DETERMINATION OF TRACES OF PLATINUM AND PALLADIUM IN THE ATMOSPHERE OF A PLATINUM REFINERY

BY A COMBINED CHEMICAL AND SPECTROGRAPHIC METHOD

BY

S. J. R. FOTHERGILL, D. F. WITHERS and F. S. CLEMENTS

An investigation carried out by Hunter and others (1945) on the health of workers at the refinery of the Mond Nickel Co., Ltd., Bashley Road, London, N.W.10, made it necessary to estimate the atmospheric content of platinum and palladium in the neighbourhood of various unit processes. The method of sampling the atmosphere and the collection of the precious metals on a particulate filter is described by Hunter and his colleagues. But we were more particularly concerned with the estimation of the traces of platinum and palladium collected on the particulate filter pads. The principle of the method we used was to collect the precious metals in a silver bead by standard smelting methods followed by cupellation and then to estimate the platinum and palladium in the silver bead spectrographically.

In 1938 Seath and Beamish published a paper entitled 'Spectrographic Examination of Assay Beads for Platinum, Palladium and Gold.' The precious metals were collected in a silver bead by smelting methods and the beads were examined spectrographically, comparison being made with standards prepared in the following way:

Lead containers were made from spectrographically pure lead foil. Solutions of precious metals were added to these from micro-burettes. After evaporating the solutions the boxes were rolled up with a weighed amount of silver foil, wrapped in more lead foil and compressed under a pressure of 100 kg. per sq. cm. The resulting 30 gm. cylinders were cupelled at 900°C. and the beads left in the muffle for 2 minutes after the 'blick' to remove most of the lead.

For the production of arc spectra the operating conditions were: current, 2 amperes; arc gap, 3 mm.; exposures, 2 minutes. Graphite electrodes 6.3 mm. diameter were used and the lower electrode was made the anode. The weight of each bead was 10 mgm. and the authors claim a sensitivity of 0.004 per cent. for platinum, using the line 3064.7 Å and 0.001 per cent. for palladium, using the line 3404.6 Å.

LABORATORY WORK

(1) Preparation of Standards

A series of silver standards containing known amounts of platinum and palladium were prepared in the form of wires. These standards were prepared by the Research and Development Department of the Mond Nickel Company and had the following compositions:

	A	B	C	D	E	F
Platinum per cent.	0.001	0.003	0.01	0.03	0.10	1.0
Palladium per cent.	0.001	0.003	0.01	0.03	0.10	1.0

The diameter of the wires was 0.056 in. and a length of 6 mm. weighed approximately 100 mgm.

All melting operations required for the preparation of the standard alloys were carried out in graphite crucibles and the molten alloys were cast into graphite moulds. The

use of graphite for these operations is important because it is shown later that contact of molten silver with refractories such as alumina and magnesia affects the arcing properties of silver.

Uniformity in composition of the wires was ensured by thorough annealing at various stages in drawing the wires.

(2) Spectrographic Examination of the Standards

Portions of 100 mgm. of each standard were arced using a current of 2 amperes and exposure time 2 minutes. The arc gap was 4 mm. and the silver bead formed the anode.

The lowest limits detected under these conditions were:

Platinum . . 0.003 per cent. (Line used: 3064.7 Å)
Palladium . . 0.001 per cent. (Line used: 3404.6 Å)

In order to see whether the process of cupellation had any effect on the behaviour of silver beads in the arc, portions of the standards were cupelled with 5 gm. of assay lead on Mabor cupels. The cupelled beads were cleaned in hydrofluoric and 1 : 1 hydrochloric acids and then submitted to the arcing treatment described above.

It was immediately noticed that the arcing behaviour of the cupelled beads differed from the original standards in that the green colour of the arc was not so strong, and usually faded right out after about 15 seconds. The arc then had the appearance of that produced by graphite electrodes alone.

Examination of the spectra showed that the intensities of the platinum and palladium lines had been affected to such an extent that, at the 0.1 per cent. level, Pt 3064.7 was only barely visible and Pd 3404.6 was not detected at all.

Thus the process of cupellation has a marked influence on the behaviour of beads in the arc.

A further experiment showed that even when the standards are simply melted on a Mabor cupel, without the addition of any lead, the same lack of sensitivity results. With 0.1 per cent. platinum and palladium standards neither element could be detected.

The cupellation experiments were repeated using bone ash in place of Mabor cupels and the beads cleaned as above and examined. The green colour of the arc did not persist for more than 15 seconds and an imperfect reproduction of the silver spectrum was obtained.

The lack of sensitivity observed in these experiments is most probably connected with the fact that the cupelled beads, on arcing, only lose a very small amount of metal by volatilization. In one test with a cupelled bead from standard 'E' only 1.1 mgm. was lost, whereas with the original wire 9.1 mgm. were volatilized.

It is possible that a thin film of refractory oxide is formed on the surface of the molten bead which prevents the arc from coming into contact with the silver itself.

In order to study this matter further the effect of various pure refractory oxides was investigated.

Three sets of cupels were prepared, each set having one of the following materials forming its top surface: (a) alumina, (b) lime, (c) magnesia. Portions of the standards 'C', 'D' and 'E' were melted on each type of refractory, and the beads, after cleaning, were arced in comparison with the original wire standards.

The bead spectra all showed reduction in the strength of the platinum and palladium lines, the effect being most marked in the case of those beads which were melted on the alumina surface and least marked where melting was done on a magnesia surface.

(3) Chemical Treatment of Beads before Arcing

Since it appeared that the abnormal behaviour of the cupelled beads might be due to some impurity picked up during the cupellation, it was decided to attempt to remove such impurities by a chemical treatment of the beads.

After a preliminary cleaning in hydrofluoric acid and in hot 1 : 1 hydrochloric acid the beads were treated by one of the following methods:

(a) The bead was dissolved in nitric acid in a small crucible, the silver was precipitated as chloride and the

entire contents of the crucible were evaporated to dryness. The platinum and palladium chlorides were thus collected on the silver chloride. The dried precipitate and wipings from the crucible were wrapped in a 7-cm. filter paper and ignited to metal in hydrogen.

(b) The bead was dissolved in a minimum of concentrated sulphuric acid and the excess acid driven off by heating. The dry silver sulphate was dissolved in boiling water and the silver and precious metals were precipitated with hydrazine sulphate. It was found that complete precipitation of the silver could be obtained only if the solution was finally made ammoniacal. The precipitate was filtered on a 7-cm. paper, dried, ignited and reduced in hydrogen.

(c) The bead was dissolved in a minimum of concentrated sulphuric acid, the solution diluted and the metals precipitated from the boiling solution with hydrogen sulphide. The precipitate was filtered on double 7-cm. paper, washed with hot distilled water, dried and ignited carefully to metal in air.

Spectrographic examination of the metals obtained by these three methods was carried out without difficulty and in all cases the platinum and palladium contents agreed well with the corresponding standards.

It was however found that the spectra of all the treated samples showed calcium, magnesium and iron lines. These impurities were found to have been introduced from the filter papers used and in later work this trouble was avoided by the use of a better paper.

TABLE 1

DETERMINATION OF PLATINUM AND PALLADIUM IN REFINERY ATMOSPHERE

Sample No.	Date	Time	Rate of sampling litres per minute	Vol. of sample cubic metres	Position of sampling and work being carried out	P.M. content of filter pad, mgm.		P.M. content of atmosphere, μ g per cubic metre	
						Pt	Pd	Pt	Pd
1	10.8.44	8.15-3.15 (7 hrs.)	70	29.4	Aqua regia treatment of crude platinum metal concentrate.	0.063	0.019	2.1	0.6
2	14.8.44	8.15-1.15 (5 hrs.) 1.15-4.45 (3½ hrs.)	70	35.7	Precipitation and filtration of impure $(\text{NH}_4)_2\text{PtCl}_6$.	0.12	0.079	3.4	2.2
3	17.8.44	8.15-3.30 (7¼ hrs.)	70	30.45	Dissolving impure platinum sponge in aqua regia.	0.11	0.16	3.6	5.3
4	11.8.44	8.15-3.15 (7 hrs.)	70	29.4	Precipitation and filtration of pure $(\text{NH}_4)_2\text{PtCl}_6$.	0.046	0.008	1.6	0.3
5	22.8.44	1.00-4.30 (3½ hrs.)	70	14.70	Discharging dry $(\text{NH}_4)_2\text{PtCl}_6$ from drying ovens.	>1.0	0.006	>68.0	0.4
6	24.8.44	8.15-10.45 (2½ hrs.) 10.45-3.45 (5 hrs.)	70	31.50	Hand crushing and packing dry $(\text{NH}_4)_2\text{PtCl}_6$ and $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in ashless filter paper.	0.26	1.0	8.3	32.0
7	15.8.44	8.15-2.15 (6 hrs.)	70	25.2	Precipitation and filtration of impure $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$.	0.050	0.051	2.0	2.0
8	21.8.44	8.15-4.30 (8¼ hrs.)	70	34.65	Purification of rhodium.	0.033	0.011	0.9	0.3
9	16.8.44	8.15-11.15 (3 hrs.) 11.15-4.45 (5½ hrs.)	70	35.7	Recovery of small amounts of precious metals from solutions by zinc reduction.	0.11	0.065	3.1	1.8
10	22.8.44	8.15-1.00 (4¾ hrs.)	70	19.95	Discharging residues from drying ovens.	0.081	0.10	4.1	5.0

Method (c) was selected as the most convenient for further work. In view of the slight enhancement of the impurity lines noticed in the spectra of the beads which had been submitted to chemical treatment, it was decided to submit the wire standards to a similar treatment to that employed in the actual tests.

(4) Application of the Method to the Determination of Platinum and Palladium in the Refinery Wet Process Atmosphere

Since it was clear that a smelt and cupellation would be necessary, filter pads were impregnated with known amounts of platinum and palladium and put through the furnace operations. The beads obtained were treated by method (c) described above. In all cases good agreement was obtained with the corresponding standards.

The esparto grass filter pads carrying the platinum and palladium from the refinery atmosphere were then treated as follows:

The pad was introduced into a size D annealing cup together with 5 gm. of assay lead foil and was ignited gently in a muffle furnace. When all carbonaceous matter had burnt off, the temperature was raised until the residue was well collected in the molten lead. Twelve gm. of flux were then added and the mixture smelted for 30 minutes and then poured. Composition of flux: 120 gm. litharge, 100 gm. borax, 50 gm. soda ash, 5 gm. carbon. The lead button obtained was cupelled on a No. 3 Mabor cupel together with 100 mgm. of proof silver.

100 mgm. portions of the wire standards were also cupelled with 5 gm. lead.

A blank test was made on the flux and proof silver.

The resulting beads from the atmosphere tests and from the standards were then submitted to the following wet treatment.

The bead was cleaned in a silver crucible with hot hydrofluoric acid and, after rinsing with distilled water, it was immersed in boiling 1 : 1 hydrochloric acid for 15 minutes. The bead was then washed thoroughly with distilled water and dissolved in a minimum of concentrated sulphuric acid. The resulting solution was diluted and washed into a 150-ml. beaker and the volume adjusted to 75 ml., 3 ml. of 1 : 1 sulphuric acid being added. The silver and platinum metals were then precipitated from the boiling solution with hydrogen sulphide. The treatment was continued until the precipitate had coagulated giving a clear supernatant solution. The precipitate was filtered on a single No. 00 Swedish 7-cm. paper and washed with hot distilled water, dried and ignited carefully to metal in air.

The silver sponge samples were then examined spectrographically under the following conditions:

Spectrograph. Hilger medium quartz (type E.3).

Spectrograph Slit Width. 0.015 mm.

Irradiation of Spectrograph Slit. The arc discharge is focussed on the prism face by means of a spherical lens (F.1026).

Arc Excitation. The arc operates on a 200-volt D.C. circuit.

Electrodes. The upper electrode consists of a rod (10 mm. dia.) of Hilger's spectroscopically pure graphite, sharpened to a point. The lower electrode consists of a similar rod of graphite having a shallow cavity formed in the top, 4 mm. in depth. The sample is placed in the cavity and forms the anode.

Arc Length. 4 mm.

Current. 2 amperes.

Exposure. 2 minutes.

No preliminary settling down period is allowed. The slit shutter is opened before the arc is struck so that the melting period of the sample forms part of the exposure.

Photographic Plate. Ilford Ordinary.

Development. 4 minutes in standard M.Q. developer at 68° F. (20° C.).

Duplicate samples were prepared from each standard and arced, and the spectra of the other samples from the atmosphere tests were obtained on the same plate under identical conditions.

Density measurements were then carried out on a Hilger non-recording microphotometer, using the lines Pt 3064.7A and Pd 3404.6A.

From the measurements relating to the standards, curves were plotted, and by using these curves, the platinum and palladium contents of the samples under test were deduced. Owing to the lack of suitable intercal standard lines in the silver spectrum, the 'log ratio' method of plotting cannot be used. Hence in this work the microphotometer readings were plotted directly against 'log concentration.'

Since the weight of silver added to each test was 100 mgm. the percentage figure obtained represents the actual weight of platinum or palladium in mgm. Thus the atmosphere content of these metals in gamma (10^{-6} gm.) per cubic metre is easily calculated.

Table I shows the results obtained for a series of tests on the refinery atmosphere in various positions in the Wet Process Building. All samples were taken at approximately head level.

Summary

An estimation was required of the platinum and palladium content of the atmosphere in the vicinity of various operations connected with the refining of platinum metals. Sampling was carried out over periods of several hours corresponding with the time required for completion of the various reactions. The atmosphere was drawn through a particulate filter designed by Hunter and his colleagues.

Estimation of the platinum and palladium collected on the filter was made by igniting the filter and smelting the residue with litharge, charcoal and flux with the addition of a known amount of proof silver, and cupelling the lead button obtained.

By this means the platinum and palladium were collected in a silver bead which was examined spectrographically and compared with synthetic standards.

The content of platinum and palladium in the atmosphere in the neighbourhood of the majority of refining operations was found to be less than $5\mu\text{g}$ /per cubic metre, due to the provision of local exhaust ventilation. In the handling of dry salts much higher concentrations of platinum and palladium were found in the atmosphere, the highest figure being in the order of $70\mu\text{g}$ /per cubic metre.

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