Ultraviolet Spectrophotometric Determination of Lead using Thiomalic Acid*

By Yasuhisa HAYASHI, Shigeo HARA and Isao MURAKI

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As has been reported,[1] thiomalic acid (henceforth abbreviated TMA) and lead form a stable, colorless complex in acidic and alkaline solutions. As can be seen from the absorption spectra of lead-TMA solutions at various pH values ranging from 5.8 to 10.5 (Fig. 1), the lead-TMA complex has a maximum absorption at 265 mμ in acidic, and at 305 mμ in alkaline solutions. As the absorption spectrum of a TMA solution is not affected by pH change,[1] the wavelength of 305 mμ is adopted for the spectrophotometric determination of small amounts of lead. Here are presented conditions for the ultraviolet spectrophotometric determination of lead; the composition of the complex is also discussed.

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[1] I. Muraki, S. Hara and Y. Hayashi, *Japan Analyst*, in press.

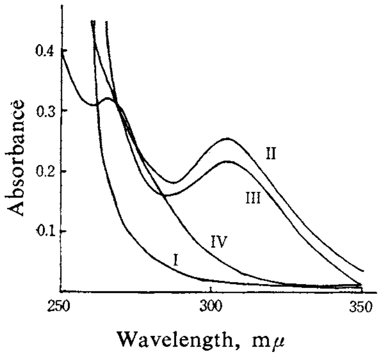

Fig. 1. Absorption spectra of lead-TMA solutions at various pH values.
Curve I 0.1% TMA soln. only, pH 10.5
Curve II Pb-TMA soln., 10 p.p.m. Pb, pH 10.5
Curve III Pb-TMA soln., 10 p.p.m. Pb, pH 9.2
Curve IV Pb-TMA soln., 10 p.p.m. Pb, pH 5.8
Buffer: 0.1 M NaOH - $Na_2B_4O_7$ system., 20 ml./100 ml.
Reference: Water Temp.: 18°C

Standard lead solution was prepared as follows: 1.0000 g. of 99.999% pure lead was dissolved in nitric acid, and the solution was evaporated to dryness; the residue was dissolved in water and diluted to 1000 ml. with water. An aliquot of this solution was then diluted with water to prepare a standard solution containing 100 p.p.m. of lead. Other materials and apparatus were the same as reported in the preceeding paper.[1] The procedure for making the calibration curve is as follows: Pipet an aliquot of the standard lead solution into a 100 ml. measuring flask, and add 20 ml. of 0.1% TMA solution and 20 ml. of buffer solution and dilute to the mark with water and then measure the absorbance of the solution at 305 mμ against water.

To obtain optimum conditions for the determination of lead, various factors were studied: In order to find an optimum pH range, the absorbances at 305 mμ were plotted against pH values. Maximum absorption was found in the pH range of 10.0—11.0. The absorbances of two series of solutions containing 5.0 and 10.0 p.p.m. of lead, respectively, and various amounts of the reagent were measured. It was found that the optimum amount of TMA was 15.0—25.0 ml. of a 0.1% solution in 100 ml.; a larger excess of TMA caused a slight increase in absorbance. The absorbance of the solutions of lead-TMA complex showed no appreciable change within about 20 hr. In order to confirm the mole ratio of the lead-TMA complex, the continuous variation method and the mole ratio method were used. In the first method, absorbances of a series of solutions containing various amounts of 5×10^{-3} M TMA were measured against the reagent blank. When the mole ratio of lead to TMA was 1 to 3, maximum absorbance resulted. The results of the second method also confirmed that the mole ratio corresponds to 1 to 3. The calibration curve (Fig. 2) shows that Beer's law is obeyed over the concentration range from 0.5 to 40.0 p.p.m. of lead. The molar absorptivity of the method is 5.2×10^3, and the sensitivity is 0.04 μg. Pb/cm^2 for $\log I_0/I=0.001$. As is shown in Table I, it is found that colored ions such as copper(II), cobalt(II), nickel(II), iron(II, III), etc., and metal ions forming precipitates in alkaline solutions such as tin interfere. The proposed method is much inferior to the

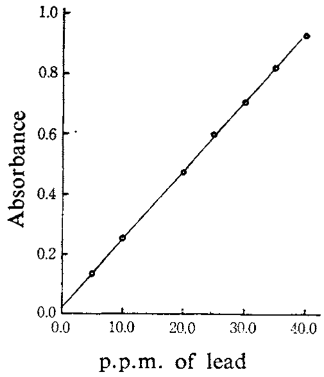

Fig. 2. Calibration curve.
TMA: 0.1% soln. 20 ml./100 ml.
Buffer: 0.1 M NaOH - $Na_2B_4O_7$ system, 20 ml./100 ml., pH 10.5
Wavelength: 305 mμ.
Reference: Water Temp.: 19°C

TABLE I. EFFECT OF DIVERSE IONS ADDED TO THE 10.0 p.p.m. SOLUTIONS OF LEAD

Ion	Added p.p.m.	Added as	Absorbance at 305 mμ
—	—	—	0.253
Cd(II)	50	Sulfate	0.247
Cd(II)	25	Sulfate	0.254
Zn(II)	30	Sulfate	0.245
Zn(II)	15	Sulfate	0.252
Al(III)	50	Chloride	0.252
As(III)	20	Chloride	0.245
As(III)	10	Chloride	0.252
Sb(III)	30	Chloride	0.485
Sn(IV)	20	Chloride	Ppt.
Cu(II)	20	Sulfate	1.08
Cu(II)	5	Sulfate	0.266
Cu(II)	2	Sulfate	0.254
NaCl	10 ml.	1 M Soln.	0.252
Na_2SO_4	10 ml.	1 M Soln.	0.332
NH_4Cl	10 ml.	1 M Soln.	0.250
$NaNO_3$	10 ml.	1 M Soln.	0.252

dithizone method[2] in sensitivity, but the procedure is simpler. As the procedure is operated in alkaline solution (pH 10.5), interferences from diverse ions must be considered.

Faculty of Science and Technology
Kinki University
Fuse, Osaka (Y. H. & I. M.)

Government Industrial Research
Institute, Osaka
Ikeda, Osaka (S. H.)

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2) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd. Ed., Interscience Pub., New York (1959), p. 563.