standard Thallium(III) Solution.*—An about 0.01 M thallium(III) nitrate solution was prepared by dissolving freshly prepared thallium(III) oxide, which had been precipitated from a thallium(III) chloride solution by adding a diluted aqueous ammonia solution and then carefully washed with water until the filtrate became free from ammonium and chloride ions, in concentrated nitric acid and diluting it with water. The solution was standardized against a standard EDTA solution.[9] The concentration of nitric acid in the solution was about 0.5 M. A working thallium(III) solution was prepared by diluting the above solution with 0.05 M nitric acid.

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1) This work was partly presented at the 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

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3) V. G. Gladyshev and G. A. Tolstikov, *Zavodskaya Lab.*, **22**, 1166 (1956); *Chem. Abstr.*, **51**, 3361 (1957).

4) H. Onishi, This Bulletin, **29**, 945 (1956).

5) C. L. Luke, *Anal. Chem.*, **31**, 1680 (1959).

6) N. T. Voskresenskaya, *Zhur. Anal. Khim.*, **11**, 585 (1956); *Chem. Abstr.*, **51**, 7230 (1957).

7) G. V. Efremov and C. Syui, *Vestnik. Leningrad Univ.*, **13**, No. 16, Ser. Fiz. i Khim. No. 3, 156 (1958).

8) A. I. Busev and V. G. Tiptsova, *Nauk. Dokladyvysshei Shkoly, Khim. i Khim. Tekknol.*, **1959**, No. 1, 105.

9) K. Ueno, "Kireto Tekiteiho (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 318.

All the other reagents and the apparatus used were the same as those reported on previously.[10]

Standard Procedure for the Determination.—To a solution in a 25 ml. volumetric flask which contained 20 to 150 μg. of thallium, 3 to 8 ml. of a 2 M acetic acid solution and 3 to 5 ml. of a 1×10^{-3} M xylenol orange solution were added. The solution was then diluted to the mark with water and mixed. After 15 min., the absorbance of the solution was measured at 520 mμ, using a reagent blank as the reference.

Results and Discussion

Absorption Curve.—The maximum absorption of the thallium - xylenol orange complex was observed at about 520 mμ, when it was measured against a reagent blank as the reference.

The Effect of the Concentration of Acetic Acid and the Color Stability.—The effect of the concentration of acetic acid on the absorbance of the solution was examined; the results are shown in Fig. 1. The maximum absorbance

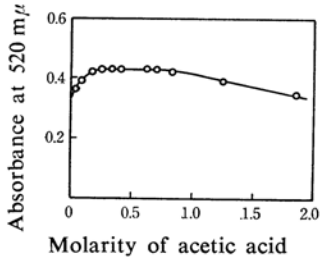

Fig. 1. Effect of concentration of acetic acid
Tl taken: 103 μg
XO concn.: 1.61×10^{-4} M

is obtained when the acid concentration is adjusted to 0.25 to 0.7 M. In all the concentrations of acetic acid, the color formation was almort instantaneous. However, the intensity of the color of the resulting solution tended to decrease slowly with time; the change in abrorbance with time is indicated in Table I.

TABLE I. EFFECT OF TIME OF STANDING

Thallium taken: 124 μg.
Xylenol orange concn.: 1.60×10^{-4} M
Acetic acid concn.: 0.41 M

Time of standing, min.	Absorbance at 520 mμ
5	0.539
10	0.536
15	0.531
20	0.528
30	0.522
45	0.517
60	0.512
120	0.500
180	0.492
240	0.489
400	0.463

10) M. Otomo, This Bulletin, 37, 504 (1964).

The effect of the concentration of other acids was also examined. At relatively lower concentrations, nitric acid and perchloric acid gave almost the same absorbance as that obtained with acetic acid. However, the color was unstable; the absorbance decreased by about 10% during the first 15 min. when the concentration of nitric acid was 0.2 M, and by about 4%, at the same concentration, of perchloric acid. Hydrochloric acid, at any concentration, is not adequate as the solvent, because thallium(III) forms stable chloro-complexes with chloride ions.

The Effect of the Addition of the Reagent.—Figure 2 shows the effect of the amount of the reagent. A high and almost constant absorbance is obtained when more than 3 ml. of a 1×10^{-3} M xylenol orange solution is added.

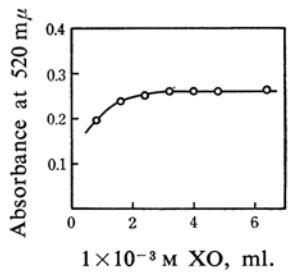

Fig. 2. Effect of addition of xylenol orange.
Tl taken: 62 μg.
CH_3CO_2H concn.: 0.41 M

Adherence to Beer's Law.—As is shown in Fig. 3, Beer's law is oveyed ober the range from 20 to 150 μg. of thallium in 25 ml.

The apparent molar extinction coefficient of the thallium(III) - xylenol orange complex is 21300 at 520 mμ. The sensitivity of the color reaction at this wavelength is 0.01 μg. of thallium per cm^2.

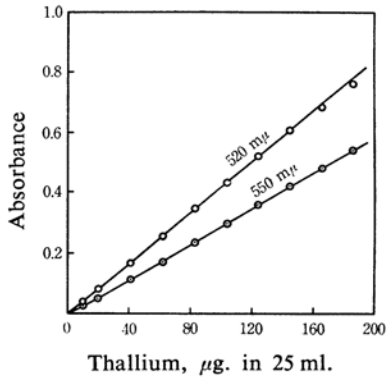

Fig. 3. Calibration curves.
XO concn.: 1.61×10^{-4} M
CH_3CO_2H concn.: 0.41 M

The Effect of Diverse Ions.—The effect of diverse ions was examined with solutions containing 103 μg. of thallium. Of the anions tested, the following did not interfere under the described conditions: fluoride up to 50 μmol., nitrate up to 500 μmol., and sulfate up to 100 μmol. Chloride, bromide, iodide, NTA and EDTA interfere seriously with the determination.

Of the 32 cations, including bi-, ter- and quadrivalent metal cations, bismuth(III), gallium(III), indium(III), iron(III), thorium(IV), vanadium(IV) and zirconium(IV) interfere with the determination by forming colored solutions. The interference of thorium and zirconium can, however, be eliminated by the addition of fluoride ions.

The proposed method, which is rapid and sensitive, seems to be applicable to the determination of traces of thallium in many samples after thallium has been preliminarily separated from the interfering ions by an appropriate method.

The Composition of the Complex.—The composition of the thallium(III) - xylenol orange complex was determined by the method of continuous variations as well as by the mole ratio method. Both methods showed that a 1 to 1 complex is formed between thallium(III) and xylenol orange at the acetic acid concentration described above.

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