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

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A satisfactory scheme of analysis has been evolved for the detection and approximate estimation of 0·25—50 mg. of mercury, 0·25—10 mg. of gold, palladium, and platinum, and 0·25—2 mg. of iridium and rhodium in mixtures containing not more than 50 mg. of the combined metals.

IN continuance of work outlined in the preceding paper, the gold group has been analysed. It is composed of the elements mercury, gold, platinum, palladium, rhodium, and iridium, which are precipitated with the tantalum and the tungsten group and certain insoluble salts, and afterwards separated and obtained as complex chlorides in a hydrochloric–nitric acid solution. The maximum amount of material under consideration was 50 mg. referred to the cations, and the amounts of the various elements to be tested for were: mercury, 0·25—50 mg.; gold, platinum, and palladium, 0·25—10 mg.; iridium and rhodium, 0·25—2 mg. Only a portion of the rhodium and iridium in the original mixture appears in this grouping (see Noyes and Bray, " A System of Qualitative Analysis for the Rare Elements," pp. 19—21, 43—53).

EXPERIMENTAL.

The following tabulated scheme of analysis incorporates Noyes and Bray's method for the initial separation together of gold and mercury, and Gilchrist and Wichers's important method (*J. Amer. Chem. Soc.*, 1935, **57**, 2565) for the separation of platinum from palladium, rhodium, and iridium, by precipitating the last three as their hydrated dioxides. Thereafter various modern reagents are utilised.

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

Gold Group.

<table>
<tr><td colspan="5"><i>Solution.</i> Contains the chlorides of Au, Hg, Pd, Pt, Rh, and Ir in HCl–HNO_3 (1 : 3). Evaporate (steam-bath) to 0·1 ml., take up in 3 ml. of water, add one drop of N-HCl, and extract with 1½ ml. of ethyl acetate. Repeat the extraction (1).</td></tr>
<tr><td colspan="2" rowspan="2"><i>Ester layer.</i> Evaporate to dryness (steam-bath) and take up in 3N-HCl. Estimate a large amount of Au from the yellow colour. To confirm, test part with rhodamine-B, and, if necessary, estimate quantity (2). Dilute the remainder with a little water and pass SO_2. Digest in hot water.</td><td colspan="3"><i>Aqueous layer.</i> Evaporate almost to dryness with HCl and take up in 20 ml. of water. Heat to b. p., add 2 ml. of 10% aq. $NaBrO_3$, and then 10% aq. $NaHCO_3$ dropwise to p_H 6. Add 1 ml. more of $NaBrO_3$, boil for 5 mins., increase the p_H to 8, add a further ml. of $NaBrO_3$ and boil for 15 mins. (4).</td></tr>
<tr><td rowspan="2"><i>Solution.</i> Add 3 ml. of 46% HBr, expel Br_2 and pass H_2S. Dissolve impure PtS_2 in <i>aqua regia</i>, expel HNO_3, take up in 4N-HCl and confirm and estimate Pt in all or part by precipitating its buff phenylbenzyldimethylammonium chloride, and heating in boiling water (5).</td><td colspan="2"><i>Precipitate.</i> Hydrated dioxides of Pd, Rh, and Ir. Dissolve in 1 ml. of hot, conc. HCl (½ hr. may be required), dilute to 30 ml. with water, and add 1% alcoholic dimethylglyoxime. Set aside for ½ hr. (6).</td></tr>
<tr><td><i>Precipitate.</i> Au.</td><td><i>Solution.</i> Evaporate to dryness (steam-bath) to remove SO_2 and HCl. Dissolve in water (½ ml. or more), add excess of NaOAc, adjust p_H to 7—8, and test with diphenylcarbazone. A purple solution or precipitate shows Hg. Assess (3).</td><td><i>Precipitate.</i> Pd as yellow dimethylglyoxime complex. Estimate by comparison with a standard. If desired, destroy organic matter with HNO_3 and H_2SO_4, and test with dithiol (7).</td><td><i>Solution.</i> Evaporate several times to dryness with HCl and HNO_3 to destroy organic matter, and take up in a minimum of HCl. Divide into two equal parts.
(<i>a</i>) Evaporate to dryness to ensure the absence of nitrate, take up in 1 ml. of 2N-HCl, heat to b. p., and precipitate black Rh with a small excess of $TiCl_3$ (15% in HCl). Assess (8).
(<i>b</i>) Evaporate to fumes with H_2SO_4. Add a few drops of HNO_3 and reheat. A blue colour shows Ir. Assess (9).</td></tr>
</table>

This scheme was applied with the following results to six mixtures submitted as " unknowns " to the junior author. All quantities are expressed in mg.

	Element.	Au.	Hg.	Pt.	Pd.	Rh.	Ir.
1	Present	—	—	0·25	10	0·25	0·25
	Found	0	0	1	15	0·5	0
2	Present	—	40	—	0·25	10	10
	Found	0	32	0	0·25	5	10
3	Present	—	—	10	—	—	5
	Found	0	0	4	0	0	10
4	Present	7·5	0·25	—	—	2·5	0·25
	Found	15	0·25	0	0	5	0·5
5	Present	2	1·5	0·25	1·5	1	0·5
	Found	6	0·5	0·5	1	2·5	0·5
6	Present	—	—	0·5	7·5	2·5	0·25
	Found	0	0	1	6	2	0·25

As with the tantalum and tungsten groups (see preceding paper) a very satisfactory feature is that no metal absent from the mixtures was reported. The failure to report iridium in No. 1 was due to the employment of the leuco-malachite-green test instead of the much more reliable reaction with sulphuric and nitric acids (see note 9). The assessments of quantity were reasonably satisfactory.

Notes on Methods and Tests.

The experimental technique was the same as that of the preceding paper.

Note 1. This process which is essentially that of Noyes and Bray (*op. cit.*, pp. 52, 113), reduced to about one-tenth of their scale, required careful control. It was important to use alcohol-free ethyl acetate, prepared by refluxing it over phosphoric oxide and fractionating it. The passage of gold into the ester layer, and the retention of palladium, in particular, in the aqueous layer were very effective. A small fraction of the mercury remained in the aqueous layer and was afterwards associated with the platinum.

Note 2. For the confirmation of gold a 1% solution of rhodamine-B in 3N-hydrochloric acid was successfully employed in the same manner as for antimony (see preceding paper), except that nitrite was omitted. Reddish-purple precipitates were obtained with amounts of gold exceeding 5γ in 0·5 ml. and 1γ in 0·05 ml. of 3N-hydrochloric acid. At least a 500-fold excess of bivalent mercury could be present. The reduction of acidity diminished the permissible excess. 1000γ of platinum, 300γ of palladium, and 50γ of rhodium or iridium did not prevent the detection of 5γ of gold in a drop of 3N-hydrochloric acid. 0·5N-Nitric acid halved the sensitivity. Gold could be estimated from the bulk of its complex. As one drop of the reagent corresponded to 25γ of gold, only a part of the test solution was usually taken.

Note 3. For confirming and estimating mercury a saturated alcoholic solution of diphenylcarbazone was employed (Hopkin and Williams, "Organic Reagents for Metals," 1938, 53). The adjustment of p_H was made by adding a drop of phenol-red indicator (0·02% alcoholic) and a dilute sodium hydroxide solution until the solution just assumed a pink tinge. Sodium acetate assisted the coagulation of the precipitate. One drop of the diphenylcarbazone reagent (0·02 ml. = *ca.* 100γ of mercury) added to 0·5 ml. of solution containing 50γ of mercury gave a deep purple colour, and a purple precipitate on centrifuging: 5γ of mercury were detectable. The bulk of a centrifuged precipitate could be used for estimating 50—5000γ of mercury. Palladium reacted similarly to mercury and had to be absent. Gold gave a black precipitate, much less bulky than that of mercury, and, unless present in minor quantity, was better removed. Platinum, rhodium, and iridium (500γ/0·5 ml.) gave no reaction.

Note 4. This procedure was essentially that of Gilchrist and Wichers (*loc. cit.*) reduced to about one-tenth of the scale. Bromocresol-purple and cresol-red test-papers were spotted with tiny drops of the solution in the adjustments of p_H.

Note 5. The centrifugate from the hydrated dioxides was liable to contain traces of rhodium and iridium and sometimes 0·5 mg. of mercury (cf. note 1). The destruction of bromate was more effectively carried out with hydrobromic than with hydrochloric acid, as used by Gilchrist and Wichers. Precipitation with hydrogen sulphide concentrated the elements, which were finally obtained in a small volume of 4N-hydrochloric acid. For the detection of platinum in the presence of the above contaminants the most reliable reagent was phenylbenzyldimethylammonium chloride (Maynard, Barber, and Sneed, *J. Chem. Educ.*, 1939, **16**, 77). A few drops of a 10% aqueous solution, added to the same amount of a solution 4N in hydrochloric acid containing platinum, gave a distinct buff precipitate with 25γ. 25γ of palladium, 250γ of mercury, 250γ of rhodium, 500γ of gold, and 125γ of iridium gave light brown, white, pale violet, yellow and red-brown precipitates, respectively, similar in bulk to those formed with 25γ of platinum. Heating in boiling water dissolved the first three, decomposed the fourth, greatly reduced the bulk of the fifth, and only slightly affected the platinum complex. Hence there was no difficulty in ascertaining the presence of platinum in the mixture under consideration. At most, iridium discoloured the platinum complex without affecting its bulk, which was compared with a standard.

Note 6. One precipitation of palladium with dimethylglyoxime, according to the method of Gilchrist and Wichers (*loc. cit.*), gave an almost complete separation from rhodium and iridium.

Note 7. Generally the formation of the yellow dimethylglyoxime complex was sufficient proof of the presence of palladium. It could be compared with a standard for an estimation of quantity, provided that the precipitates were centrifuged for 10 mins. to render them compact. For the confirmation of a small precipitate, after the destruction of organic matter, a 0·5% solution in 0·5N-sodium hydroxide of toluene-3 : 4-dithiol ("dithiol") was an excellent reagent (see Hopkin and Williams, *op. cit.*, p. 138). It gave in acid solutions (~2N) a dark brown complex with palladium, and no outstanding reaction with any other metal of the gold group. The former was readily soluble in butyl acetate to a brown solution. Even 5γ of palladium were easily detected in 0·5 ml. of an aqueous solution. Comparisons with standards were best made in butyl acetate extracts.

Note 8. The reduction of rhodium chloride by means of titanous chloride was used by Gilchrist and Wichers (*loc. cit.*), and the bulk of the precipitated rhodium served for the assessment of quantity. Iridium did not interfere, but gold, platinum, and palladium had to be absent from the solution.

Note 9. This test, which was used by Maynard, Barber, and Sneed (*loc. cit.*), was very satisfactory, and the colour of the solution served for the estimation of iridium. When a ten-fold excess of rhodium was present a brownish-purple colour could safely be interpreted as indicating the admixture of iridium. Traces of other metals did not interfere.

In a few experiments a 1% solution of leuco-malachite-green in acetic acid was employed to detect iridium (Chugaev, *Chem. Abstr.*, 1930, 2689). It was turned green by *neutral* solutions. The other strongly-coloured metal ions of the gold group interfered by masking the colour produced by iridium; 50γ of iridium could, however, be detected in association with 500γ of rhodium. This test was less satisfactory than the first, for the detection of a minimal amount of iridium.

This work will be continued when circumstances permit.

We thank the Carnegie Trustees for a Teaching Fellowship (to C. C. M.) and the Trustees of the Moray Fund for several grants, which have facilitated the work described in this and the preceding paper.

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[*Received, July 5th,* 1940.]