395. *The Micro-determination of Platinum and Iridium, and of Associated Chlorine and Potassium.*

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Micro-analytical methods are specially advantageous in work on the compounds of noble metals, owing to the high cost of preparation of these substances on the macro-scale. The methods now described are, so far as possible, general in character for the complex compounds of platinum and of iridium; they relate to determinations upon some 5—20 mg. of initial material (all weights given are in mg.).

Platinum.—In previous papers (J., 1930, 349; *et seq.*) numerous examples of the determination of platinum in its ammine and sulphine derivatives have been given; these analyses were carried out by Pregl's method (ignition with sulphuric acid in a platinum boat, in a current of air). The results show the high accuracy and wide scope of the method, but a few cases have been encountered where the results vary owing to the volatility of appreciable traces of platinum in certain conditions; again, the method is not applicable to the common case in which an alkali metal is present. We have, therefore, worked out the following more general method, in which the substance is decomposed by fusion with sodium carbonate–sodium nitrate, and the liberated platinum collected and weighed. For the fusion, we experimented with porcelain and platinum crucibles, and found a method of procedure suitable to both cases. For the filtration, a Pregl filter tube with capillary cap (Drew and Porter, J., 1929, 2092) was employed, but it was also shown that a platinum micro-Neubauer crucible can be used. Porcelain crucibles can be employed for the fusion in spite of the usual avoidance of them in accurate work on a macro-scale. The micro-experiments showed that as much as 5 mg. of silica may be removed from the crucible by the fusion mixture, but that no ponderable quantity is associated with the platinum weighed. Similarly, when a platinum crucible is used, none of the metal dissolves off the walls, nor does the precipitated platinum adhere to the crucible; the attack of the nitrate on the crucible, which might, from certain statements in the literature, be thought of importance, is negligible, being confined to a minute superficial oxidation of the metal, afterwards easily reversed by ignition in the Bunsen flame. Again, the literature would lead to the anticipation that platinum must be ignited at a high temperature before being weighed, a process only convenient when the rather expensive micro-Neubauer filter-crucible is available: but we found that a temperature of only 130°, or even less, suffices if the platinum is first washed on the Pregl filter with a little hot concentrated nitric acid, which probably removes traces of occluded carbonates. Hydrochloric acid must on no account be used to wash precipitated platinum, for it is appreciably soluble in that acid in the presence of oxygen, forming chloroplatinic acid, in spite of the absence of oxides of platinum (proved by comparative experiments using high-temperature ignition with a platinum micro-Neubauer crucible). The point of greatest difficulty was the behaviour of the Pregl filter tube towards concentrated nitric acid: these filters, after adequate preliminary washing with the hot acid, underwent no change in weight during many successive washings with the acid, but if left for a day or two (in some cases, much longer) the glass or the asbestos of the filters recovered the property of losing weight (usually about 0·1 mg.) when once more washed with the acid. However, it was ultimately found that the difficulty did not arise if the filters were always rewashed with the acid on the day of use. The micro-Neubauer crucible retained constancy of weight when washed with hot concentrated nitric acid. The experimental details are therefore relatively simple:

An acorn-size (1 c.c.) crucible, of Bavaria porcelain or of platinum, is covered with a thin layer of melted fusion mixture (sodium carbonate : sodium nitrate = 2 : 1), allowed to cool, and the substance (5—20 mg., previously finely powdered in an agate mortar) is added from a "grasshopper" weighing-tube; more fusion mixture is added, admixture is effected with a fine glass rod, and the mixture finally covered with a further layer of fusion mixture, so that the crucible is about one-third full; the crucible, with lid always on, is heated on a stout platinum sheet by means of a Bunsen burner, at first very gently and finally at red heat for about 20 minutes, until gas is no longer evolved. After cooling, the lid is immersed in some 10 c.c. of warm water in a 30 c.c. covered beaker, rinsed with a fine-jet wash-bottle, and removed with platinum forceps; then the crucible is immersed upside-down and the beaker warmed on the water-bath till the salt dissolves and the platinum particles fall to the bottom of the beaker; the crucible is rinsed and removed, care being taken that none of the minute granules of platinum remains on it; the beaker is cooled and the contents cautiously acidified with pure concentrated nitric acid; should particles of platinum adhere to the crucible, the acidification may be conducted before the crucible is removed. The liquid should now be perfectly transparent; it is heated on the water-bath for about ½ hour and then poured directly through the Pregl filter tube [previously washed with some 3 c.c. of hot concentrated nitric acid, water, and alcohol, dried at 130° (¼ hr.) in the usual apparatus, and weighed after cooling for 20 mins.] with moderate suction at the pump, the transference being completed by rinsing with alcohol and with water; the filter is well washed with hot water, then washed, dried, and weighed as initially. The results of analyses are shown below :

Substance.	Amount taken.	Pt, found.	Pt, calc.	Pt, %. Found.	Pt, %. Calc.
K_2PtCl_4	7·921	3·748	3·724	47·3	47·0
K_2PtCl_6	9·510	3·860	3·819	40·6	40·2
,,	10·257	4·134	4·118	40·3	,,
α-$Pt(NH_3)_2Cl_2$	8·887	5·788	5·779	65·1	65·0
,,	13·106	8·537	8·523	65·1	,,
,,	24·983 *	16·389	16·248	65·6	,,
β-$Pt(NH_3)_2Cl_2$	29·251	19·020	19·023	65·0	,,
$PtC_2H_4(NH_2)_2Cl_2$	11·619	6·997	6·954	60·2	59·9
,,	11·784	7·102	7·053	60·3	,,
α-$Pt(NH_3)_2Cl_4$	13·544	7·178	7·123	53·0	52·6

* This analysis was carried out with a Neubauer crucible.

The contents of the filter need not be changed for further determinations, and if successive estimations are carried out on the same day, the previous weight of the filter can be taken as the initial weight for the next analysis.

The following data show the effect of repeatedly washing a filter with hot concentrated nitric acid, water, and alcohol, drying at 130°, and weighing as described; the weights are those after successive washings : fractions of a mg. only are quoted, the tare being constant.

1st Filter, ·657, ·640, ·651.
2nd Filter, ·791, ·791, ·794.
,, (on another day), ·782, ·782, ·790, ·784, ·790.
3rd Filter, ·008, ·020, ·016, ·015.

Fuming nitric acid should not be used to wash the filters.

Blank experiments with the fusion mixture and a porcelain crucible showed a negligible increase in weight (less than 0·01 mg.) of the Pregl filter tube after the procedure described above, showing that no insoluble material was derived from the crucible.

Chlorine in the Presence of Platinum.—Experiments showed that two methods are available : (1) fusion as above, in a platinum crucible, filtration of platinum from the alkaline extract, and precipitation of the filtrate with a solution of silver nitrate in concentrated nitric acid; (2) a micro-Carius method. Only the latter was studied in detail. A single experiment carried out by the first method, using β-$Pt(NH_3)_2Cl_2$ (11 mg.), gave Cl, 24·0 (Calc. : Cl, 23·6%).

In the second method, the substance (about 5—12 mg.) was heated in the usual way to 270° for some 6 hours with an excess of silver nitrate and about 4 drops of fuming nitric acid, a mixture of silver chloride and a reddish platinum compound being formed. The contents of the tube were washed out as far as possible into a small beaker with water and the washings evaporated to dryness; the tube and glass capsule and the residue in the beaker were then extracted repeatedly with concentrated ammonia (some 10 c.c. in all), the extracts being filtered through a Pregl filter tube, which retained the insoluble reddish substance. The filtrate was then evaporated on the water-bath to remove most of the ammonia, acidified with nitric acid, again heated, cooled, and the precipitated silver chloride filtered off and weighed in the usual manner (Pregl). The method depends upon the fact that the red platinum compound, the nature of which has not been examined, is quite insoluble in ammonia. The results (below) appear to be of the same order of accuracy as that attained in the simple Carius estimation in the absence of platinum (compare Drew and Porter, *loc. cit.*) :

Substance.	Cl, %. Found.	Cl, %. Calc.	Substance.	Cl, %. Found.	Cl, %. Calc.
β-$Pt(NH_3)_2Cl_2$	23·5	23·6	$PtC_2H_4(NH_2)_2Cl_4$	35·7	35·7
γ-$Pt(NH_3)_2Cl_2$	23·55	,,	$PtC_3H_6(NH_2)_2Cl_4$	34·3	34·5

Iridium.—The determination of iridium (see Palmaer, *Z. anorg. Chem.*, 1895, **10**, 320) is more complicated than that of platinum or of palladium, because this metal is oxidised when heated in air; therefore simple ignition with sulphuric acid fails unless followed by some form of reduction. Our object was to obtain a micro-method applicable not only to simple co-ordination compounds of iridium and those with organic groupings, but also to those containing alkali metals; hence it was necessary to use a method of filtration at some stage in the process. In order to allow of subsequent reduction of the filtered iridium, the filter had also to be capable of ignition. A platinum micro-Neubauer crucible was found most suitable for the purpose, but a porcelain crucible with porous base (so-called " porcelain micro-Neubauer ") can be used instead, although filtration is then slower and a longer period of cooling is necessary.

The procedure first tried was to weigh the material into a small platinum capsule (0·6 cm. diam., 0·3 cm. height), which was then placed in the weighed filter-crucible; two drops of residue-free 10% sulphuric acid were added to the capsule, and crucible and capsule were slowly ignited in hydrogen, cooled in carbon dioxide, and weighed; the potassium sulphate was then washed out with water through the Neubauer crucible without displacing the capsule, and the vessels were ignited as before and again weighed. It was found, however, that in the presence of hydrogen considerable reduction of potassium sulphate to sulphite occurred, and therefore the method was useless for the determination of potassium. If, on the other hand, the ignition with sulphuric acid was conducted in air, the potassium was accurately estimated as sulphate by subsequently washing out and igniting the vessels in carbon dioxide, the state of oxidation of the iridium meanwhile remaining unchanged; the iridium was itself then accurately determined after reduction in hydrogen.

FIG. 1.

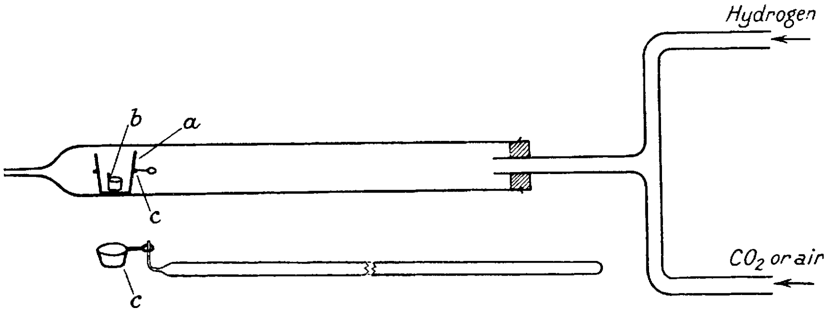

FIG. 2.

The procedure finally adopted was as follows. The filter-crucible (*a*) and inner capsule (*b*) were ignited in a current of purified hydrogen (15 mins.) in the hard-glass combustion tube shown in Fig. 1, the air having first been displaced by carbon dioxide, and were then cooled in a current of dry carbon dioxide (10 mins.); they were next allowed to cool in a micro-desiccator (20 mins.) and weighed after 5 mins. in the balance case. The capsule was removed from the crucible, dusted on the outside, and weighed together with the filter crucible (with lower cap in place, in the case of the Neubauer crucible); then the substance was placed in the capsule, the latter in the filter-crucible, and the weight again taken; the sulphuric acid (2 drops) was now added to the capsule, and the whole inserted in the combustion tube by means of the cradle (*c*) of platinum wire and the hooked glass rod (Fig. 2). The mixture was gradually heated to redness in a current of air, the tube allowed to cool until the crucible ceased to glow, the air replaced by carbon dioxide, and the cooling and weighing conducted as before. The filter crucible (without lower cap) was then placed in the rubber gasket of the usual suction apparatus (see Pregl, on the filtration of barium sulphate) and a fine jet of warm water was directed on the capsule and its surroundings until all alkali sulphate was removed (some 40 c.c. of water are required), as little iridium as possible being displaced from the capsule; the crucible (with lower cap replaced, in the case of the Neubauer pattern) was then wiped, ignited in the combustion tube as before in a current of carbon dioxide, and again weighed. Thus the weight of potassium sulphate was available, but the iridium was still partially in the form of oxide; therefore the crucible was again ignited in hydrogen, cooled in carbon dioxide, and weighed as before described, giving the weight of iridium.

This procedure is much simplified if the compound to be analysed contains no metal other than iridium, for it is then only necessary to ignite with sulphuric acid in a current of air, and to heat first in carbon dioxide and then in hydrogen, cool in carbon dioxide, and weigh. In these circumstances the filter crucible and capsule could doubtless be replaced by a platinum boat.

It is evident that the foregoing method could be applied also to the analysis of platinum compounds containing alkali metals; in that case, filtration only would be necessary, reduction in hydrogen becoming superfluous owing to the stability of platinum in presence of oxygen. However, no tests on platinum compounds have yet been carried out.

The following table shows the results of repeated analyses with several iridium compounds, and also with artificial mixtures of potassium chloride and an iridium compound. Analyses marked (P) were carried out with the porcelain filter crucible, the remainder being with the platinum Neubauer.

Substance.	Amount taken.	Ir, found.	Ir, %.		Amount taken.	Ir, found.	Ir, %.	
			Found.	Calc.			Found.	Calc.
$[Ir(NH_3)_5Cl]Cl_2$	4·641 (P)	2·314	49·85	50·2	8·189 (P)	4·110	50·2	50·2
	5·766 (P)	2·878	49·9	,,	5·651 (P)	2·814	49·8	,,
	8·805 (P)	4·409	50·1	,,	13·923	6·981	50·15	,,
(pyH)[Ir py_2Cl_4], orange isomeride	2·684 (P)	0·886	33·45	33·7	5·612	1·879	33·5	33·7
	4·409 (P)	1·495	33·85	,,	7·110	2·388	33·6	,,
red isomeride	4·531	1·507	33·25	,,	4·356	1·479	33·95	,,

Substance.	Amount taken.	KCl added.	Ir, found.	K_2SO_4, found.	Ir, %.		K, %.	
					Found.	Calc.	Found.	Calc.
K(pyH)[Ir $pyCl_5$]	5·401	—	1·807	0·823	33·45	33·95	6·8	6·9
	7·101	—	2·382	1·157	33·55	,,	7·3	,,
	8·805	—	2·993	1·391	34·0	,,	7·1	,,
	12·684	—	4·285	1·971	33·8	,,	6·95	,,
$[Ir(NH_3)_5Cl]Cl_2$	4·136	3·130 (P)	2·076	3·651	28·6	28·6	22·55	22·6
	4·817	2·888 (P)	2·436	3·372	31·6	31·4	19·65	19·65
	6·435	5·838	3·215	6·789	26·2	26·3	24·8	24·95

(py = C_5H_5N.)

Chlorine in the Presence of Iridium.—This determination was carried out by fusion in a platinum crucible with sodium carbonate–sodium nitrate as described on p. **1787**; the melt was dissolved in cold water, the insoluble iridium and iridium oxide filtered off, the filtrate precipitated with a solution of silver nitrate in concentrated nitric acid, and the silver chloride estimated as usual {Found, with **6·140** mg. of K(py H)[Ir py Cl_5] : **7·795** mg. AgCl; Cl, **31·45**; with **5·096** mg. : **6·386** mg. AgCl; Cl, **31·0**. Calc. : Cl, **31·2**%}.

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