17. *Qualitative Semimicro-analysis with Reference to Noyes and Bray's System : The Thallium Group.*

By Christina C. Miller.

A scheme of analysis differing from that of Noyes and Bray has been evolved for the detection and estimation of 0·25—50 mg. of silver and lead, 0·25—10 mg. of thallium, and some bismuth in mixtures containing a maximum of 50 mg. of the combined metals. The main features are the dissolution of the metallic bromides in hydrobromic acid, the detection of thallium with rhodamine-B in the presence of lead and bismuth and some silver, the extraction of thallium (III) bromide by means of *n*-butyl acetate, the detection of silver in a cyanide solution with *p*-dimethylaminobenzylidenerhodanine, the simultaneous detection of bismuth and lead with thiourea, and the final confirmation of lead as lead rhodizonate.

In two recent papers (Miller and Lowe, J., 1940, 1258, 1263) schemes of semimicro-analysis were submitted for three groups of Noyes and Bray's system (" A System of Qualitative Analysis for the Rare Elements," 1927). The present paper describes an extension of the methods to the thallium group, which has already been analysed on the micro-scale by Benedetti-Pichler and Spikes (*Mikrochem.*, 1936, **19**, 239).

The essential components of the thallium group are thallium (I), lead, and silver, with perhaps some bismuth, which are precipitated as their bromides when hydrobromic acid is added to the filtrate from the precipitate composing the tantalum, the tungsten, and the gold group. Although it was anticipated from a consideration of Noyes and Bray's work (*op. cit.*, pp. 44, 48, 123, 371) that only a fraction of the silver in a mixture would be present at this stage, that 1—2 mg. of lead would remain in the solution, and that bismuth precipitated in excess of 25 mg. might be completely removed in the subsequent washing process (see, however, p. 74), yet provision was made for the detection and estimation of 0·25—50 mg. of lead and silver, 0·25—10 mg. of thallium, and a moderate amount of bismuth.

EXPERIMENTAL.

Preparation of the Group for Analysis.—In order to precipitate the bromides in solutions comparable with those of Noyes and Bray, mixtures of the nitrates of lead, silver, and bismuth were evaporated to fumes with 0·35 ml. of 9N-perchloric acid. Thallium (I) perchlorate, 0·5 ml. of 24N-formic acid, and water were then added to make a volume of 1·2 ml. The bromides were precipitated and washed with dilute, bromine-free hydrobromic acid, one-tenth of Noyes and Bray's quantities being used, and analysed according to the tabulated scheme. As a check on the recovery of bismuth and lead, the centrifugates containing bismuth and unprecipitated lead were treated with nitric acid and evaporated to dryness, dissolved in 2N-nitric acid, and examined for the metals as described in the group analysis.

Thallium Group.

(The figures in parentheses are referred to in " Notes on Methods and Tests.")

<table>
<tr><td colspan="2"><i>Precipitate.</i> Pb, Tl^I, Ag, and Bi (probably) bromides. Boil with 0·5 ml. of 9N-HBr and a small excess of Br_2 to form Tl^{III}. Gradually dilute with 1 ml. of water and remove precipitated AgBr by centrifuging (1). To 0·05 ml. of the solution add 0·05 ml. each of 9N-HBr, H_2O, and then 2% aq. Na_2HAsO_3. Finally, add dropwise a small excess of rhodamine-B (1% in 3N-HBr), and centrifuge. A red precipitate shows Tl (2). Assess. If Tl is present, remove $TlBr_3$ from the remainder of the solution by extracting thrice with 0·5 ml. of <i>n</i>-butyl acetate (3). Evaporate the aq. layer to $\sim$0·5 ml., cautiously add concentrated HNO_3 in excess, expel Br_2, and take just to dryness. Extract once with 0·5 ml. of hot 2N-HNO_3, and twice with 0·25 ml. of the cold acid (4). Wash the precipitate of AgBr with a little water and reject the washing.</td></tr>
<tr><td rowspan="3"><i>Precipitate.</i> AgBr. Estimate roughly. Dissolve in 0·2—1·5 ml. of 5% aq. KCN, according to the bulk of the precipitate (1 ml. dissolves $\sim$40 mg. of Ag), and centrifuge. Mix 0·05 ml. with 0·5 ml. of <i>p</i>-dimethylaminobenzylidenerhodanine (saturated in $CH_3{\cdot}OH$), add 2 drops of 2N-HNO_3, and centrifuge. A reddish-purple precipitate shows Ag. If an excess of reagent is not indicated (yellow centrifugate), repeat the test with 2·5 ml. of the reagent. Assess (5).
Any residue in the KCN extract may be dissolved in 2N-HNO_3 and examined for Pb and Bi.
<i>Note.</i>—If desired, part of the group precipitate may be at once treated with HNO_3 to remove Pb, Bi, and Tl, and tested for Ag as above.</td><td><i>Solution.</i> Contains $Pb(NO_3)_2$ and $Bi(NO_3)_3$ in 1 ml. Test portions as follows.</td></tr>
<tr><td>(<i>a</i>) To 0·5 ml. of the <i>cold</i> solution add $\nless$0·5 ml. of thiourea (saturated in N-HNO_3 at 20°), stir, and centrifuge. A precipitate, white in the absence of Bi, yellow in its presence, shows Pb, and a yellow solution, Bi. Estimate Pb (6). To confirm a small amount of Pb ($<$1 mg.) wash the precipitate once with the reagent, and twice with ethyl alcohol to remove free acid. Dissolve in 1—2 drops of hot water, add excess of a fresh, saturated aq. solution of sodium rhodizonate, and centrifuge. A reddish-purple precipitate shows Pb. Estimate. Finally, add to the separated precipitate, without stirring, a drop of 2N-HCl, which changes its colour to blue-purple and partly dissolves it (7).</td></tr>
<tr><td>(<i>b</i>) If the presence of Bi has been shown in (<i>a</i>), dilute 0·1—0·5 ml. to 2 ml. with 1—2N-HNO_3, and add an excess of solid thiourea. If necessary, warm to keep Pb in solution, and compare with standards for Bi (8).</td></tr>
</table>

Notes on Methods and Tests.

Note 1. 0·5 Ml. of 9N-hydrobromic acid, which dissolved large amounts of lead and thallium (III) bromides, and $\sim$10 mg. of silver as silver bromide, was ample for the extraction of all the thallium, but more could be used, if desired. Dilution to 3N reprecipitated most of the silver, and gave appropriate conditions for the rhodamine-B test and the removal of thallium bromide.

Note 2. Eegriwe (*Z. anal. Chem.*, 1927, **70**, 400) found a 0·01% aqueous solution of rhodamine-B to be a sensitive reagent for thallium (III) and certain other metals. Miller and Lowe (*loc. cit.*) enhanced the selectivity of the reagent by employing it in fairly concentrated hydrochloric acid solutions. For the detection and estimation of thallium (III), in the presence of large amounts of lead, excellent results were obtained by substituting 3N-hydrobromic acid, in which lead bromide was somewhat soluble. As little as 2γ of thallium was detectable in 1 ml. of 3N-hydrobromic acid containing 10 mg. of lead or bismuth, and silver bromide to saturate the solution. One drop of the 1% reagent solution precipitated 25γ of thallium. Bromine, which formed a red precipitate with the reagent, was instantaneously destroyed by sodium arsenite, which did not reduce thallium (III) in the strongly acid solution.

Note 3. This method of extraction was extremely simple, and the removal of thallium ($\nless$10 mg.) virtually complete. Lead bromide was insoluble and bismuth bromide only slightly soluble.

Note 4. The evaporation was rapidly effected in the centrifuge tube, placed in a boiling water-bath, if a current of air played on the surface. The nitric acid treatment separated even minimal amounts of lead and bismuth nitrates very satisfactorily from 50 mg. of silver, and small amounts of silver bromide were retained as such. Although large quantities of lead and bismuth might leave large precipitates of silver bromide slightly contaminated, the subsequent test for silver was unaffected.

Note 5. The test for silver with *p*-dimethylaminobenzylidenerhodanine was based on that described by Feigl ("Qualitative Analyse mit Hilfe von Tüpfelreaktionen," 1938, 159), but provided for an estimation. The reagent was prepared in methyl alcohol because it gave a clear solution with a cyanide solution of silver bromide, and was more sensitive than the acetonic reagent. For the estimation of silver it was essential to add an excess of the reagent *before* the nitric acid, and to compare with standards prepared from silver bromide, *not* silver nitrate, dissolved in aqueous potassium cyanide. Although the test was at least five times less sensitive with the bromide, it was adequate for the present purpose, and simple to apply. As somewhat erratic results were occasionally obtained in testing for silver bromide in very small amounts, it was inadvisable to have $< 25\gamma$ of silver per drop of the cyanide solution. 0·5 Ml. of the reagent served for 200γ of silver. The large proportion of methyl alcohol in the final solution prevented deposition of the reagent itself.

Note 6. Mahr and Ohle's method of separating lead from a large number of metals by precipitating its bulky complex with thiourea, in a solution 1—2N in nitric acid, was very successful (*Z. anorg. Chem.*, 1937, **234**, 224). Thallium reacted similarly and more readily and had to be absent. The presence of silver was unlikely, but its complex is soluble in an excess of the reagent. 5 Mg. of bismuth gave only a yellow solution, but coloured the lead precipitates yellow, and slightly retarded their formation. It did not seriously affect their bulk, and 50γ of lead were detectable. It was advisable to confirm the presence of lead in a small precipitate (see Note 7).

Note 7. The thiourea complex of lead was not obviously soluble in ethyl alcohol, but dissolved readily in a small volume of water, giving an approximately neutral solution. As a distinctive confirmatory test for lead its complexes with sodium rhodizonate were formed. Very weakly acid solutions of lead salts give reddish-purple precipitates with sodium rhodizonate (cf. Kolthoff, *Pharm. Weekblad*, 1925, **62**, 1017, through *Chem. Zentr.*, 1926, I, **97**, 448). Just as treatment with 2N-hydrochloric acid caused the brownish-red rhodizonate complex of barium to change to carmine (cf. Miller, J., 1940, 401), so the reddish-purple complex of lead was changed to a characteristic blue-purple one, which slowly dissolved. No other metal examined behaved in this manner. The dissolved thiourea complex of lead was readily transformed into the reddish-purple rhodizonate complex, on the bulk of which lead could be assessed, and thence to the highly distinctive blue-purple complex as a final check. Although the presence of thallium and silver in the lead–thiourea complex was unlikely, the behaviour of their corresponding complexes was examined. The thallium complex remained acid and decolorised sodium rhodizonate, and the silver complex gave a dirty-brown, non-settling precipitate. Bismuth contaminating the lead–thiourea complex exerted no influence. It was unnecessary to have more than 500γ of lead for the test (one drop of the reagent solution sufficed for $40—50\gamma$), and 50γ could be carried through the whole process. Attempts to detect and estimate lead directly with sodium rhodizonate, in the presence of thallium and bismuth, were not successful.

Note 8. Amounts of bismuth ranging from 5γ to 2·5 mg. could be satisfactorily detected and estimated in 2 ml. of 1—2N-nitric acid, provided that an excess of thiourea was added, and that a short time was allowed for full colour development (cf. Dubský, Okáč, and Trtílek, *Mikrochem.*, 1935, **17**, 332). Suitable portions of solutions containing large amounts of bismuth were examined. The dissolved complexes of lead (and thallium) were without influence.

Analysis of Mixtures.—In order to test the analytical scheme a number of mixtures were prepared and selected at random. The results are given in the table, the figures referring to the weights in mg.

It will be noted that a maximum of 1 mg. of lead was found in the solution from the group precipitation. An amount of lead well below this figure was, however, actually found in the group, presumably because it was carried down by a large group precipitate (No. 7). The removal of bismuth, by washing the group precipitate with cold N-hydrobromic acid, might be by no means complete (No. 3), and bismuth must be allowed for in the group analysis. Noyes and Bray's experiments on the solvent effect of hydrobromic acid on bismuth bromide (cf. p. 72) were made in the absence of the other metallic bromides.

The estimations of all the metals were considered satisfactory, and no metal absent from the mixtures was erroneously reported.

	Element.	Tl.	Ag.	Pb.		Bi.	
				In group precipitate.	In solution from group.	In group precipitate.	In solution from group.
1	Present	7	—	20		20	
	Found	7·5	0	20	0·5	1	20
2	Present	10	3	—		—	
	Found	10	2	0	0	0	0
3	Present	0·5	5	0·5		40	
	Found	0·5	10	0·1	0·05	10 †	25
4	Present	0·25	20	2		20	
	Found	0·25	20	0·5	1	2 ‡	22
5	Present	—	15	25		10	
	Found	0	12	22 *	0·5	0·15	10
6	Present	2	0·25	35		10	
	Found	2·5	0·3	34	0·5	0·5	10
7	Present	10	40	0·25		—	
	Found	10	40	0·5	Trace	0	0
8	Present	0·25	50	—		—	
	Found	0·25	50	0	0	0	0

* 1·5 mg. in AgBr. † 50γ in AgBr. ‡ 25γ in AgBr.

The author is indebted to the Carnegie Trustees for a Teaching Fellowship, and to the Trustees of the Moray Fund for a grant.

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[*Received, December 4th,* 1940.]