Determination of Lead and Thallium(I) in Presence of Each Other by Amperometric Titrations

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Thallium in presence of lead has been determined by Winn1) in urine by digesting a sample of urine with a mixture of sulphuric, perchloric and nitric acids. Thallium was oxidised to the trivalent state with bromine water and then extracted with a chloroform solution of dithiozone, while lead under these conditions, remained in the water phase. The chloroform extract was used for the polarographic estimation of thallium.

In supporting electrolytes which do not complex lead ions, the thallium and lead waves coincide. The half-wave potentials of lead and thallous ion in 1 M potassium nitrate has been found to be -0.38 V.2) and -0.46V.3) respectively against SCE at 25°C and thus their polarographic determination in presence of each other presents some difficulty, but by employing sodium or potassium hydroxide supporting electrolyte the half-wave potential of lead shifts to -0.76 V.4) Thallium can thus easily be determined in presence of lead. In the present communication a method will be described by which lead and thallium (ous) can be determined in presence of each other amperometrically without oxidizing thallous to thallic ion.

Apparatus and Experimental

Heyrovsky LP55 polarograph was used. The dropping mercury electrode had the following characteristics: $m=2.12$ mg./sec., $t=3.6$ sec. (at -1.0 V. vs. SCE in 0.1 M potassium nitrate solution).

All measurements were done at 20°C, purified hydrogen was used for the removal of dissolved oxygen.

All reagents employed were of A. R. grade. Purity of the samples was checked by standard methods.

Determination of Lead in Presence of Thallium Ion.—The principles involved in the method are as follows: (i) Tl^+ does not form a complex with potassium ferrocyanide5) in concentrations below 0.1 M, but lead does at all concentration; and (ii) when a potential of -0.4 V. vs. SCE is applied to a solution containing both lead and thallium ion, it is the thallous ion which can be reduced.

Solutions of different strength containing Pb^{2+} and Tl^+ were prepared in 1 M potassium nitrate. One thousandth percent solution of triton×100 was used as maxima suppressor in the final solution. The mixture was titrated with a standard potassium ferrocyanide solution at an applied voltage of -0.4 V. vs. SCE. Hydrogen was passed after every addition. Titrations were performed both by the direct and reverse methods. The results are recorded in Tables I and II.

Determination of Thallium in Presence of Lead.—(i) In alkaline solution (pH 11.5) of

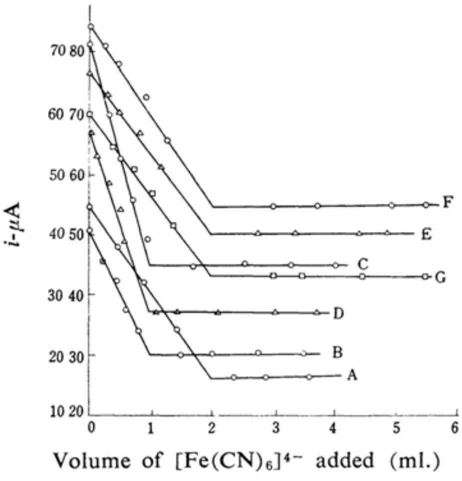

Fig. 1. Direct titration of Pb^{2+} in presence of Tl^+ with 0.1 M $K_4Fe(CN)_6$.

Curve A: 1 ml. of 0.2 M Pb^{2+}+0.2 ml. of 0.1 M Tl^+.
B: 0.5 ml. of 0.2 M Pb^{2+}+0.2 ml. of 0.1 M Tl^+.
C: 0.5 ml. of 0.2 M Pb^{2+}+1 ml. of 0.1 M Tl^+.
D: 0.5 ml. of 0.2 M Pb^{2+}+0.4 ml. of 0.1 M Tl^+.
E: 1.0 ml. of 0.2 M Pb^{2+}+2 ml. of 0.1 M Tl^+.
F: 1.0 ml. of 0.2 M Pb^{2+}+5 ml. of 0.1 M Tl^+.
G: 1.0 ml. of 0.2 M Pb^{2+}+10 ml. of 0.1 M Tl^+.

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1) G. S. Winn, F. L. Godfrey and K. W. Nelson, *Arch. Ind. Hyg. Occupational Med.*, 6, 14 (1952).

2) H. M. Hershenson, M. E. Smith and D. N. Hume, *J. Am. Chem. Soc.*, 75, 507 (1953).

3) L. Meites, ibid., 73, 4155 (1951).

4) J. Heyrovsky and D. Ilkovic, *Collection Czechoslov. Chem. Communs.*, 7, 198 (1935).

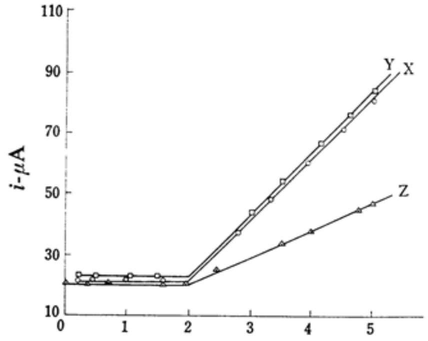
5) J. N. Gaur, H. C. Gaur and A. K. Bhattacharya, *J. Indian Chem. Soc.*, 35, 144 (1958).

TABLE I. DIRECT TITRATION OF Pb IN PRESENCE OF THALLIUM

Sample No.	Composition of mixture (10 ml.) in 1 M KNO_3	Volume of sol. taken in cell ml.	Volume of 0.1 M $K_4Fe(CN)_6$ used ml.	Amount of Pb^{2+} found g.	Amount of Pb^{2+} actually present (calcd.) g.
A	5 ml. of 0.2 M Pb^{2+} 1 ml. of 0.1 M Tl^+	20	2.0	0.04144	0.04144
B	2.5 ml. of 0.2 M Pb^{2+} 1 ml. of 0.1 M Tl^+	10	1.0	0.02072	0.02072
C	2.5 ml. of 0.2 M Pb^{2+} 5 ml. of 0.1 M Tl^+	10	1.0	0.02072	0.02072
D	2.5 ml. of 0.2 M Pb^{2+} 2 ml. of 0.1 M Tl^+	10	1.0	0.02072	0.02072
E	5 ml. of 0.2 M Pb^{2+} 10 ml. of 0.1 M Tl^+	20	2.0	0.04144	0.04144
F	5 ml. of 0.2 M Pb^{2+} 25 ml. of 0.1 M Tl^+	20	2.0	0.04144	0.04144
G	5 ml. of 0.2 M Pb^{2+} 50 ml. of 0.1 M Tl^+	20	2.0	0.04144	0.04144

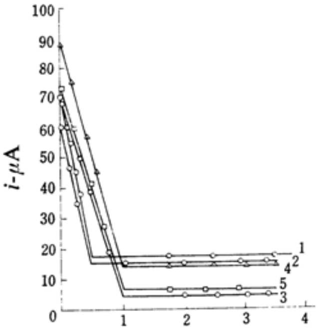
TABLE II. REVERSE TITRATION OF Pb^{2+} IN PRESENCE OF Tl^+

Sample No.	Composition of mixture (100 ml.) in 1 M KNO_3	Strength and volume of $K_4Fe(CN)_6$ in the cell	Volume of mixture used ml.	Amount of Pb^{2+} found g.	Amount of Pb^{2+} present (calcd.) g.
1	50 ml. of 0.2 M Pb^{2+} 5 ml. of 0.2 M Tl^+	40 ml. of 5 mM	2.0	0.04144	0.04144
2	50 ml. of 0.2 M Pb^{2+} 10 ml. of 0.2 M Tl^+	40 ml. of 5 mM	2.0	0.04144	0.04144
3	20 ml. of 0.2 M Pb^{2+} 20 ml. of 0.2 M Tl^+	40 ml. of 2 mM	2.00	0.01666	0.01666



Volume of Pb^{2+} added (in ml.)

Fig. 2. Reverse titration of Pb^{2+} in presence of Tl^+ with $K_4Fe(CN)_6$.
Curve X: 0.1 M Pb^{2+} + 0.01 M Tl^+ added to 40 ml. of 5 mM $K_4Fe(CN)_6$.
Y: 0.1 M Pb^{2+} + 0.02 M Tl^+ added to 40 ml. of 5 mM $K_4Fe(CN)_6$.
Z: 0.04 M Pb^{2+} + 0.04 M Tl^+ added to 40 ml. of 2 mM $K_4Fe(CN)_6$.



Volume of $[CrO_4]^{2-}$ added (in ml.)

Fig. 3. Direct titration of Tl^+ in presence of Pb^{2+} with K_2CrO_4.
Curve 1: 0.25 ml. of 0.2 M Tl^+ + 0.25 ml. of 0.2 M Pb^{2+} titrated with 0.05 M K_2CrO_4.
2: 0.5 ml. of 0.2 M Tl^+ + 0.5 ml. of 0.2 M Pb^{2+} titrated with 0.1 M K_2CrO_4.
3: 5.0 ml. of 0.2 M Tl^+ + 5.0 ml. of 0.2 M Pb^{2+} titrated with 0.5 M K_2CrO_4.
4: 1.0 ml. of 0.2 M Tl^+ + 1.0 ml. of 0.2 M Pb^{2+} titrated with 0.5 M K_2CrO_4.

thallium and lead, only thallium is precipitated as thallous chromate and lead remains in solution as sodium plumbate. (ii) As a potential of −0.5 V. vs. SCE is applied, only thallium is reduced in the alkaline medium. After adjusting the pH of the solution of 11.5 by adding sodium hydroxide the mixture was titrated with a standard solution of potassium chromate. Titrations were done by the direct as well as reverse methods. The results are recorded in Tables III and IV.

TABLE III. DIRECT TITRATION OF Tl^+ IN PRESENCE OF Pb^{2+}

Sample No.	Composition of the mixture (50 ml.) in NaOH (pH=11.5)	Volume of mixture in the cell ml.	Strength and volume of K_2CrO_4 used	Amount of Tl^+ found g.	Amount of Tl^+ present (calcd.) g.
1	1.25 ml. of 0.2 M Tl^+ 1.25 ml. of 0.2 M Pb^{2+}	10	0.5 ml. of 0.05 M	0.01022	0.01022
2	2.5 ml. of 0.2 M Tl^+ 2.5 ml. of 0.2 M Pb^{2+}	10	0.5 ml. of 0.1 M	0.02044	0.02044
3	12.5 ml. of 0.2 M Tl^+ 12.5 ml. of 0.2 M Pb^{2+}	20	1.0 ml. of 0.5 M	0.20439	0.20439
4	2.5 ml. of 0.2 M Tl^+ 2.5 ml. of 0.2 M Pb^{2+}	20	1.0 ml. of 0.1 M	0.40878	0.40878
5	12.5 ml. of 0.2 M Tl^+ 25.0 ml. of 0.2 M Pb^{2+}	20	1.0 ml. of 0.5 M	0.20439	0.20439

TABLE IV. REVERSE TITRATION OF Tl^+ IN PRESENCE OF Pb^{2+}

Sample No.	Composition of the mixture (50 ml.) in NaOH (pH=11.5)	Strength and volume of K_2CrO_4 in cell	Volume of mixture used ml.	Amount of Tl^+ found g.	Amount of Tl^+ present (calcd.) g.
1	1.25 ml. of 0.2 M Tl^+ 1.25 ml. of 0.2 M Pb^{2+}	10 ml. of 1.0 mM	4.0	0.00409	0.00409
2	2.5 ml. of 0.2 M Tl^+ 2.5 ml. of 0.2 M Pb^{2+}	10 ml. of 0.5 mM	1.0	0.00204	0.00204
3	12.5 ml. of 0.2 M Tl^+ 12.5 ml. of 0.2 M Pb^{2+}	10 ml. of 1.0 mM	4.0	0.04087	0.04087
4	2.5 ml. of 0.2 M Tl^+ 25.00 ml. of 0.2 M Pb^{2+}	20 ml. of 1.0 mM	2.0	0.00409	0.00409
5	12.5 ml. of 0.2 M Tl^+ 25.0 ml. of 0.2 M Pb^{2+}	10 ml. of 1.0 mM	4.0	0.04087	0.04087

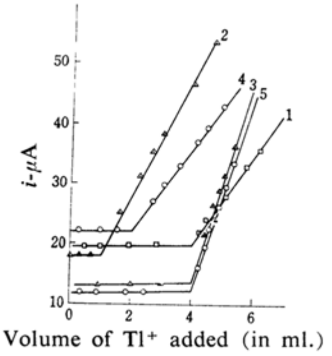


Fig. 4. Reverse titration of Tl^+ in presence of Pb^{2+} with K_2CrO_4.

Curve 1: 0.005 M Tl^++0.005 M Pb^{2+} titrated with 10 ml. of 1.0 mM of K_2CrO_4.
2: 0.01 M Tl^++0.01 M Pb^{2+} titrated with 10 ml. of 0.5 mM of K_2CrO_4.
3: 0.05 M Tl^++0.05 M Pb^{2+} titrated with 10 ml. of 1.0 mM of K_2CrO_4.
4: 0.01 M Tl^++0.1 M Pb^{2+} titrated with 20 ml. of 1.0 mM of K_2CrO_4.
5: 0.05 M Tl^++0.1 M Pb^{2+} titrated with 10 ml. of 1.0 mM of K_2CrO_4.

Discussion

It has been found that the results obtained by the direct and reverse titrations of thallium by potassium ferrocyanide suggest an excellent method of determining lead in presence of thallium in small concentrations (0.01 M Pb^{2+} in 0.05 M Tl^+). The concentration of the thallium ion should not go beyond 0.1 M, since it reacts with potassium ferrocyanide. At pH 11.5 it has been possible to determine thallous ion in presence of lead by titration with potassium chromate. Under these conditions lead does not interfere. It is possible to determine accurately as small as 0.005 M Tl^+ in 0.1 M of Pb^{2+}.

Summary

A method has been described in which thallium(I) can be determined in presence of lead and vice versa. Thallium is determined amperometrically in presence of lead at pH 11.5 and is titrated with potassium chromate, while lead is determined in presence of thallium by titrating with potassium ferrocyanide. It is possible to determine small amounts of lead in large quantities of thallium and vice versa.

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