THE DETERMINATION OF PLATINUM IN ORES.

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by

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ABSTRACT.

Fire assay and wet extraction methods of determining platinum in ores were evaluated. Losses by each procedure were investigated for milligram and microgram amounts of platinum.

The fire assay procedure using lead as a collector was used in combination with flame and flameless atomic absorption, emission spectroscopy and x-ray fluorescence. For the latter method flattened silver beads were analysed directly, whereas for the other methods beads were dissolved in aqua regia and solutions made up with strong hydrochloric acid before analysis.

The wet procedures involved treatment of ores with acids and subsequent analysis by flame atomic absorption or spectrophotometry with tin (II) chloride. Chromatographic, ion exchange and solvent extraction procedures were used to isolate platinum and the platinum group metals.

Results for each ore by fire assay-flame atomic absorption, fire assay-emission spectroscopy and wet extraction showed no difference at the 99 per cent confidence level. X-ray fluorescence and flameless atomic absorption results tended to be high and low respectively. The most precise method was wet extraction followed by spectrophotometric analysis. Emission spectroscopy and x-ray fluorescence generally yielded the lowest precision. Wet extraction methods were time consuming and since no advantage was gained in accuracy over fire assay, a combined fire assay-flame atomic absorption was the preferred method of analysis.

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The Determination of Platinum in Ores.

Introduction.

Platinum was discovered in 1735. However, the metal contained traces of palladium, rhodium, iridium, osmium and ruthenium, and it was not until 1844 when the latter metal was isolated, that platinum was obtained in pure form. These early researchers, in their task to purify platinum, laid the foundation to much of the analytical chemistry known today about platinum and the other platinum metals. Today these metals in various forms find ever increasing uses in industry as catalysts for a wide variety of reactions. Because of its resistance to corrosion the platinum crucible and platinum electrodes are common laboratory equipment. Platinum has also found extensive use in jewelry and decorative wear. Its high melting point and stability make it ideal for materials of construction that will not contaminate products at high temperature. Frequently, platinum is alloyed with rhodium, iridium, osmium or ruthenium to increase its hardness and corrosion resistance.

The principal source of platinum and the other platinum metals is in the several native alloys of the metals found in various parts of the world. The correct determination of these metals is considered one of the most difficult analyses in inorganic chemistry. Its rare occurrence, difficulty in isolating and unique properties have helped to make platinum a very expensive metal. In business transactions involving the use of platinum, the accurate determination of

platinum content is important. A relatively small error in an assay can result in a large monetary gain or loss.

Extraction methods for platinum include fire assay and wet procedures. The use of fire assay has grown out of an irrational assumption that platinum is as noble as gold. The efficiency of the fire assay procedure for platinum has never been completely evaluated.

Early determinations for platinum included gravimetric methods - in which platinum was weighed or was precipitated and the precipitate ignited to the metal and weighed - and volumetric methods. However, spectrophotometric methods and the more recent spectrochemical, atomic absorption and x-ray techniques have extended determinations to the microgram and in some cases even sub-microgram levels. This is of considerable importance, because as it becomes economically feasible to extract lower grade ores, more sensitive methods of analysis must be utilized.

It is the purpose of this study to evaluate fire assay and wet procedures for milligram and microgram amounts of platinum, and to provide a comparison of accuracy and precision to be expected using spectrophotometric, flame and flameless atomic absorption, emission spectroscopic and x-ray fluorescence methods for the determination of platinum in ores.

Standard platinum solutions.

Approximately 1 g of platinum wire was accurately weighed out on a Sartorius microgram balance and dissolved in aqua regia. Nitrous oxides were removed by repeated evaporations with hydrochloric acid. The solution was filtered into a one litre flask and made up to the mark with 0.1 M hydrochloric acid. This solution was standardized with thiophenol (1). A second solution was prepared in the same manner, and standardized with tin (II) chloride (2) against the first standard, using all calibrated glassware. Dilute platinum solutions were prepared by dilution of stock solutions.

Apparatus.

Perkin-Elmer 306 Atomic Absorption Spectrophotometer.

Perkin-Elmer 403 Atomic Absorption Spectrophotometer fitted with the HGA-70 flameless atomization device and a deuterium background corrector.

Unicam SP 500 U.V. - Visible Spectrophotometer.

U. of Manitoba Physics Dept. - component parts X-ray Fluorescence Spectrometer.

Jarell Ash Spectrograph with 3.4 M Ebert mounted grating with 5,000 lines/inch, giving a reciprocal linear dispersion of 5 Å/mm in the first order.

Densitometer - Jarell Ash Model 21-000. Non-recording.

Varian and Intensitron Platinum Hollow Cathode Lamps.

Lindberg Hevi-duty 20KW electric furnace.

Sartorius Type 1802 microbalance.

Mettler Type H6 milligram balance.

Ohaus Harvard trip balance.

Magnesia cupels produced by Leonard Light Industries, (Benoni, South Africa).

Crucibles produced by A.P. Green Refractories (Ontario, Canada).

Ion-exchange columns: Large column 2.5 cm diameter, 40 cm length, Small column - 1.2 cm diameter, 30 cm length.

Porasil C columns: 1.2 cm diameter, 30 cm length.

Cellulose columns: 1.5 cm diameter, 40 cm length.

All the above columns were fitted with sintered glass discs at the bottom.

Apparatus continued.

Sieves: Endecott (Test Sieves) Ltd., London, England.

Mesh size 44	Aperture 355 microns.
" " 100	" 150 "
" " 200	" 75 "

Reagents.

Platinum wire 0.008" thick (Johnson, Matthey & Mallory).

Platinum powder obtained by reduction of platinum oxide (The American Platinum Works., Newark, N.J.).

Silver, precipitated powder(Johnson, Matthey & Mallory).

Lead, 0.004" foil (Matheson, Coleman & Bell).

BIO-RAD AG-50W-X8 analytical grade, 50 mesh hydrogen form cation exchange resin. (BIO-RAD Laboratories, Richmond, California).

Whatman cellulose, fibrous powder CF 11 medium fibres.

Porasil C, mesh size 80-100 (Waters Associates, Inc., Massachusetts, U.S.A.).

Palladium and gold standards prepared by dissolving pure metals in aqua regia, evaporating to dryness several times with concentrated HCl and making up in 0.1 M HCl.

Sodium hexachlororhodate (Alfa Inorganics., Ventron, Mass., U.S.A.).

Sodium chloroiridate (Johnson Matthey, Chemicals Ltd., London).

Tin (II) chloride solution - 1.0 M in $SnCl_2$ and 3 M in HCl.

Lanthanum chloride solution - 6.45 g La_2O_3 (reagent grade) in 100 ml of 6 M HCl.

Reagents continued.

"Buffer" solution - mix 50 ml of 4 M sodium acetate with 53 ml of 4M HCl to give a pH of 2.2±0.2. References (9,87).

Tri-n-butyl phosphate (TBP) was equilibrated with 6 M HCl before use, in the solvent extraction procedure.

Thiophenol - (Aldrich Chemical Company, Inc.).

Molybdenum trioxide (Spex Industries, New Jersey, U.S.A.). 0.15 g dissolved in 100 ml 3 M HCl.

All other chemicals were reagent grade.

Preparation of Chromatographic columns.

I. Column for BIO-RAD 50W-X8.

The resin was cleaned by gently heating with 50% (v/v) hydrochloric acid, and washed several times by decantation with water. The column was filled to a height of 25 cm with the resin, and washed with water until the pH value of the eluate was the same as that of the water.

The resin was regenerated with 35% (v/v) hydrochloric acid and again washed until the pH value of the eluate was the same as that of water.

II. Columns for TBP-treated Porasil C.

5 g of the TBP dissolved in chloroform was added to 15 g Porasil C, that had previously been washed with concentrated hydrochloric acid, water, and dried. The slurry was stirred to remove most of the chloroform, and then placed in a drying oven overnight at 75°C.

Preparation of Chromatographic columns - continued.

1.5 g of the TBP treated Porasil C was weighed, and transferred to the column with water. The column was conditioned with 10 ml of 0.1 M hydrochloric acid before use.

III. Cellulose column.

The column was silanized with a 5% (v/v) solution of dichlorodimethylsilane in toluene before use. 20 g of cellulose was mixed with enough TBP/toluene solution to give a thin slurry. 13.3 ml of 5 N hydrochloric acid was added and the slurry stirred continuously for three minutes. The column was filled with approximately 10 ml of TBP/toluene solution, and the slurry transferred to the column in small portions. Each portion was pressed down firmly by an up and down movement with a glass plunger.

General considerations.

Rejection of discordant results.

Whenever an experimental source of error was noticed results were rejected. Frozen beads, careless pouring of molten charge, and spilled solutions are examples of such experimental errors. When no such errors were in evidence, discordant results were statistically rejected at the 95 per cent confidence level.

FIRE ASSAY.

Introduction.

Fire assaying is a method of quantitative determination in which a metal or metals are separated from impurities by fusion processes. It is the oldest analytical procedure in use today (3). Probably the earliest reference to the fire-assay process is to be found in the Tel al Arma tablets dated about 1380 B.C. (4). A cupellation process for gold is mentioned by Siculus as being in use in the second century B.C. (4). The "parting" assay i.e. the separation of silver from gold was known to Geber (777 A.D.) (4).

Thus it can be seen that fire assaying was known long before the discovery of platinum. The first application of fire assay for platinum appears to be by Deville and Debray (5), who melted solid platinum between blocks of quick-lime using a coal-gas/oxygen flame. The heat insulating properties of the lime were excellent and at the same time its basic nature allowed it to take up any slag formed by oxidation of impurities in the metal. Further refinement of platinum was found to be possible by alloying with lead. Platinum, palladium and rhodium were freely soluble in molten lead, whereas iridium and osmium were not.

Much data has been collected to demonstrate the quantitative nature of fire assay for milligram and microgram amounts of gold(6,7). Very little such data has been collected for platinum. This author

found only one reference concerned solely with the fire assay for platinum (8). The report was concerned mainly with finding an optimum flux for platinum recovery, and evaluation of the fire assay for milligram and microgram amounts of platinum. However, very few results were quoted evaluating the cupellation process, and evaluation of the fire assay process was not undertaken for amounts under 90 micrograms (important for many ore assays). Also few results were quoted for varying milligram quantities of platinum. It is the intention of the author, in this part of the thesis, to fill in these gaps, and so provide complete data on the efficiency of the fire assay for platinum.

Classically lead has been used as the collector in fire assay procedures. However, the claim has been made that lead is not a particularly suitable collector, at least not for some of the more "insoluble" platinum metals such as iridium and osmium. These new collectors such as tin (9), copper (10), iron-nickel-copper (11), and nickel sulfide (12), have been used, but as stated in a recent book (13), "despite the availability of new collectors for the noble metals, the classical lead collection remains clearly superior for the determination of platinum, palladium, gold and perhaps rhodium".

Fire assay for platinum.

The classical fire assay procedure requires the collection of the precious metals from an ore into a lead button. The lead button is produced by interactions of the ore with several flux components. The majority of ores are by themselves infusible, or nearly so, at easily attainable temperatures. However, thorough mixing with flux components yields a mixture readily fusible at such temperatures. Ores should be ground as fine as possible to ensure intimate contact with the reagents. After fusion is complete the molten mass is poured into a metal mould and allowed to cool. The lead button may then be removed from the slag by gentle tapping with a hammer.

Materials commonly used for fluxing include litharge (PbO), silica (SiO_2), borax ($Na_2B_4O_7$), soda (Na_2CO_3) and flour. The proportions of each material used will depend on the nature of the ore and the individual preference of the assayer. According to Bugbee (14); "no two assayers working on the same ore will agree exactly on the flux proportions to use, so it is safe to say that, for any given ore there is a comparatively wide range within which the four common flux constituents may be varied and still, in the hands of an able assayer, yield practically identical results." This is borne out by the work of Hoffman and Beamish (8), who studied platinum recovery using fluxes varying in nature from very acidic to very basic. They reported that "there appears to be no outstandingly successful flux for the overall recovery of platinum." Fluxes high in silica content were found to give the lowest recovery of platinum, presumably because of the high viscosity of such fluxes.

The chemistry of the interactions between the ore and flux components is not known to any degree of certainty, but reasonable assumptions may be made. At low temperatures some of the litharge is reduced to elemental lead by reduction with carbon (flour):

$$2PbO + C = 2Pb + CO_2.$$

The lead droplets thus formed are homogeneously mixed with the charge, and a lead-platinum alloy formed by liquid-liquid extraction. Carbon dioxide is evolved and provides some measure of mixing between flux components, thereby increasing ease of extraction. As the temperature is raised, lead slowly falls to the bottom of the charge, collecting platinum, and the other noble metals if present, as it does so. The temperature is finally raised to approximately 1100-1200°C. At this temperature the charge is very fluid and any platinum not already alloyed with lead will simply fall through the charge because of its high density and be collected by the lead.

Lead may also be formed by litharge reacting with other components of the ore. In silicate ores, for example, the reaction may proceed with the initial formation of lead silicate, followed by reaction of the lead silicate with bases in the presence of a reducing agent:

$$2PbO + SiO_2 = Pb_2SiO_4$$

$$Pb_2SiO_4 + 2\,FeO + C = Fe_2SiO_4 + CO_2 + 2Pb.$$

Litharge also oxidises base metal sulfides, the reaction being promoted by the presence of soda which aids in the desulfurization.

$$2FeS_2 + 15PbO = Fe_2O_3 + 4SO_3 + 15Pb.$$

$$Na_2CO_3 + SO_3 = Na_2SO_4 + CO_2.$$

Ores with high sulfide content can lead to the formation of unsuitably large lead buttons, because of the excess litharge required for oxidation. In such cases a nitre assay is performed, and the ore is treated with potassium nitrate:

$$2FeS_2 + 6KNO_3 = Fe_2O_3 + 2K_2SO_4 + SO_3 + 3N_2.$$

$$4FeS_2 + 10KNO_3 = 4FeO + 5K_2SO_4 + 3SO_2 + 5N_2.$$

Opinions vary as the proper size of the lead button. Many assayers hold that it should be proportional to the total volume of charge; others vary the lead-fall according to the quantity of precious metals to be collected (14). It would appear that a button weight between 20-35 g is considered optimum in most cases.

Cupellation.

Cupellation involves the selective removal of lead as lead oxide from the silver and platinum collected in the lead button during fusion. Silver exerts a protective effect on platinum, and consequently is usually added to reduce losses.

Cupellation is accomplished in porous vessels called cupels. Cupels are commonly made from bone-ash, cement or magnesia. Magnesia cupels, used in this work, can absorb three-quarters of their weight

in litharge. It is necessary to cupel at higher temperatures when using magnesia cupels, because of the more rapid dispersion of heat of oxidation of lead on such cupels.

On addition of the lead button to the cupel (pre-heated for at least 10 minutes), at 950°C or higher, a dark scum is initially formed. This scum quickly disappears, and the molten lead becomes bright. This is referred to as "opening", and is usually complete within 5 minutes, with the furnace door closed. When the button has "opened", the furnace door is opened slightly, and air allowed to pass over the cupels. This causes oxidation of lead to lead oxide, which "wets" the cupel. Lead oxide is absorbed into the cupel, leaving the silver-platinum bead or prill on the surface. Silver and platinum are not oxidised and do not "wet" the cupel, and consequently are not absorbed. "Driving", as this process is called, is continued to remove all of the lead.

Towards the end of cupellation, the furnace door is closed, and the cupellation "finished" for a further 5 minutes. Closing the furnace door raises the temperature, which is necessary to maintain the button in a molten state.

After the cupellation has "finished", cupels are slowly removed from the furnace. This is necessary, because molten silver absorbs large quantities of oxygen, which can be violently expelled on cooling too rapidly. Such beads are said to "sprout" or "spit". Sprouting can be accompanied by mechanical losses of platinum.

Temperature should be strictly controlled during cupellation, in order to minimise losses of platinum. Low temperatures can cause buttons to become "frozen". Freezing occurs when crystals of litharge cover the button, preventing further oxidation of lead. Such buttons can be made to drive again by raising the temperature, but should be rejected as results obtained from them are usually low (14). Increasing temperature increases loss of platinum by absorption into the cupel (15). According to the same source, loss occurs during the last minute of cupellation. Thus the optimum temperature for cupellation is one just high enough to prevent freezing.

Increasing the silver content is also used to minimise losses, and silver-platinum ratios of 100:1 and 250:1 are common. Hoffman (8) reports loss of platinum when the ratios are as low as 10:1 and 20:1. A ratio of 10:1 (Ag:Pt) is also recommended for the removal of lead (4), although according to one source, the complete elimination of lead is unlikely (16).

Parting.

Parting involves separation of silver from the silver-platinum bead obtained in the cupellation process. This is achieved by leaching with acids, and any base metals carried over in the bead will also be dissolved.

Sulfuric acid and nitric acid have been used for parting. Both these acids leave platinum in a finely divided state. Solutions are filtered off and residues washed with hot ammonium acetate or hot

water. Ammonium acetate removes lead sulfate which may remain with the platinum residue. The sulfuric acid should be free of nitric and hydrochloric acids.

Using a double parting with hot concentrated sulfuric acid, Thompson and Miller (17) found that a ratio of at least ten parts silver to one part platinum was necessary for complete removal of silver. In some cases, platinum was found in the filtrate, indicating limited solubility of platinum in sulfuric acid. In another study as much as 50 parts per 1,000 parts of platinum have been found in the filtrate after boiling with concentrated sulfuric acid (4). To prevent losses slightly diluted acid was used (82 volumes concentrated sulfuric acid to 18 volumes of water). According to Bugbee (14), it is probable that a little silver will always remain undissolved regardless of the ratio of silver used in the alloy. This could lead to errors in the determination of platinum by weighing.

Thompson and Miller (17) also studied the parting of silver-platinum beads of various ratios by nitric acid. 0.5 - 57 per cent of platinum was used in the beads and tests were made with 1:1 and 1:4 nitric acid. In all cases, platinum was found in the filtrate, the amount varying with the ratio of silver to platinum and also with the strength of acid. It was also found that silver was invariably retained in the platinum residue, the amount increasing with increasing platinum content.

To complicate matters a little further, the above results for sulfuric and nitric acid partings are subject to alteration by the

presence of gold and the other noble metals. In the ternary system, silver-gold-platinum, silver is only quantitatively separated by concentrated sulfuric acid when the three metals are present in very definite ratios (4). An increase in separation is achieved when the ratio of gold to platinum is increased. In the case of nitric acid, the presence of gold accelerates dissolution of platinum, whilst dissolution is decreased in the presence of rhodium, iridium and ruthenium (4).

It can be seen that parting with nitric acid will involve a re-assay of the acid filtrate for quantitative recovery of platinum. Parting with concentrated sulfuric acid has been shown to be quantitative for platinum in the presence (18) and absence (8) of the other noble metals.

Fire assay of standard platinum samples.

The fire assay procedure was evaluated for milligram and microgram quantities of platinum by salting a blank ore, and fusing with flux A (Table I). 15 g of silica was used as the blank ore.

Flux components were weighed out on a Harvard trip balance and placed in polythene bags known as "baggies" (made in Canada by Colgate Palmolive). The flour was weighed on a milligram balance, as better precision with lead button weights could be obtained this way. The flux components were mixed in the baggie by shaking and tumbling for approximately 1 minute. Each flux sample was then salted with a known amount of platinum. Some samples were salted with weighed, milligram quantities of platinum, and some samples salted with milligram and microgram quantitites of platinum added as a solution. A maximum of 10 ml of solution was added to reduce the chances of the liquid passing through the flux, and possibly being lost to the crucible. Silver was added to each sample, so that the silver-platinum ratio was at least 10:1. Silver was added as a powder or as a solution of silver nitrate. Samples containing solutions of platinum and silver were dried by placing in a drying oven and leaving overnight at 70°C. Higher temperatures ($\sim$85°C) were not used, as some of the baggies developed holes, thus increasing the chances of mechanical loss of sample. When dry, lumps were broken up and the contents of the baggie thoroughly mixed for 4-5 minutes. Longer mixing times were found to have no effect on platinum recovery.

Table I: Composition of fluxes.

	A	B	C
Ore	15.0g	30.0[b]	40[c]
PbO	85.0	77.0	30
SiO_2	(15.0)g[a]	6.3	80
Na_2CO_3	21.1	30.0	80
CaO	4.5	18.8	—
Borax	—	6.3	40
Flour	2.0	2.0	2.5

a. For blanks, 15g SiO_2 replaced 15g of platinum ore.

b. 30g of crucible pot used as a sample.

c. 40g of cupel material used as a sample.

The crucibles containing the assay samples were placed in the furnace at 950°C and heated to 1200°C at the maximum rate of the furnace. This normally required between 75-90 minutes. After holding at this temperature for 15 minutes, the crucibles were removed from the furnace and the molten contents poured into conical iron moulds. When cool, slags could be separated from the lead buttons by gentle tapping with a small hammer.

Lead buttons were cupelled and the silver beads analysed for platinum. Some beads were parted with concentrated sulfuric acid and analysed spectrophotometrically with tin (II) chloride using 1 cm and 4 cm cells, and other beads were dissolved in 6 M hydrochloric acid and determined by atomic absorption. Results of these analyses are shown in Table II. In both methods, standard solutions were always measured with each set of samples. These procedures will be described in detail in later sections. Blanks were run with each set of samples. This corrected for any platinum contamination of the reagents. In all blanks determined no platinum was detected. Under the conditions used a detection limit of 0.14 μg/ml can be set for 1 cm cells and 0.09 μg/ml for 4 cm cells. Similarly a detection limit of 0.4μg/ml can be set for atomic absorption analysis.

Recoveries for milligram amounts of platinum added as a powder and microgram amounts of platinum are on average 97-99 per cent. Recovery for milligram amounts of platinum added as a solution are a little lower than this (~95%). It was noticed for these samples that total heating time in the furnace was approximately 120 minutes. This was due to replacement of a high tension lead in the furnace, and as a result the heating rate of the furnace was lowered somewhat. This was

Table II: Fire assay of platinum standards.

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
3.60 mg [(a)]		3.59 mg	99.7%
4.67		4.75	101.7%
5.42		5.24	96.7%
8.16		7.94	97.3%
10.90		10.77	98.8%
11.66		11.21	96.1%
13.09		12.65	96.6%
14.30		14.05	98.3%
21.42		21.22	99.1%
21.52		21.23	98.7%
25.02		25.12	100.4%
34.01		33.35	98.1%
54.00		52.68	97.6%
63.17		61.88	98.0%
	9.90 mg [(a)]	9.36 mg	
	"	9.42	
	"	9.57	
	"	9.45	
	"	9.42	
	"	9.38	
	"	9.38	
	"	9.33	

Table II(Cont'd).

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
	9.90 mg [a]	9.52 mg	
	"	9.45	
	"	9.31	
	"	9.31	9.41±0.05mg (95.0±0.5%)
	4.95 μg [a]	4.67 mg	
	"	4.73	
	"	4.76	
	"	4.71	
	"	4.73	
	"	4.76	
	"	4.68	4.72±0.03mg (95.4±0.6%)
	891.2 μg [b]	878.8 μg	98.6%
	594.1 μg [b]	593.0 μg	
	"	582.2 *	
	"	593.0	
	"	589.5	
	"	589.5	591.3±3.2 μg(99.5±0.5%)
	495.1 μg [b]	488.2 μg	
	"	491.2	
	"	485.3	488.2±7.33 μg(98.6±1.5%)

Table II (Cont'd).

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
	396.1 μg [b]	389.0 μg	
	"	392.5	
	"	378.3	
	"	389.6	
	"	389.6	
	"	389.6	
	"	405.5	390.6±7.4 μg (98.6±1.9%)
	118.6 μg [a]	119.5 μg	
	"	116.5	
	"	118.2	
	"	108.0 *	118.1±3.7 μg (99.6±3.1%)
	98.9 μg [a]	94.0 μg	
	"	93.0	
	"	99.5	
	"	91.0	
	"	98.7	
	"	100.7	96.2±4.2 μg (97.3±4.3%)
	29.6 μg [a]	30.0 μg	
	"	27.5	
	"	28.0	28.5±3.3 μg (96.3±11.2%)

Table II (Cont'd).

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
	19.8 μg (a)	20.2 μg	
	"	20.4	
	"	18.9	
	"	18.0	
	"	18.1	
	"	18.4	
	"	20.1	
	"	19.8	
	"	19.9	
	"	19.9	
	"	18.4	
	"	18.4	19.2±0.6 μg (97.0±3.0%)

* Value rejected on statistical grounds.

(a) $SnCl_2$ spectrophotometric analysis.

(b) A.A. analysis.

± Values quoted at the 95% confidence level.

later rectified. It was felt that this extra heating time could increase losses of platinum to the slag and to the walls of the crucible. To test this assumption, slags and crucibles were assayed.

Six crucibles from both 9.90 mg and 4.95 mg samples were weighed and crushed fine enough to pass through a sieve of mesh size 44. Samples at each level were combined, mixed thoroughly and sampled in a manner to be described later for ores. Six 30 g samples from each level were assayed with flux B. The silver beads obtained from cupellation were combined, parted in concentrated sulfuric acid and analysed spectrophotometrically. 0.86 mg platinum was found for the six 9.90 mg samples and 0.26 mg platinum for the six 4.95 mg samples.

Slags were crushed to mesh size 44, and assayed with an extra 30 g litharge and 2 g flour. Beads were analysed as above and 128 μg platinum found for the six 9.90 mg samples and 44 μg for the six 4.95 mg samples. These results when added to the original values represent an average recovery of $\sim$96.5 per cent.

Cupellation of platinum standards.

Evaluation of the cupellation process was accomplished by salting artificial lead buttons with known amounts of platinum and silver.

A boat shaped container was made from a 5" x 5" square of lead foil of 0.004" thickness. Carefully weighed amounts of platinum and silver powders were added, and the boat carefully formed into a cube, small enough to fit into the mouth of a cupel. The weight of the lead cube was approximately 25 g. Silver to platinum ratios were 10:1 or higher.

Magnesia cupels were placed in the furnace at 960°C and preheated for at least 10 minutes before use. Lead buttons were added to these cupels as quickly as possible, to prevent "freezing". After "opening" of the buttons (5 minutes), the furnace door was slightly opened, and a 1/4" plate placed under the door to control the draft. To prevent air from flowing directly over the cupels, thus causing too large a temperature drop, blank cupels were placed between these cupels and the draft. Under these conditions the driving of the lead occurred at the rate of approximately 1 gram per minute. When driving was complete, the furnace door was closed and the cupellation finished for a further 5 minutes. Cupels were then slowly withdrawn from the furnace to prevent sprouting, and allowed to cool. When cool the silver beads were removed from the cupel and weighed, after first carefully scraping away adhering cupel material with a spatula.

The recovery of platinum and silver is recorded in Table III. On average, the beads are 2-3 mg heavier than the platinum and silver added.

Blank cupellations on 25 g lead foil revealed the presence of 2 mg silver. There is evidence that as the silver and platinum contents were increased more lead was retained. However, all silver beads were shiny and hemi-spherical and no visual indication of lead was present.

The variations in recovery are probably due to fluctuations in temperature within the furnace. This author found on occasion considerable lead retained in beads cupelled near the furnace walls. Thus all cupellations were performed in the central area of the furnace hearth.

Table III: Cupellation of platinum standards.

Platinum added (mg).	Silver added (mg).	Platinum + Silver (mg).	Platinum + Silver recovered (mg).
2.93	39.5	42.4	43.9
4.10	45.6	49.7	51.9
6.70	82.9	89.6	90.3
10.64	118.0	128.6	128.7
12.70	132.1	144.7	148.3
14.78	176.3	191.1	190.0
19.59	232.3	251.9	253.5
20.36	212.5	232.8	230.0
21.67	222.3	243.9	247.9
23.26	284.5	307.8	308.8
25.98	297.3	323.3	326.9
26.91	271.1	298.0	302.5
30.63	329.6	360.2	364.2
31.78	381.4	413.2	417.6
42.07	515.5	557.5	560.3
52.56	539.9	592.4	604.4

Cupellation and parting of platinum standards.

As in the previous section, evaluation of the combined cupellation and parting procedure was accomplished using artificial lead buttons salted with known amounts of platinum and silver powders. Other buttons were prepared by salting with milligram and microgram amounts of platinum added as a solution. Silver was added as a powder or as a solution of silver nitrate, and in all cases the silver-platinum ratio was kept at 10:1 or higher. The acidity of the solution was kept at 0.1 M or lower to prevent possible corrosion of the lead, thus increasing chances of mechanical loss. Solutions were evaporated by placing in a drying oven at 85°C for several hours. Boats were then folded into cubes and cupelled as described previously.

Three acids were evaluated for parting. 1:4 nitric acid was found to dissolve as much as 60 per cent of the platinum and so was not considered further. Concentrated sulfuric acid and slightly diluted sulfuric acid (80 volumes acid and 20 volumes water) were both found to yield the same recovery for platinum. It was decided to use concentrated sulfuric acid for all partings as no advantage could be gained by dilution. Beads were placed in 30 ml beakers and an appropriate volume of concentrated sulfuric acid added. (2 ml acid was added for beads of silver content up to 50 mg; 5 ml added for 200 mg silver and 10 ml for higher silver content). A glass cover was placed on top of the beaker, and the beakers' contents heated on a hot plate until the rapid evolution of bubbles had ceased. The beaker and contents were allowed to cool and then diluted with an equal volume of

water, and filtered through a Whatman No. 42. 7 cm filter paper, whilst still hot. In this way, silver and any lead present will remain in the filtrate. After being washed well with hot water, the filter paper was transferred to the original 30 ml beaker and ignited overnight in an electric oven at 400°C. The residue was treated with aqua regia and the solution evaporated to dryness on a steam bath. The treatment with aqua regia was repeated twice more, followed by three treatments with concentrated hydrochloric acid, and the residue finally dissolved in water, and filtered through a Whatman No. 42 paper to remove the last traces of silver. Platinum was determined gravimetrically with thiophenol or spectrophotometrically by tin (II) chloride. These results are recorded in Table IV.

A number of beads were placed in 10 ml volumetric flasks and parted with concentrated nitric acid. Solutions were made up with 6 M hydrochloric acid in the presence of lanthanum and platinum determined by atomic absorption. These results are also shown in Table IV.

In both the above procedures, blanks were always run with each set of samples. As before, no platinum was detected.

It is interesting to compare results obtained by atomic absorption with results obtained by the other methods. Since beads analysed by atomic absorption were parted and analysed in the same flask, results obtained should be independent of any parting losses i.e. losses to the filtrate or mechanical losses on filtration. These results, on average, show greater than 99.5 per cent recovery for platinum indicating that losses to the cupel are insignificant. Recovery of platinum by

Table IV: Cupellation and parting of platinum standards.

Platinum added as a solid.	Platinum added as a solution	Platinum recovered.	Average Platinum recovered.
2.93 mg[a]		2.99 mg	102.1%
4.10		4.05	98.8%
6.70		6.54	97.6%
10.64		10.28	96.6%
12.70		12.97	102.1%
14.78		14.30	96.8%
19.59		19.14	97.7%
20.36		19.72	96.9%
21.67		21.64	99.9%
23.26		22.56	97.0%
25.98		25.22	97.1%
26.91		26.18	97.3%
30.63		29.38	95.9%
31.78		30.96	97.4%
42.07		41.97	99.8%
52.56		54.10	102.9%
	19.77 mg[b]	20.01 mg	
	"	19.56	
	"	20.05	
	"	19.97	
	"	20.30	19,98 $\pm$0,33mg(101,1$\pm$1,7%)

Table IV (Cont'd).

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
	10.13 mg[a]	10.03 mg	
	"	9.96	
	"	9.91	
	"	9.82	9.93 ± 0.14mg(98.0 ±1.4%)
	9.90 mg[a]	9.62 mg	
	"	9.48	
	"	9.66	
	"	9.62	
	"	9.69	
	"	9.52	
	"	9.66	
	"	9.76	
	"	9.78	9.64 ± 0.08mg(97.4 ±0.8%)
	4.95 mg[a]	5.02 mg	
	"	4.82	
	"	4.92	
	"	4.90	
	"	4.82	
	"	5.09	4.93 ± 0.11mg(99.6 ±2.2%)
	594.1 µg[c]	595.7 µg	
	"	583.5*	
	"	592.7	

Table IV (Cont'd).

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
	594.1 μg[c]	592.7 μg	
	"	592.7	
	"	589.7	592.7±2.7 μg(99.8±0.5%)
	495.1 μg[c]	501.5 μg	
	"	498.5	
	"	501.5	
	"	495.5	
	"	495.5	498.5±3.7 μg(100.7±0.8%)
	396.1 μg[c]	389.0 μg	
	"	389.0	
	"	383.0	
	"	392.0	
	"	395.2	
	"	386.0	389.0±4.5 μg(98.2±1.1%)
	197.9 μg[a]	190.5 μg	
	"	202.5	
	"	188.0	
	"	197.5	
	"	196.5	195.0±7.2 μg(98.5±3.6%)
	118.6 μg[a]	116.3 μg	
	"	119.5	
	"	115.2	

Table IV (Cont'd).

Platinum added as a solid.	Platinum added as a solution.	Platinum recovered.	Average Platinum recovered.
	118.6 μg(a)	113.2 μg	
	"	113.2	
	"	111.0	114.7±3.1 μg(96.7±2.6%)
	98.9 μg(a)	98.2 μg	
	"	98.2	
	"	91.0 *	
	"	100.0	
	"	103.0	
	"	98.8	99.6±2.5 μg(100.7±2.5%)
	29.6 μg(a)	28.9 μg	
	"	28.3	
	"	29.3	28.8±1.3 μg(97.3±4.5%)
	19.8 μg(a)	20.2 μg	
	"	18.5	
	"	19.8	
	"	21.3	
	"	18.4	
	"	19.2	
	"	18.4	
	"	19.5	
	"	20.5	19.5±0.8 μg(98.5±4.0%)

* Value rejected on statistical grounds.

(a) $SnCl_2$ spectrophotometric analysis.

(b) Thiophenol gravimetric analysis.

(c) A.A. analysis.

± Values quoted at the 95% confidence level.

parting in concentrated sulfuric acid is on average lower - 98.4 per cent. Gravimetric results were not included, because as will be explained in a later section,these results are subject to high positive errors. These averages seem to indicate that the main loss of platinum in a combined cupellation and parting procedure is in the parting stage. However, tests of significance at the 95 per cent confidence level show no significant difference between the averages..

In an attempt to identify losses, cupels and filtrates from beads parted in concentrated sulfuric acid were analysed for platinum.

Cupels were weighed and then crushed to pass through mesh size 44, combined and thoroughly mixed on a cellophane sheet. Several samples were assayed, beads parted and platinum determined spectrophotometrically using 4 cm cells. A cupel previously used for cupelling lead and silver was used as a blank. No platinum was found in this blank. Of 308 μg platinum lost, only 62 μg (20 per cent) was recovered.

Fifteen filtrates were slowly evaporated on a steam bath, to a small volume. The contents of the beakers were taken to dryness by fuming off the sulfuric acid on a hot plate. Aqua regia, concentrated hydrochloric acid and water were added as described above. The solutions were filtered into flasks containing concentrated hydrochloric acid, and tin (II) chloride, and platinum determined spectrophotometrically using 4 cm cells. Only on one occasion was platinum found in the filtrate, the amount found, 50 μg, constituting 0.12 per cent of the platinum added - 42.07 mg.

It is seen that recovery of 9.90 mg and 4.95 mg samples in the cupellation and parting procedure is 98-99 per cent. This seems to verify

the earlier assumption made that the main losses for these samples during the fire assay process were to the slag and crucible walls.

The weight of lead buttons used in this work was generally kept at 25-28 g. However, button weights were varied from 15-40 g with no difference in the recovery of platinum.

Variation of platinum recovery with silver.

It was anticipated that silver beads obtained by fire assay of ore samples would be analysed for platinum by atomic absorption in a manner identical to that used for standard beads. This necessitates dissolving the bead in 6 M hydrochloric acid. Increasing acid strengths may be used, but this decreases platinum sensitivity. To obtain quantities of platinum in the range necessary for atomic absorption analysis, small bead weights should be used so that smaller dilutions with acid are possible. It was thus advantageous to test recovery of platinum with varying bead weights - especially in the 2-6 mg range - and varying silver to platinum ratios. These results are shown in Table V.

Quantitative recovery of platinum is obtained using a bead weight as low as 1.4 mg. The recovery of platinum with silver-platinum ratios of 10:1 - 15:1 are significant, since these ratios are expected in the analysis of the float concentrate. Although not recorded the silver-platinum ratio was varied from 10:1 to 200:1 with no difference in recovery.

Table V: Variation of platinum recovery with silver.

Platinum added (μg)	Silver added (μg)	Silver/Platinum ratio	Platinum recovered (%)
594.1[a]	6.0	10:1	100.3
"	"	"	99.8
"	"	"	99.8
"	"	"	99.3
"	"	"	99.8
495.1[a]	5.0	10:1	101.3
"	"	"	101.3
"	"	"	100.7
"	"	"	100.1
"	"	"	100.1
396.1[a]	4.0	10:1	98.2
"	"	"	98.2
"	"	"	96.7
"	"	"	99.0
"	"	"	99.8
"	"	"	97.5
197.9[b]	2.9	15:1	102.3
"	3.5	18:1	95.0
"	2.7	14:1	99.8
"	5.5	28:1	99.3

Table V (Cont'd)

Platinum added (µg)	Silver added (µg)	Silver/Platinum ratio	Platinum recovered (%).
118.6(b)	6.6	55:1	95.5
"	10.5	88:1	93.6
"	1.4	12:1	100.7
"	"	"	98.2
"	"	"	99.7
98.9(b)	8.4	84:1	99.4
"	4.1	41:1	99.4
"	5.2	52:1	104.1
"	1.4	14:1	94.9
"	"	"	93.9
"	"	"	100.5
"	"	"	91.9
"	"	"	99.7
"	"	"	101.7

(a) A.A. analysis.

(b) $SnCl_2$ spectrophotometric analysis.

Conclusion.

The fire assay procedure has been shown to be quantitative for platinum, results in most cases showing 98-99 per cent recovery. No difference is in evidence between milligram amounts of platinum added as a powder and a solution, and microgram amounts of platinum.

The results obtained from the assay of crucibles and slags, and the fact that cupellation and filtrate losses have been shown to be insignificant, suggest that the main loss of platinum during the fire assay is by migration to the walls of the crucible.

Silver-platinum ratios as low as 10:1 and silver weights as low as 1.4 mg have been shown to effect quantitative recovery of platinum.

It is unlikely that the accuracy and precision found for synthetic samples as shown in Table II will be duplicated by an ore assay. Problems of homogeneity and sampling must be taken into account an any analysis for an ore, and "ideal" conditions as found in synthetic samples are rarely encountered.

Fire assay for platinum using tin as a collector.

The precious metals are collected in molten tin when the sample is fused at 1200 - 1250°C with a flux containing stannic oxide, sodium carbonate, silica, borax and flour (9). The resultant tin alloy is granulated by melting in a stream of nitrogen and quickly pouring into approximately one litre of water. The water is removed by decantation, and the residue treated with concentrated hydrochloric acid which volatilizes most of the tin. The precious metals are dissolved and isolated by various procedures prior to determination.

The success of tin in collecting platinum and the other precious metals is due to the formation of intermetallic compounds of the type Pt-Sn and $Pt-Sn_2$.

It was the author's intention to "simulate" the cupellation procedure, by forming the intermetallic compounds of tin and platinum independent of fluxing and evaluating the procedure for platinum. If successful the entire fire assay procedure could then be evaluated and compared in efficiency to the fire assay using lead.

Artificial buttons were prepared by salting tin foil with milligram amounts of platinum added as a solution. After evaporation of the platinum aliquot, the tin foil, weighing approximately 25 g was carefully folded into a ball, small enough to fit in a Vycor tube. Air was purged from the tube by nitrogen gas delivered through a smaller Vycor tube placed directly over the button. The Vycor tube was held in an open flame until the button had melted. The

nitrogen delivery tube was withdrawn and the molten tin alloy poured quickly into approximately one litre of water. The water was decanted off and the residue heated to dryness on a hot plate. The contents were then transferred to a 400 ml beaker and treated with concentrated hydrochloric acid to volatilize most of the tin. Complete volatilization was achieved with 3-4 ml of a 7:2 mixture of concentrated hydrochloric and hydrobromic acids. The remaining residue was treated three times with aqua regia, three times with concentrated hydrochloric acid and finally with water, and platinum determined by atomic absorption. The above procedure was repeated once more. Recovery of platinum was 85-90 per cent. The remaining platinum could be removed from the Vycor tube by leaching with aqua regia.

Visual inspection of the Vycor tube during heating showed that platinum was "sticking" to the walls, and there appeared to be two metallic phases at all times. It was considered that a true intermetallic compound was not being formed under these conditions and this line of work was discontinued.

Fire-assay of Platinum ores.

Introduction.

As with any method of analysis, the accuracy and precision obtained by fire-assay is very dependent of the sampling procedures used. The importance of proper sampling methods has been emphasized by Bugbee (14), who states "when it is considered that the final sample for fire-assay usually weighs somewhat less than 15 g, and that each must truly represent from 1 to 5 car-loads of ore weighing from 50-250 tons, the enormous practical difficulty of the problem may be appreciated." The problems of such sampling are discussed in various textbooks on fire-assaying (4,14). The analytical chemist has usually no control over this method of sampling and is concerned more with laboratory sampling. In this case, ores should be ground to a high fineness. This not only aids in every particle having an equal chance of appearing in the sample, but also ensures conditions for an initial optimum fusion.

Optimum sample size has been related to the physical characteristics of the ore, such as particle size (16). However, the size of sample taken by this author for each ore was determined by the method of analysis used.

Laboratory sampling of ores.

The ores received for assaying had been previously crushed and sieved, and weighed approximately 1-2 lbs. In order to ensure adequate

fineness, it was attempted to pass each ore through sieves of 100 and 200 mesh. However, very little ore came through either mesh. This was surprising since the ores already showed a high degree of fineness. The sieves were placed on vibrators for several minutes, but this failed to collect anymore ore. Inspection of the sieves under a microscope showed that the holes of the sieves were free and that small globules of ore were sticking to the fine wire, probably by electrostatic force. This was taken as evidence that the ores were fine enough to pass through the sieves, and required no more crushing.

The entire ore sample was placed on a large sheet of cellophane and rolled or tumbled by lifting alternate corners of the sheet. After twenty-five minutes of mixing, the ore was spread out evenly on the cellophane, and marked off into one inch squares. The sample for assaying was then obtained by taking a small portion on a spatula from each of the squares. The spatula was extended down to the bottom each time. With practice, approximately equal portions could be taken from each square, thus, keeping variations to a minimum.

This procedure was repeated to obtain ore samples for future determinations, except that the rolling and tumbling was reduced to five minutes.

Determination of platinum in ores.

The ores to be analysed were obtained from the Merensky Reef in the Bushveld Igneous Complex, South Africa. The major component of such ores is pyroxene (silicates of calcium, magnesium, iron, aluminum, sodium and and lithium), mainly bronzite $(Mg, Fe)_2Si_2O_6$. Minor components include chromite $(Fe(Cr,Fe)_2O_4)$, chalcopyrite $(CuFeS_2)$, pyrrhotite (Fe S) and

pentlandite ($(Fe,Ni)_9S_8$). Trace constituents include a variety of sulfides of iron, copper and nickel. The platinum metals are present as native platinum, sperrylite($PtAs_2$), braggite (Pt_2PdNiS_4), stibiopalladinite (Pd_3S_6), copperite (PtS) and laurite (RuS_2). A proportion of the platinum metals is also present in solid solution in the sulfides of iron, copper and nickel. Each ore - designated by name or number - had been previously analysed for platinum metals and gold. Results of these analyses for platinum are shown in Table VI, together with the methods of analysis. Fifteen laboratories were furnished samples of ore USBM 31 by the United States Bureau of Mines as part of a "round robin" analysis and twelve laboratories submitted analytical results. The values rejected in the averaging of ore USBM 31 were rejected by the United States Bureau of Mines and not by this author. Where possible precision has been quoted at the 95 per cent confidence level. It should be made clear that the laboratories that analysed ore USBM 31 did not analyse ore S4 and the float concentrate. A complete analysis of these ores for the platinum metals and gold is shown in Table VII.

The approximate weights of the ores taken were S4 - 15 g; float concentrate - 8 g and USBM 31 - 11 g. Silica (15g)was used as a blank ore. In order that the flux was not too basic approximately 7 g of silica was added to the float concentrate and 4 g to USBM 31. From previous experience of an identical ore, it was deemed necessary to roast USBM 31 before fire assaying. This was achieved by placing ore samples in porcelain dishes and placing in the furnace at 700°C. The furnace door was left slightly open to create a draft, necessary for the oxidation of sulfur to sulfur dioxide. The samples were stirred at frequent intervals

Table VI: Previous analysis of ores for platinum.

Concentration of platinum (ppm).

Method of analysis	S4 (19)	Float concentrate (19)	USBM 31 (20)
Fire assay-atomic absorption	5.23	82.60	5.04 ± 0.17
" "			8.1 *
" "			2.1 *
Fire assay-emission spectrographic			4.6 ± 1.0
" "			5.04 ± 0.28
" "			4.78 ± 0.96 +
" "			5.1 ± 0.2
" "			3.4 *
Fire assay-spectrophotometric			4.63
" "			4.5 ± 0.2
" "			5.61 ± 0.32

* Not included in average value for platinum.

\+ No confidence limits quoted.

Table VII: Previous analysis of ores for platinum group metals and gold.

	Concentration of metal (ppm).		
	S4 (19)	Float concentrate (19)	USBM 31 (20)
Platinum	5.23	82.60	4.9 (7.3%) +
Palladium	0.91	49.90	(a) 2.1 (5.3%)
Ruthenium	0.05	1.00	(b) 0.53
Rhodium	0.35	9.55	(c) 0.34 (17.8%)
Iridium	0.10	1.35	(d) 0.13 (15.0%)
Gold	0.23	2.55	(e) 0.41 (20.5%)

(a) Average value from 9 laboratories.

(b) Tentative value from United States Bureau of Mines.

(c) Average value from 7 laboratories.

(d) Average of 12 determinations from United States Bureau of Mines.

(e) Average value from 8 laboratories.

\+ Figures in brackets represent relative standard deviation.

whilst roasting. Loss in weight on roasting was on average 0.003g/g. Samples of S_4 and the float concentrate were weighed directly into baggies and mixed with the flux components (flux A).. Six milligrams of silver as silver nitrate was added to the float concentrate and 2 mg added to the other two ores. The samples were dried, usually by leaving in a drying oven overnight at 70°C. After drying, lumps were broken up and the mixture thoroughly shaken for five minutes. The crucibles were placed in the furnace and samples fire assayed in an identical manner to that already outlined for synthetic samples.

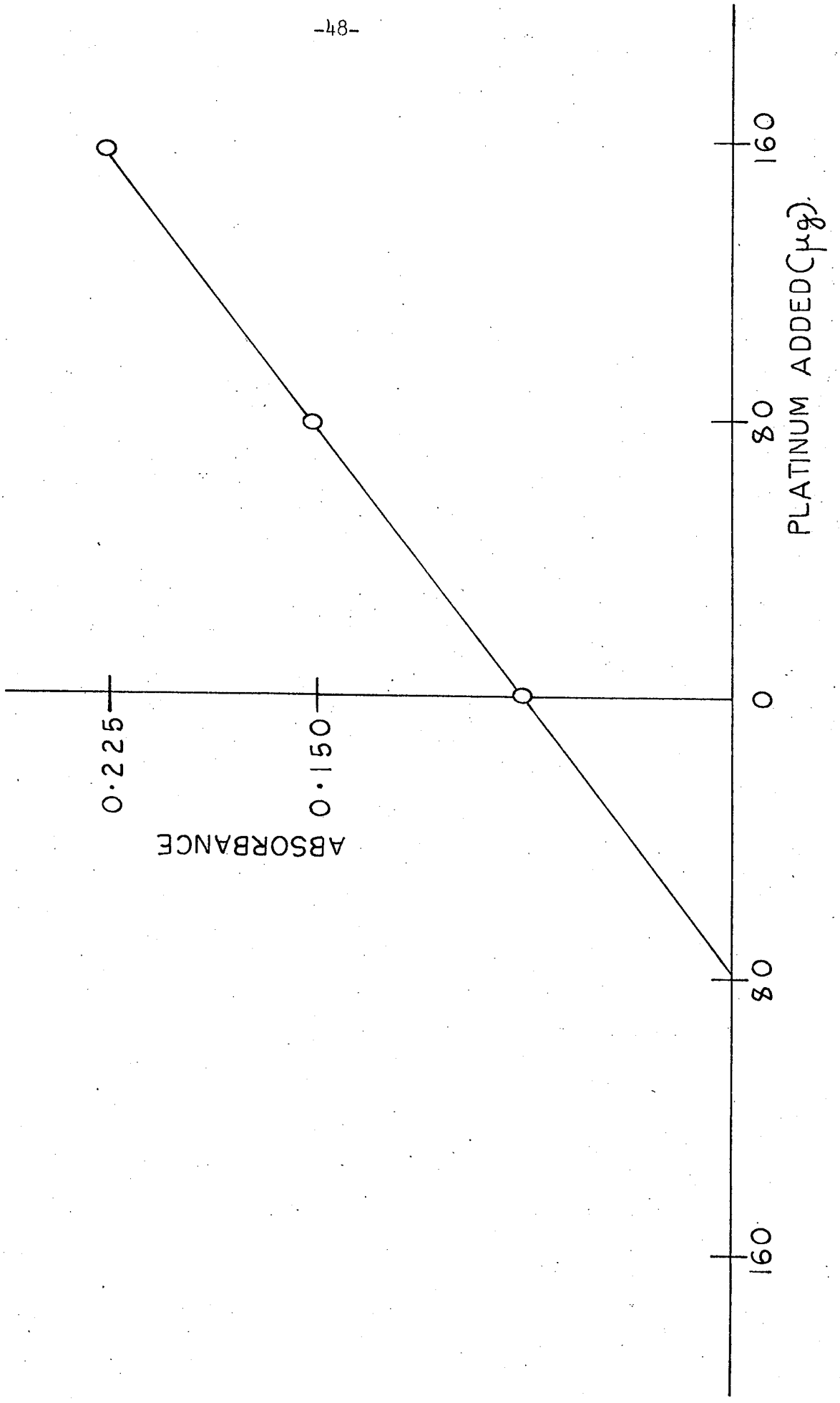
The silver beads obtained were analysed by atomic absorption and results are shown in Table VIII. Initial results for the float concentrate were low and so samples were roasted as described above before fire assaying. Loss in weight on roasting was on average 0.013g/g. These results also appear in Table VIII. Several S4 ore samples were also roasted to see if recovery could be improved. Although loss in weight was 0.030g/g, results obtained were the same as previous analysis. The procedure was checked using the method of standard additions. Three beads obtained from the fire assay of equal amounts of ore were placed in 10 ml flasks and treated as described above. Additions of 0, 79.2 and 158.4 μg platinum were made to respective flasks, and the absorbance of each solution was measured, using a blank to zero the instrument. A plot of absorbance versus amount of platinum added yielded a straight line as shown in Figure I. Extrapolation of the line to the abscissa yielded 78.4 μg platinum which when divided by the sample weight (15.9 g) gave a value of 4.93 ppm for ore S4.

Table VIII: Determination of platinum in ores by combined fire assay-flame atomic absorption.

	Concentration of platinum (ppm).			
Ore designation:	S4	Float concentrate		USBM 31
		Before roasting	After roasting	
	5.21	76.4	79.2	5.73
	5.78	73.4	79.6	5.84
	5.36	77.1	81.8	5.03
	4.91	74.4	80.0	5.30
	4.59 *	77.1	78.3	5.39
	5.03	76.1	79.9	5.95
	4.93	77.5	78.6	5.83
	5.37	77.5	79.3	5.07
	5.47	74.4	77.5	
	5.51	74.0	85.2*	
	5.07		81.2	
Averages:	5.26±0.20	75.8±1.1	79.5±0.9	5.52±0.31

* Value rejected on statistical grounds.
± Value quoted at the 95% confidence level.

Figure I. Standard addition method for the determination of platinum in ore S4. (Scale expansion X5).


ABSORBANCE
0·225
0·150
0
80
160
80
160
PLATINUM ADDED(μg).

Methods for the determination of platinum.

a). Gravimetric methods.

Probably the easiest and most convenient method for the determination of platinum after removal of silver by parting is by direct weighing. The filter paper containing the platinum residue could be ignited by leaving in a tared crucible overnight at 400°C. The crucible could then be weighed and the amount of platinum determined. Blanks would have to be run to correct for residual ash from the filter paper. However, it was invariably found that, even after double parting with concentrated sulfuric acid, the platinum residue contained traces of silver. Blanks could not be relied upon to correct this, since the amount of silver retained probably varied from bead to bead. Because of this reason a direct weighing procedure was not used.

A gravimetric method using thiophenol (1) was used for milligram amounts of platinum. After igniting the filter paper at 400°C, the platinum residue was alternately treated with aqua regia three times, concentrated hydrochloric acid three times and finally water. The solution was filtered into a 400 ml beaker and made up to 200 ml with water. Dissolving in water and filtering removes the last traces of silver. The solution was acidified with four drops of concentrated hydrochloric acid and five drops of thiophenol then added. A cover glass was placed over the beaker and the mixture digested on a steam bath until the supernatant liquid was clear. This period may extend

to twelve hours or possibly more depending on the temperature of the steam bath. The solution was filtered through a 7 cm Whatman No. 44 paper and the residue washed with water. The filter paper was transferred to a tared Coors 000 porcelain crucible and placed in an electric oven. The temperature was slowly raised to 400°C and held there for three hours, and then raised to 800°C and held for twenty minutes. Crucibles were then removed and the residue weighed as platinum. Blanks which were run simultaneously with samples in all cases were consistent at between 100 - 200 μg. Results obtained are shown in Table IX.

It can be seen that most results are high. This has been the usual experience of the author using platinum standards. Table IX shows the values obtained on one set of platinum standards. Beamish (16) remarks that there is a marked tendency towards positive errors using this method. However, these errors should be at maximum 0.2 per cent and certainly not 3 - 8 per cent. In an attempt to determine the reason for high values, these platinum residues were heated in a stream of hydrogen at 800°C. Losses in weight occured as shown in Table IX . Heating was continued until no further loss in weight was obtained. Blanks were also heated in hydrogen but no loss in weight occurred.

Two reasonable explanations may be put forward to explain these losses in weight:

a) Further removal of sulfur as hydrogen sulfide.

b) Formation of oxides of platinum on heating in the electric oven followed by reduction in hydrogen.

Table IX: Results of thiophenol gravimetric analysis and losses in weight of platinum residues by reduction in hydrogen.

Platinum added (mg)	Platinum found (mg)	% increase	Platinum weight on reduction (mg)	Loss in weight (mg)	% loss
10.131	10.631	4.9	10.222	0.409	3.8
"	10.658	5.2	10.326	0.332	3.1
"	10.744	6.1	10.380	0.364	3.4
"	10.458	3.2	10.183	0.275	2.6
"	10.912	7.7	10.401	0.511	4.7
"	10.848	7.1	10.413	0.435	4.0

Explanation (a) would seem most valid especially as yellow specks were in evidence in the black residue. The temperature in the electric oven (800°C.) does not seem high enough for formation of platinum oxides (16). Even if such oxides are formed, they are volatile and one would not expect their presence in the residue.

Other precipitants were examined and only zinc was found to be recommended (21). The method outlined for zinc was then used for standard platinum solutions. Again results were very high - probably because of contamination by zinc.

Because of these high results, a second platinum solution was standardized spectrophotometrically against the original standard using all calibrated glassware. Also milligram samples of platinum from the fire assay and cupellation procedures were determined in the same way.

b). Spectrophotometric method.

The colour formed by the reaction of platinum with tin (II) chloride was used for spectrophotometric analysis (2). After parting, the platinum residue was ignited and treated with aqua regia, hydrochloric acid and water as described in the previous sections.

Platinum solutions were added to volumetric flasks containing concentrated hydrochloric acid and tin (II) chloride and the absorbance measured at 400 nm in 1 or 4 cm cells as determined by the concentration. Optimum reagent concentrations were 10 ml concentrated hydrochloric acid and 20 ml tin (II) chloride per 100 ml of solution. Using 1 cm cells the concentration was linear over the range 3-23 ppm

and using 4 cm cells linear over the range 0.5 - 8 ppm. Absorbances were corrected for blanks containing hydrochloric acid and tin (II) chloride. From blank measurements detection limits were calculated to be 0.14 μg/ml for 1 cm cells and 0.09 μg/ml for 4 cm cells. The precision obtainable in both cases was ± 0.5 per cent. Standard graphs are shown in Figures II and III. In all analyses standard solutions were measured with sample solutions to check the calibration.

The nature of the coloured product formed in the above reaction has been the centre of considerable interest. Ayers and Meyer (22), using the methods of continuous variations and mole ratios, found evidence for the formation of several complexes. Some of the reactions were slow, others rapid. In aqueous solution, the principal product was believed to be a tetrapositive ion of formula $(PtSn_4Cl_4)^{4+}$ in which platinum exists in the zero oxidation state.

A later study by Lederer and Shukla (23) disagrees with the above conclusion, claiming the complex is anionic in nature. Using adsorption paper chromatography, they suggested that trichlorostannate ligands ($SnCl_3$) were coordinated to platinum and that zero valent platinum was highly unlikely. Support for this has been given in correspondence on the subject (24,25).

Davies et at (24) confirmed the complex was anionic by ion-exchange and gave evidence for the presence of $\left[Pt\ (SnCl_3)_2Cl_2\right]^{2-}$.

Cramer et al (25) isolated two substances from solutions in which the tin (II) - platinum ratio was greater than 5:1:

Figure II. Tin (II) chloride spectrophotometric calibration curve for 0.8 - 5 ppm platinum using 4 cm cells.

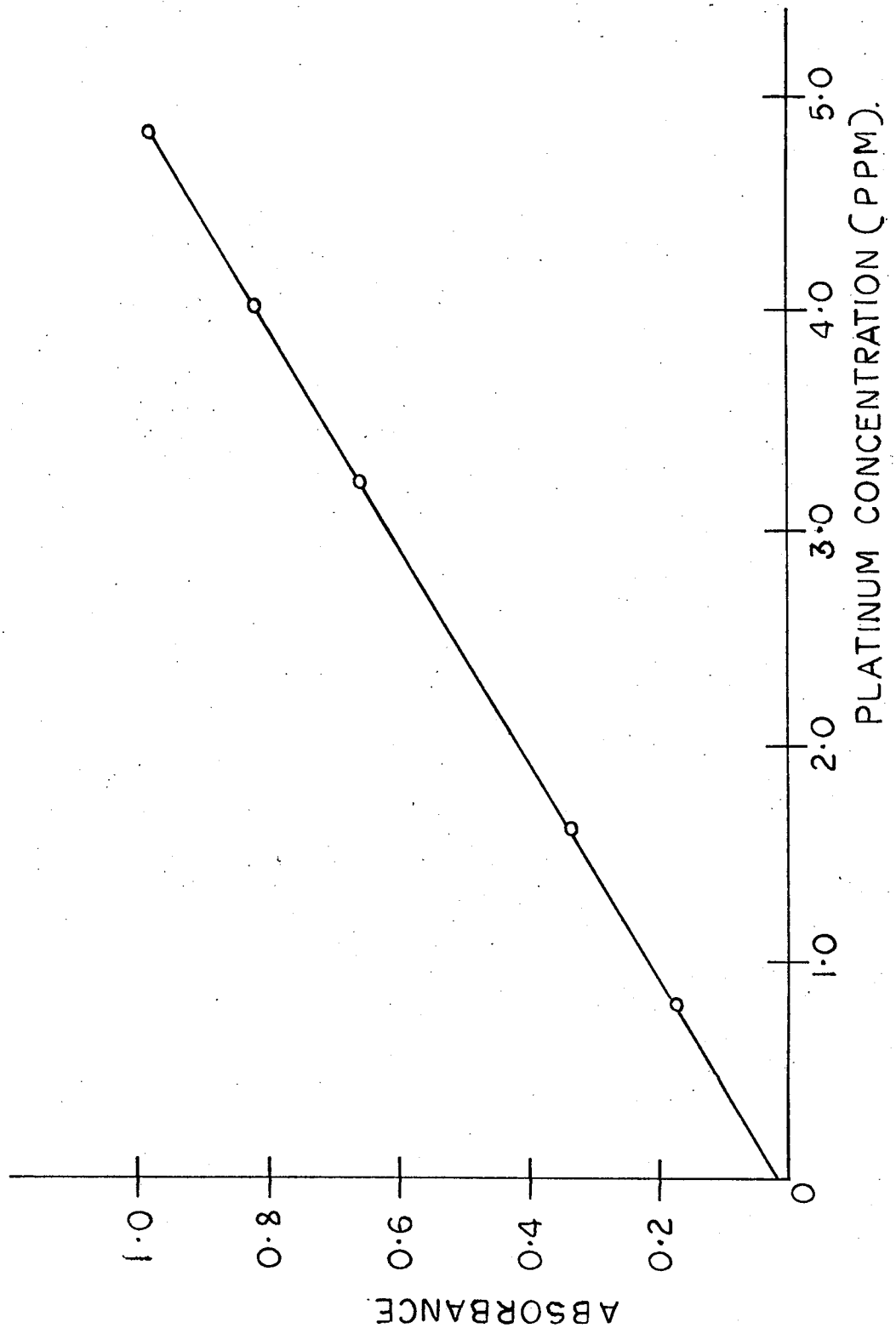
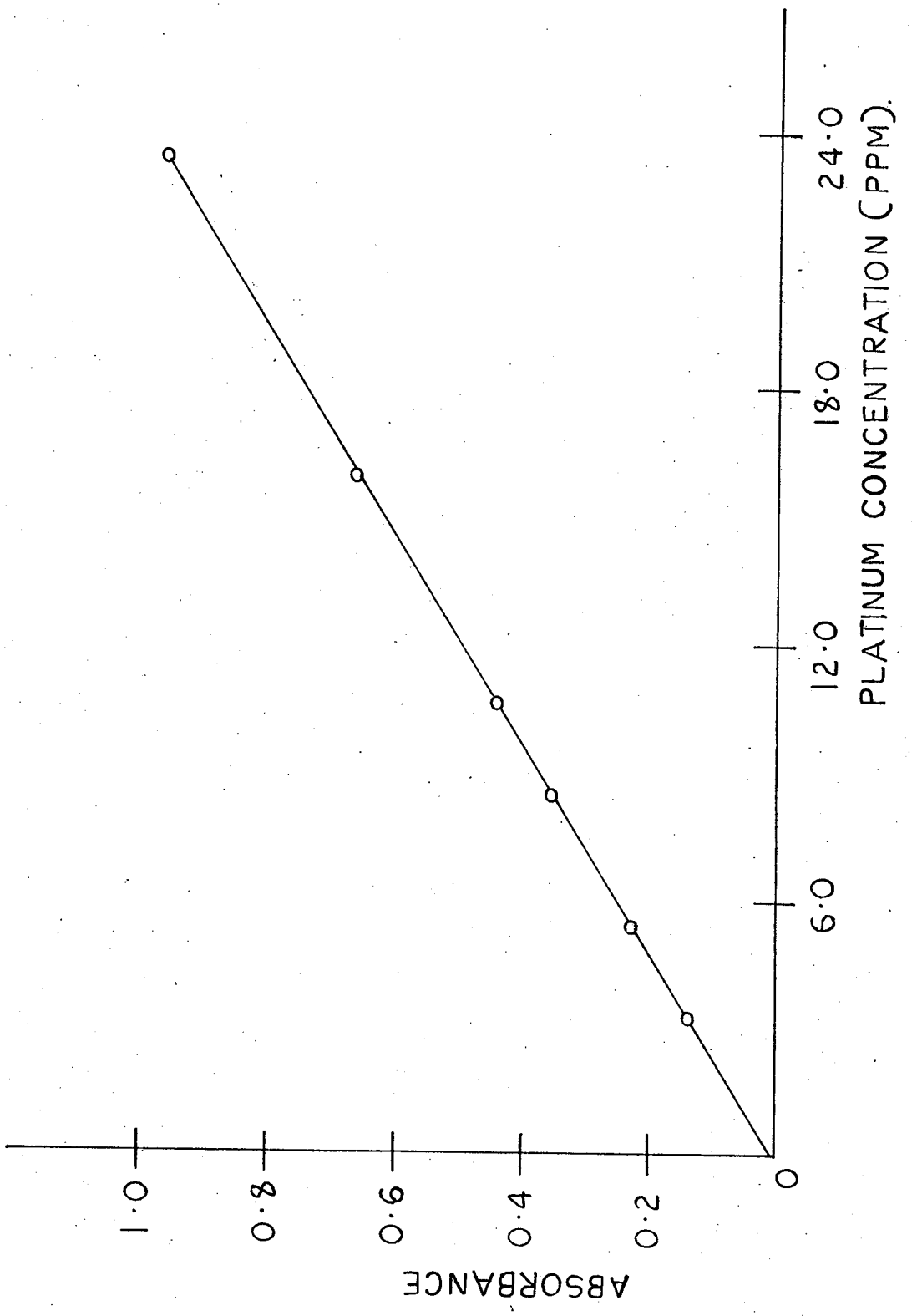

ABSORBANCE
0·2
0·4
0·6
0·8
1·0
0
1·0
2·0
3·0
4·0
5·0
PLATINUM CONCENTRATION (PPM).

Figure III. Tin (II) chloride spectrophotometric calibration curve for 3 - 23 ppm platinum using 1 cm cells.


ABSORBANCE
0·2
0·4
0·6
0·8
1·0
0
6·0
12·0
18·0
24·0
PLATINUM CONCENTRATION (PPM).

$[(C_6H_5)_3\ PCH_3]_3\ Pt(SnCl_3)_5$ (red crystalline) and $[(C_6H_5)_3\ PCH_3]_2\ PtCl_2\ (SnCl_3)_2$. (yellow crystalline)

Further evidence for the $Pt(SnCl_3)_5^{3-}$ anion comes from the work of Pietropaola et al (26) who studied the reaction of $PtCl_4^{2-}$ with ethylene in the presence of $SnCl_3^-$. These authors claim no ethylene adsorption is detectable at high tin-platinum ratios, at which the predominant species is the five coordinated $Pt(SnCl_3)_5^{3-}$. Their study also shows that $SnCl_3^-$ behaves as a weak σ- donor, but is a strong $d\pi$ - $d\pi$ metal to tin bond acceptor ligand.

Young et al (27) have proposed the possibility of cis and trans isomers formed in the following stepwise manner.

$$SnCl_2 + Cl^- \rightleftharpoons SnCl_3^-$$

$$PtCl_4^{2-} + SnCl_3^- \rightleftharpoons PtCl_3(SnCl_3)^{2-} + Cl^-$$

$$PtCl_3(SnCl_3)^{2-} + SnCl_3^- \rightleftharpoons \text{trans} - PtCl_2(SnCl_3)_2^{2-} + Cl^-$$

$$\text{trans} - PtCl_2(SnCl_3)_2^{2-} \rightleftharpoons \text{cis} - PtCl_2(SnCl_3)_2^{2-}.$$

Lindsay et al (28) found evidence for the anion $[Pt_3Sn_8Cl_{20}]^{4-}$ in acetone solution. Platinum is presumably in the zero valent state.

In a recent polarographic and spectrophotometric study in this laboratory, Dugan (29) found evidence of reduction of platinum (IV) to platinum (II) and possibly platinum (0) in perchloric acid medium. At tin-platinum ratios greater than 1:1 at least two complexes

were formed. At low and intermediate tin to platinum ratios, one complex is initially formed followed by rearrangement or dissociation to another complex. This rearrangement was suppressed at high tin-platinum ratios (50:1). These results were interpreted as initial formation of a trans complex followed by rearrangement to the cis isomer. At high tin-platinum ratios, this rearrangement was suppressed by the large excess of tin (II) chloride.

Thus it can be seen that while the colour formed between platinum and tin (II) chloride in acid solution is the basis of a sensitive, quantitative method of determination, the exact nature of the system is as yet not completely understood.

c). Atomic absorption.

The method described by Van Loon (30) was used to determine platinum in silver beads obtained from the cupellation process.

Each bead, obtained from fire assay of ores S4 and USBM 31, was placed in a 10 ml volumetric flask and 0.5 ml concentrated nitric acid added. The flask was heated by immersion in a beaker of hot water, and heating continued until dissolution of the bead was complete. Concentrated hydrochloric acid (3.75 ml) was then added, and the flask heated once more to dissolve the silver. The flask was allowed to cool, usually overnight, and lanthanum as lanthanum chloride added so as to make the final concentration in the flask 1 per cent. The flask was made up to the mark with distilled water, and platinum absorbance determined versus standards containing silver, 1 per cent lanthanum and

6 M hydrochloric acid by running, closely, a lower concentration standard, followed by two samples and a higher concentration standard in quick succession.

The beads obtained from fire assay of the float concentrate were placed in 25 ml volumetric flasks. Solutions were still made 6 M in hydrochloric acid and the final concentration of lanthanum in the flask was still 1 per cent.

Blanks were run with each set of samples and under the conditions used it is possible to detect 0.4 μg/ml of platinum.

Addition of excess concentrated hydrochloric acid serves not only to dissolve the platinum but also to keep silver in solution. Silver is soluble because of the formation of anionic complexes of the type $AgCl_2^-$, $AgCl_3^{2-}$, and $AgCl_4^{3-}$.

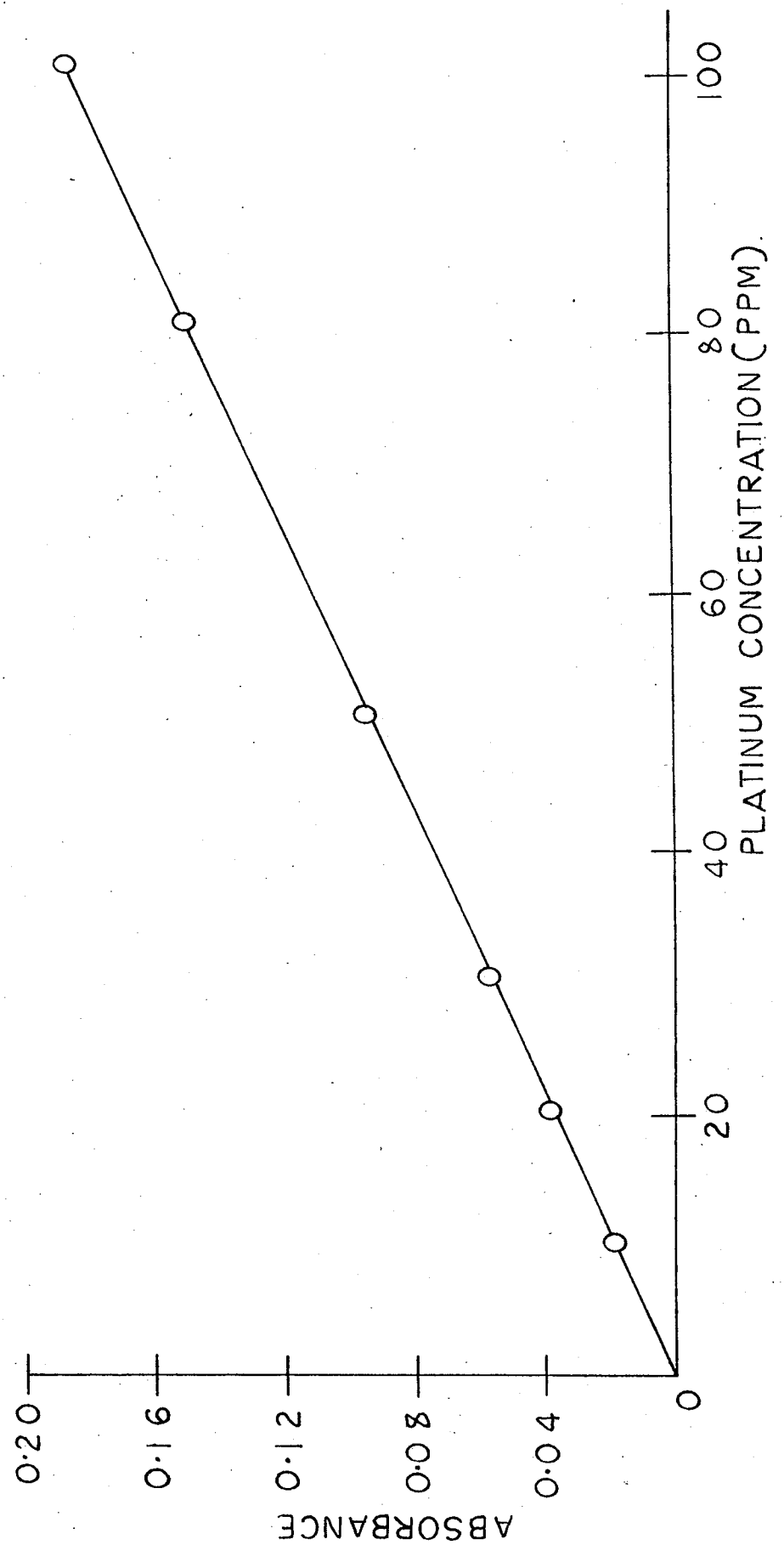
The following instrument settings were used according to the Perkin-Elmer Handbook (31):

Wavelength:	2659Å
Lamp current:	25mA
Slit setting:	4
Fuel (Acetylene) flow rate:	3.8 litres / minute.
Air flow rate:	24 litres / minute.

Burner positions and aspiration rate were adjusted for optimum absorbance each time.

Precision obtainable using scale expansion X5 is of the order of ± 2%, over the concentration range 5-100 ppm. The standard graph is shown is Figure IV.

Figure IV. Atomic absorption calibration curve for 0 - 100 ppm platinum (no scale expansion).


ABSORBANCE
0·20
0·16
0·12
0·08
0·04
0
20
40
60
80
100
PLATINUM CONCENTRATION (PPM).

It is of interest to consider the interferences on platinum, due to the other noble metals. Van Loon (28) found platinum absorbance depressed 30 per cent by 1 per cent silver. Other studies (32,33,34) have shown interference from palladium, gold and particularly rhodium and iridium. All interferences due to these metals may be removed by the addition of 1 per cent lanthanum.

Gilbert (35) divides chemical interferences into two types:

I) Vapour-phase interferences including ionization, excitation and dissociation.

II) Condensed-phase interference due to the formation of an involatile species of the analyte.

Type (II) would seem to be more applicable in this work. Ionization is not expected to any great extent in an air-acetylene flame, because of the relatively low temperature of such a flame. Excitation interference is due to a shift in population of several energy levels in an atom. Since the ground state does the absorbing in atomic absorption, this type of interference is negligible. Interference can also be encountered due to insufficient dissociation of molecules at ordinary flame temperatures. Hotter flames can be used, but this increases chances of ionization.

The work of Van Loon et al (32) lends credence to the above assumption concerning type (II) interferences. Plots of absorbance versus (M^{n+}) / (Pt^{4+}), where (M^{n+}) is the concentration of contaminant, showed distinct breaks in absorbance depression at (M^{n+}) / (Pt^{4+}) = 2 for sodium and potassium and a value of 1 for magnesium and calcium. This suggests the formation of an involatile species of platinum as shown below:

$$(2/n)M^{n+} + H_2(PtCl_6) \rightleftharpoons M_{2/n}PtCl_6 + 2H^+.$$

Interference by a cation would depend on the extent of the displacement and the volatility of the platinum salt formed as compared to $H_2(PtCl_6)$. In strong hydrochloric acid solution, all the noble metals form anionic complexes. Of the noble metals considered in this work, the least stable are rhodium (36) and iridium (37). Thus it is expected that rhodium will cause the greatest interference followed by iridium. This is borne out by the work cited above (32,34). All metals will cause interference when present in large amounts.

Lanthanum (III) depresses platinum absorbance reaching a minimum at $(La^{3+}) / (Pt^{4+}) = 0.7$. This is possibly due to the following reaction:

$$2La^{3+} + 3H_2(PtCl_6) \rightleftharpoons La_2(PtCl_6)_3 + 2H^+$$

Increasing concentrations of lanthanum release more platinum leading to enchancement of absorbance.

The suggestion was also made that oxides of platinum may be present in the flame. Lanthanum could prevent interference from such species by one of the following reactions:

$$4La(g) + 3O_2(g) \rightleftharpoons 2La_2O_3(g)$$

$$La(g) + Pt_xO_2 \rightleftharpoons La_2O_3 + x\ Pt(g)$$

Hotter flames may also be used to reduce condensed-phase interferences. Van Loon et al (38) studied the above system in nitrous oxide-acetylene flames and found interferences were indeed removed. However, sensitivity was lowered by a factor of 4, presumably because of ionization effects.

EMISSION SPECTROSCOPY.

Introduction.

Atomic emission spectra are observed when photons are emitted by atoms in an excited energy state. The frequencies of the lines are characteristic of the elements present and can, therefore, be utilized in qualitative and quantitative analysis.

Various energy sources may be used to excite electrons in atoms. In emission spectroscopy electric arc and spark discharges are commonly used. With such powerful excitation sources, high resolution instruments are required to resolve the complex spectra generated. The spectra originate from excitation of outer or valency electrons, and are studied in the visible and near U.V. regions.

The sample for analysis is vapourised into the excitation source, and the light thus produced is dispersed by a prism or a grating and recorded, usually, on a photographic plate. The intensity of an emitted line depends on the number of excited atoms and hence the concentration of the particular element in the sample.

Many spectrographic methods have been employed for the determination of platinum. Samples have been in the form of silver beads (39,40); lead buttons from arrested cupellations (41,42); and as solutions (43,44).

Initial studies were performed with silver beads. It was thought that since no parting or dissolution of the beads was necessary, arcing of the beads would provide the simplest and most convenient method for platinum determination.

Arcing of silver beads.

Silver beads weighing approximately 20 mg and containing 0 (blank), 10, 20, 40 and 60 μg of platinum were prepared by cupellation as described in a previous section. These beads were placed in standard 3/16" cupped graphite electrodes and 6 mg lithium fluoride added as a buffer to prevent bead ejection during arcing. The beads were excited by means of an uninterrupted d.c. arc (11.5A), in an argon-oxygen atmosphere, followed by three photographic exposures. The first exposure was completed at 120 seconds, the second exposure completed when the intense silver coloration of the arc began to decrease and the third terminated when the arc characteristics indicated that complete volatilization of the electrodes contents had been achieved. Total exposure time was approximately 240 seconds. Exploratory results showed a linear relationship between concentration of platinum and intensity of spectral line (3064.71Å), when plotted on log-log coordinates.

All beads to be used in further emission spectrographic work were, therefore prepared containing 20 mg silver. Standard beads were prepared by cupellation, and synthetic fire assay beads and ore beads prepared by fire assaying with flux A as described previously. Ores designated float concentrate and USBM 31 were roasted at 700°C for one hour before fire assaying. Ore weights were such that between 20-50 μg of platinum were taken.

Arcing of these beads failed to reproduced the linear relationship found in earlier work. Indeed, in some instances, no platinum was found at all. Close examination of the beads during arcing showed that after

all the silver had volatilized, platinum was left on the electrode in the form of a "leaf". This leaf either burnt to completion on the electrode, or was ejected at random intervals causing erratic results. Copper powder was added to the electrodes to try to prevent ejection of the platinum. Copper electrodes have successfully been used for arcing silver beads (45). However, copper failed to overcome the problem, ejection still taking place after the volatilization of copper. Reduction of the arc current to 7A also proved unsuccessful. It now appears that early success with this method was purely fortuitous and this line of work was discontinued.

Beads were then dissolved and applied to the electrodes as solutions. Synthetic fire assay beads and ore beads were placed in 25 ml volumetric flasks and 0.5 ml concentrated nitric acid added to dissolve the silver. Two millilitres of concentrated hydrochloric acid was then added to dissolve the platinum. Flasks were gently heated to encourage dissolution. When cool flasks were made up to the mark with concentrated hydrochloric acid, and allowed to stand for several hours. This ensures complete dissolution of the silver. Standard solutions were made by pipetting microlitre quantities of stock platinum and silver solutions into 25 ml flasks and adding nitric acid and hydrochloric acid as above. These solutions contained 0, 10, 20, 40 and 60 µg platinum and 20 mg silver. A calibration was attempted by running each standard in triplicate. 200µl of solution was placed on each electrode in 20µl aliquots, after first waterproofing the electrode with 40µl of a 1% solution of polystyrene in benzene. The aliquots were evaporated onto the electrode, by placing the electrode under a heat lamp. A final

20 µl of polystyrene solution was applied just before arcing. The electrode was then mounted against a conically tipped graphite electrode and arced at 11.5A in an argon-oxygen atmosphere, using an analytical gap of 4 mm. A 45 second pre-burn followed by a 35 second exposure was used. Results were very erratic, especially at low loadings of platinum (80 ng and 160 ng). Precision at these levels was ± 50%. Platinum 2659.45 and 3064.71 Å lines were used. Internal standardization was not attempted. Most of the elements considered were volatilized before platinum during the pre-burn. Those that were desirable - the noble metals - were considered unsuitable because of their presence in ore samples. This was not considered critical since the arc burned very quietly and steadily with minimum wandering and was constantly focussed on the slit.

Because of the lack of success with a d.c. arc, it was decided to utilize the method of Haffty and Riley (43) and use an ignited a.c. arc to excite the platinum.

Ignited a.c. arc of platinum solutions.

The same solutions prepared above were used, except that 40 µl of a 1,000 ppm molybdenum solution was added to each flask. Molybdenum serves as an internal standard. Instrumental conditions are given in Table X.

Standard solutions were run in triplicate by adding 200 µl in 50 µl aliquots to the flat end of the electrodes. Electrodes were

Table X: Instrumental conditions for ignited a.c. arc.

Excitation source - ignited a.c. arc. Primary power source - full wave rectified 230V, 60Hz power supply - initiated by a high-voltage condensed spark synchronized to initiate each half cycle.

Radio frequency current:	2.0 A
Capacitance:	0.0025 μF.
Inductance:	15 μH (residual).
Primary resistance:	16 Ω.
Secondary resistance:	0.5 Ω.
Discharge voltage:	15,000V.
Current, radio frequency:	7.5 A
Slitwidth:	40 μ.
Analytical gap:	3mm.
Transmission:	Steps 3 & 6 of a 7 step filter.(a)
Exposure:	20 seconds.
Emulsion:	Kodak SA-1
Electrodes:	Anode - ASTM 8 (flat end)
	Cathode - ASTM 5 (flat end)

(a) Neutral filter with bands of differing transmittance placed at the slit of the spectrograph. It was prepared at A.E.C.L., Pinawa, Manitoba from thin aluminum sheet and painted black. Transmission of step 3 is 40.7% and for step 6 - 11.2%.

waterproofed and aliquots evaporated under a heat lamp as already described. Residues were excited by an ignited a.c. arc for twenty seconds. Photographic plates were calibrated with an iron spectrum, excited by a d.c. arc at 7A for eight seconds using a slit width of 20μ. Intensities of spectral lines were measured using a non-recording densitometer. Calibration plots of concentration versus intensity ratios of Pt 2659.45 / Mo 2816.15 and Pt 3064.71 / Mo 2816.16 gave straight lines, when plotted on log-log coordinates. Precision was much improved using the Pt 2659.45 / Mo 2816.15 ratio.

Synthetic fire assay solutions and ore solutions were run and results were very low when compared to the standard graph. However, when cupellation beads were dissolved and used as standards, results indicated quantitative recovery, as shown in Table XI and XII. It was found that accuracy and precision were much improved using the Pt 3064.71 / Mo 2816.15 intensity ratio. This is in contrast to the previous standards. Several plates were used to accomodate all samples, and cupellation standards were run on each plate to check the calibration. Each plate was developed by the procedure recommended by Kodak, and developing solutions were changed once weekly.

Conclusion.

It is surprising that so much trouble was experienced using a d.c. arc on silver beads after a report successfully accomplishing the same (39). However, other workers have had the problem of bead ejection when arcing on graphite electrodes. Sim (45) overcame the problem by using copper electrodes. Although these electrodes seem best for arcing silver

Table XI: Ignited a.c. arc of synthetic fire assay samples.

Platinum added (μg)	Platinum recovered (μg)	Average recovery.
16.1	17.1	
"	17.1	
"	16.0	
"	14.4	16.2 ± 2.0 μg (100.6 ± 12.4%)
24.1	24.5	
"	20.0	
"	20.0	
"	24.0	22.1 ± 3.9 μg (91.7 ± 16.2%)
32.2	40.0 *	
"	31.3	
"	31.3	31.3 μg (97.2%)
48.3	46.0	
"	49.0	
"	49.0	
"	46.5	47.6 ± 2.6 μg (98.6 ± 5.4%)

* value rejected on statistical grounds.

± Values quoted at the 95% confidence level.

Table XII: Determination of platinum in ores by combined fire assay-ignited a.c. arc.

	Concentration of platinum (ppm).		
Ore designation:	S4	Float concentrate	USBM 31
	5.67	78.9	5.98
	4.76	79.4	4.38
	4.79	84.7	6.10
	5.60	78.8	4.52
	6.02	69.6	4.03
	6.04	71.2	5.09
	5.79	77.2	4.79
	4.76		
Average:	5.43 ± 0.49	77.1 ± 5.0	4.98 ± 0.73

± Values quoted at the 95% confidence level.

beads, they were not used for this work. Whitehead and Heady (46) used 10 mg rhodium powder as a buffer to prevent bead ejection. It was felt that a platinum metal would likely be contaminated with platinum and the presence of only 0.0001 per cent platinum would be detected. Thus, it was not considered good practice to use another platinum metal in the determination of platinum.

Poor results obtained for solutions using a d.c. arc may be due to the small amount of sample being added to the electrode cf. 80 ng. This is close to the detection limit. If results had not initially been so fortuituous, smaller bead weights would have been used, and smaller dilutions utilized. Thus, more platinum would have been added to the electrode with a probable increase in precision.

No explanation can be forwarded to explain why cupellation standards were necessary using an ignited a.c. arc. Results using synthetic standards were approximately 30-50 per cent low. It is inconceivable that such losses will occur for platinum in all samples in the cupellation or fire assay procedure.

The precision obtained at 80 ng (±13 ng) agrees well with that obtained in another study (±10 ng) at 79 ng (44).

X RAY FLUORESCENCE SPECTROMETRY.

Introduction.

When high voltage electrons impinge on a target they are retarded and quickly lose energy. The energy these electrons lose is radiated in a spectrum that ranges from the x-ray region into the infra-red and is generally referred to as a "continuum". If the voltage across the x-ray tube is raised to a critical level, which is a function of the target, sharp peaks are superimposed on the "continuum". For a given target these spectra occur at the same wavelength and so are referred to as "characteristic line" spectra.

Characteristic radiation arises from the energy transference involved in the arrangement of orbital electrons of the target element following ejections of one or more electrons in the excitation process. Line spectra are named according to the transitions involved. Thus, if an electron moves into an empty K shell the characteristic radiation emitted is designated $K\alpha$, $K\beta$ etc depending on whether the electron originated from the L or M etc shell. The relative simplicity of characteristic x-ray spectra is explained by the limited numbers of energy levels in the atom, the fact that certain electron transitions are prohibited and that for those that are possible different probabilities exist.

The characteristic x-ray spectrum of an element can also be excited by x-rays, if this primary x-radiation is sufficiently energetic to ionize an inner shell. This is known as "secondary excitation".

Secondary excitation is also known as fluorescent x-ray spectrography.

In quantitative analysis the intensity of the "characteristic line" is related to the concentration of the element.

Commonly secondary x-radiation is scattered from the crystal surface and by suitable collimation and selection of Bragg angle of reflection, the radiation is analysed into its component wavelengths. The number of photons scattered at each Bragg angle is registered by a Geiger counter or proportional counter.

In more recent years solid-state detectors have been used to distinguish and measure individual lines by means of energy discrimination (47,48). These solid-state detectors are prepared by doping impurities such as phosphorus or boron into otherwise pure silicon or germanium crystals. Impurities that add electrons such as phosphorus are termed donors; impurities that create "holes" such as boron are termed acceptors. An n-type material contains free electrons for conduction whereas a p-type has an abundance of holes. The joining together of n-type and p-type crystals produces a p-n junction. Application of reverse bias to this p-n crystal creates a depletion zone within the crystal which is practically free of mobile charge. Ionizing radiation on entering the depletion zone creates electron-hole pairs, which produce pulses of electric current. Pulse height analysis allows the sorting of the energy pulses into different channels for counting. Pulses are directly proportional to the energy of the incident x-ray photon.

Lithium differs from the usual doping agents in that lithium atoms occupy interstitial sites and not substitutional sites. For

this reason the diffusion coefficient in lithium drifted silicon is greater by a factor of approximately 10^7. Solid-state detectors offer the advantage that all x-rays from elements in a specimen may be counted simultaneously.

Several examples are documented demonstrating the applicability of using x-rays for the determination of platinum in ores and mattes.

Strasheim and Wybenga(49) determined platinum, gold and iridium in matte solutions by a correction method and an internal standard method. The results obtained agreed well with one another and also with atomic absorption and chemical values, although the latter were not described.

Russell et al (50) determined noble metals in nickel sulfide buttons, ion-exchange resins and matte-leach residues by x-ray analysis. Floatation concentrates and nickel sulfide mattes were analysed for noble metals by concentration in nickel sulfide buttons. Results were compared with standards prepared by adding solutions of the noble metals to pure nickel sulfide, the mixture then dried, homogenised and pelleted. Results for platinum and palladium were satifactory when compared with atomic absorption analysis. Matrix effects were found to be insignificant.

In the analysis of ion-exchange resins and solutions of matte-leach residues, matrices were found to vary significantly so that net peak intensities could not be related to concentration. To overcome this, internal standardization was utilized, mercury being used as an internal standard for platinum. In both cases, synthetic standards

were prepared as identical as possible to samples. The procedures are capable of a high degree of accuracy and precision.

Bapat (51) described a method for the simultaneous determination of platinum and palladium, by isolating the metals on an anion-exchange resin-loaded paper disc. In this way, microgram quantities of platinum and palladium could be determined in the presence of milligram quantities of base metals. The method was extended to a nickel matte, and results obtained agreed well with spectrophotometric analysis.

To determine platinum in ores, Losev (52) dissolved the silver assay bead in dilute nitric acid, added tantalum as a comparison element, evaporated the solution, ignited the residue and then ground it. The analytical lines used were platinum $L\alpha_1$, and tantalum $L\beta_1$ and $L\beta_2$. For concentrations of platinum less than 0.5 per cent, the bead was first treated with dilute sulfuric acid to dissolve the silver. The error quoted was 3-4 per cent.

Chow (6) developed a procedure for the determination of gold in silver assay beads. Beads were flattened and a constant area exposed to the x-ray beam. Although results were very promising for synthetic samples, ore samples were not analysed. Other noble metals were found not to interfere.

It is hoped to extend Chow's method to the analysis of platinum in synthetic silver assay beads and if successful to further extend the method to ore samples.

Experimental.

Tube:	Molybdenum
Voltage:	40 Kv
Filament:	20 mA
Detector:	Kevex Si(Li) with an active area of 30mm^2 and resolution of 195ev full width at half maximum (FWHM) at 5.9 Kev.
Counting Time:	8 minutes.

X-rays from the molybdenum tube are filtered so as to be largely monochromatic, collimated and allowed to fall on the sample to be analysed. The Si(Li) detector is placed immediately below the sample out of the path of the main beam. The detector is operated at liquid nitrogen temperatures. The detector output signals are amplified and shaped for sorting by a 1024 channel pulse height analyser. The memory of the pulse height analyser may be continuously monitored by a display oscilloscope allowing the entire range to be inspected at a single glance. The data are recorded in digital form as a teletype readout of the memory.

X-ray fluorescence of standard silver-platinum beads.

Silver beads weighing approximately 11 mg and containing 0.2-4 per cent platinum were prepared in triplicate by cupellation of lead boats as described previously. Blanks were also included. Both platinum

and silver were added as solutions. The hemi-spherical beads so prepared were flattened between two steel blocks in order to present as large a surface area as possible to the x-ray beam. This was accomplished in two stages. After cupellation any adhering cupel material was carefully scraped away with a spatula and the beads flattened to approximately 0.5 mm. The beads were then annealed by heating in a porcelain crucible at red heat for 2 to 3 minutes and finally flattened to a pressure of 10 tons with a hydraulic press. Annealing prevented the beads from splitting or cracking. Bead thickness was constant at 0.10 - 0.12 mm. Diameters of beads varied from 3.70 - 4.10 mm.

The beads were mounted on mylar foil of 450 $\mu g\ cm^{-2}$ thickness stretched over an aluminum foil and held in position by vacuum grease. The holder was placed in the specimen chamber which was then evacuated. The sample made a 45° angle to the x-ray beam. Initially tube voltage and tube current were varied and 40Kv and 20mA found to give the best peak to background ratio. Each bead was counted for 8 minutes. This was long enough to obtain 10% counting statistics for 0.18% platinum. Figure V shows the spectrum obtained from a bead containing 100 μg platinum. Only channels 256 - 768 are shown. Resolutions calculated for 9.44 Kev (PtLα_1 peak) and 11.07 Kev (PtLβ_1 peak) are 330ev and 365ev, respectively. Thus it is not possible to resolve Lα_1, and Lα_2 peaks nor Lβ_1 and Lβ_2 peaks (Table XIII). However, PtLα and PtLβ peaks are easily resolved. Similar calculations show that Kα_1, and Kα_2 peaks of silver will appear as a single Kα peak. This is also the case with the Kβ line. AgKα and AgKβ peaks are easily resolved.

Figure V. X-ray fluorescence spectrum of a silver bead containing 100 μg platinum.

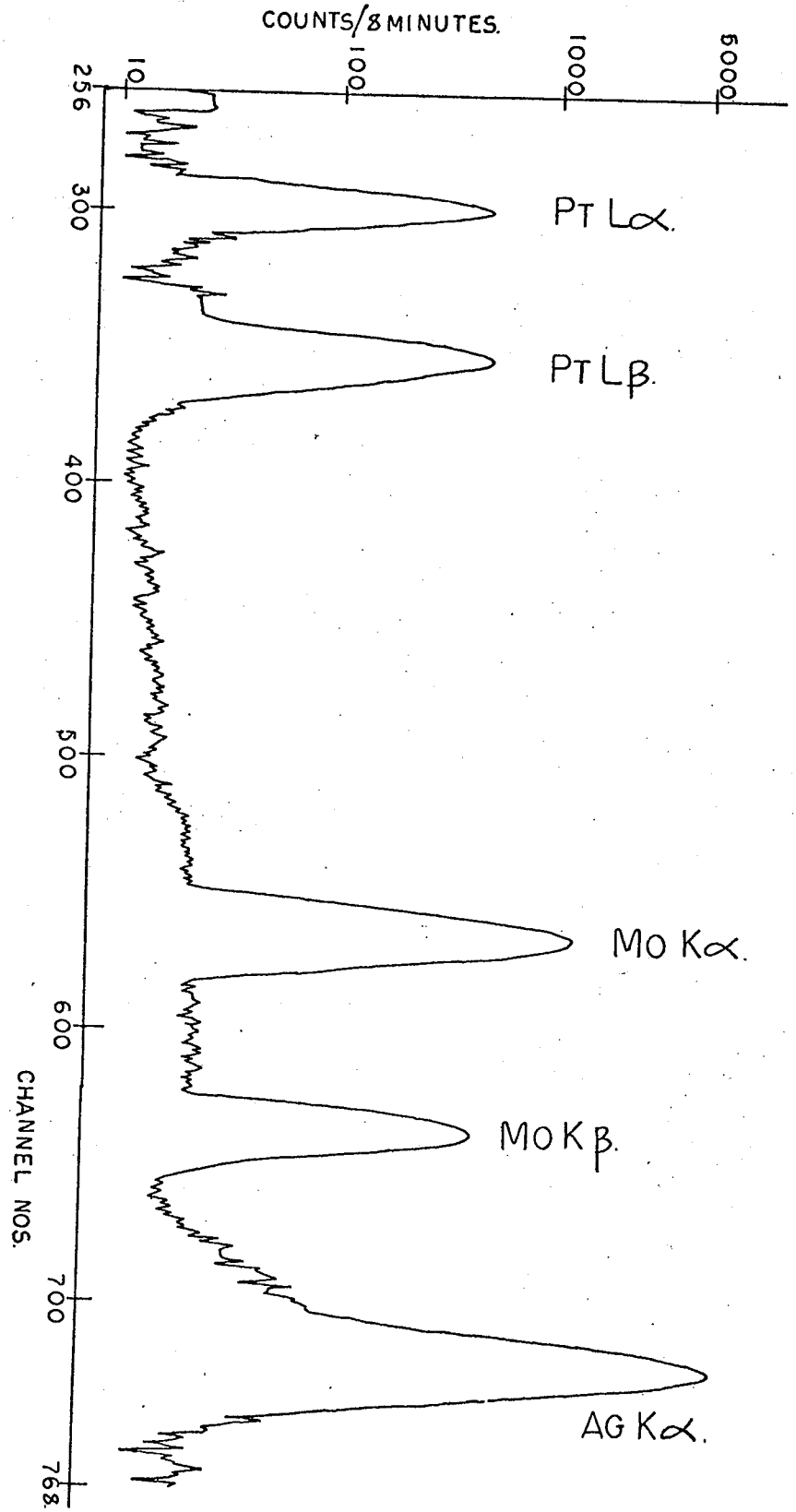

COUNTS/8 MINUTES.
10
100
1000
5000
256
300
400
500
600
700
768
CHANNEL NOS.
PT Lα.
PT Lβ.
MO Kα.
MO Kβ.
AG Kα.

Table XIII: Energies and wavelengths of $L\alpha$ and $L\beta$ peaks of iridium, platinum and gold.

	$L\alpha_1$		$L\alpha_2$		$L\beta_1$		$L\beta_2$	
	E	λ	E	λ	E	λ	E	λ
Iridium	9178.4	1.351	9104.3	1.362	10708.1	1.158	10925.1	1.135
Platinum	9444.0	1.313	9365.6	1.324	11071.4	1.120	11252.3	1.102
Gold	9717.9	1.276	9627.3	1.288	11439.1	1.084	11588.8	1.070

E = Energy in ev.

λ = Wavelength in Å.

A calibration curve was drawn of percentage platinum against PtLα/AgKα intensity ratio using the method of least squares. (Appendix A). This is shown in Figure VI. The concentration of platinum in the silver beads was calculated from the platinum added and the weight of the bead after cupellation. Intensity ratio was chosen as this ratio is independent of instrumental errors such as sample size, sample position and x-ray tube current.

Blanks contributed a constant 10 counts / 8 minutes at the PtLα line, and hence all platinum intensities were corrected by this amount. This correction made very little difference at high platinum intensities, but was significant at low count rates. No correction was applied to the AgKα line. The results for standard beads are shown in Table XIV.

The method was tested using synthetic fire assay samples prepared by salting flux A. Recoveries are listed in Table XV. As was the case with standards, bead thickness was constant at 0.10 - 0.12 mm. Bead diameters varied from 3.40 - 3.90 mm.

Homogeneity of beads.

To obtain quantitative results using an intensity ratio method, it is essential that platinum is uniformly distributed throughout the silver matrix. To test this uniform distribution two beads, one at low concentration and one at high concentration, were chosen at random, and both sides of the beads counted five times for the same length of time. Results are shown in Table XVI. Application of the Student "t" test for significance at the 95 per cent confidence level shows that the averages for each bead are statistically the same (Appendix B). This indicates complete bead homogeneity and justifies the use of intensity ratios.

Figure VI. X-ray fluorescence calibration curve for silver beads containing 0.18 - 4.2% platinum.

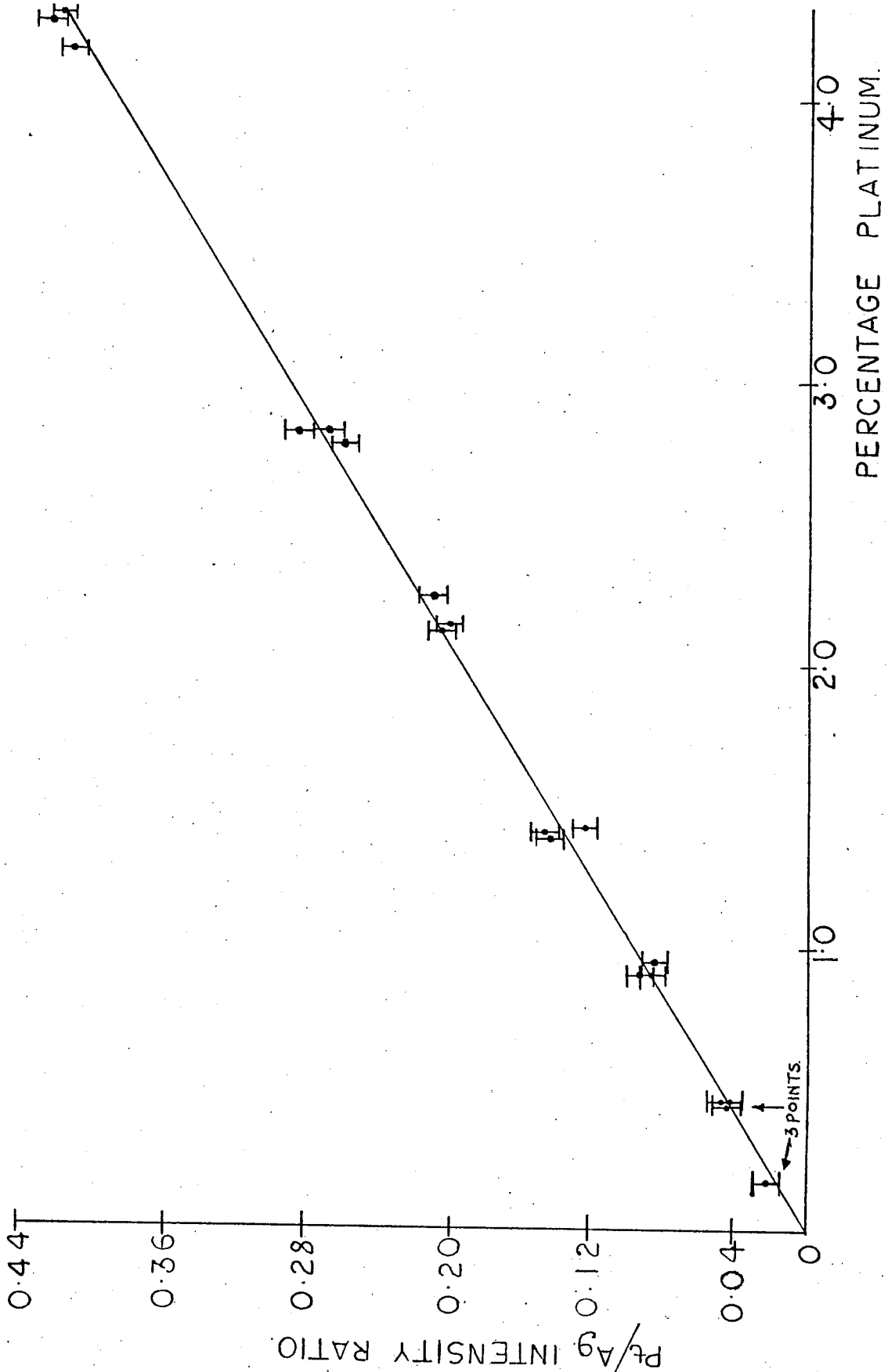

Pt/Ag INTENSITY RATIO
0·44
0·36
0·28
0·20
0·12
0·04
0
1·0
2·0
3·0
4·0
PERCENTAGE PLATINUM.
3 POINTS

Table XIV: X-ray fluorescence of standard silver-platinum beads.

Pt added (μg)	Wt of bead (mg)	%Pt	Net Peak Height Intensities counts / 8 minutes			
			Pt	Ag	Pt/Ag	A
20.1	11.45	0.176	224	10508*	0.0213	0.1210
20.1	11.25	0.179	114	5459	0.0209	0.1168
20.1	11.11	0.181	110	5302	0.0207	0.1144
50.2	11.23	0.447	255	5749	0.0444	0.0993
50.2	11.07	0.454	253	5295	0.0478	0.1053
50.2	11.11	0.452	232	5382	0.0431	0.0954
100.4	11.33	0.886	944	10933*	0.0863	0.0974
100.4	10.69	0.939	476	5578	0.0853	0.0908
100.4	11.10	0.905	488	5194	0.0940	0.1039

Table XIV (Cont'd).

Pt added (µg)	Wt of bead (mg)	%Pt	Net Peak Height Intensities counts / 8 minutes. Pt	Ag	Pt/Ag	A
160.1	11.44	1.400	755	5093	0.1482	0.1059
160.1	11.61	1.379	711	4888	0.1455	0.1055
160.1	11.29	1.418	710	5668	0.1253	0.0884
240.1	11.30	2.125	982	4838	0.2030	0.0955
240.1	11.43	2.101	1003	4838	0.2073	0.0987
240.1	10.85	2.213	1058	4996	0.2118	0.0957
320.1	11.42	2.803	2606	9640*	0.2703	0.0964
320.1	11.51	2.781	1356	4727	0.2869	0.1032
320.1	11.60	2.760	1275	4884	0.2611	0.0946
480.3	11.28	4.258	1943	4625	0.4201	0.0987
480.3	11.61	4.137	1944	4703	0.4134	0.0999
480.3	11.40	4.213	1910	4472	0.4271	0.1014

* Counting time 16 minutes.

A = Intensity ratio divided by platinum concentration.

Table XV: X-ray fluorescence of synthetic fire assay samples.

Pt added (μg)	Wt of bead (mg)	Net Peak Height Intensities counts / 8 minutes. Pt	Ag	Pt/Ag	%Pt	Pt recovered (μg)	Average
20.1	9.66	116	4850	0.0239	0.241	23.3	
"	9.54	109	5175	0.0211	0.213	20.3	
"	9.50	116	4959	0.0234	0.236	22.4	
"	9.61	112	5454	0.0205	0.207	19.9	
"	9.59	108	5085	0.0212	0.215	20.6	21.3±1.8 μg (106.0±9.0%)
40.2	9.67	198	5012	0.0395	0.399	38.6	
"	9.46	199	5159	0.0386	0.390	36.9	
"	9.83	203	4867	0.0417	0.421	41.4	
"	9.53	217	5122	0.0424	0.428	40.8	
"	9.52	187	5084	0.0365	0.369	35.1	38.6±3.3 μg (96.0±8.2%)

Table XV (Cont'd). Net Peak Height Intensities

counts / 8 minutes.

Pt added (µg)	Wt of bead (mg)	Pt	Ag	Pt/Ag	%Pt	Pt recovered (µg)	Average
60.3	10.54	306	4952	0.0618	0.624	65.8	
"	10.76	351	5971	0.0588	0.594	63.9	
"	10.63	309	5897	0.0524	0.529	56.2	
"	10.44	309	5462	0.0566	0.571	59.7	61.4±6.8 µg (101.8±11.3%)
200.1	10.71	922	5211	0.1769	1.787	191.4	
"	10.72	1089	5628	0.1935	1.955	209.5	
"	10.81	956	5190	0.1842	1.861	201.1	
"	10.70	1093	5240	0.2086	2.107	225.4	
"	10.59	1104	5800	0.1903	1.923	203.6	206.2±15.6 g (103.1±7.8%)

Table XV (Cont'd). Net Peak Height Intensities
counts / 8 minutes.

Pt added (μg)	Wt of bead (mg)	Pt	Ag	Pt/Ag	%Pt	Pt recovered (μg)	Average
400.2	10.92	1939	5446	0.3560	3.596	392.7	
"	10.99	1874	4905	0.3821	3.859	424.1	
"	10.93	1818	4636	0.3921	3.961	432.9	
"	11.00	1879	5045	0.3724	3.762	413.8	
"	10.84	1841	5330	0.3454	3.489	378.2	408.3±27.9 μg (102.0±7.0%)

± Values quoted at the 95% confidence level.

Table XVI: Homogeneity of silver-platinum beads.

Sample: 50.2 μgPt.

Side A			Side B		
Pt	Ag	Pt/Ag	Pt	Ag	Pt/Ag
255	5749	0.0444	263	5752	0.0457
268	5679	0.0472	257	6018	0.0427
269	5879	0.0458	281	6062	0.0464
269	6036	0.0446	260	6016	0.0432
268	6141	0.0436	272	6010	0.0453

Average ratio Side A: 0.0451±0.0017

Side B: 0.0447±0.0020

Sample: 480.3 μgPt

Side A			Side B		
Pt	Ag	Pt/Ag	Pt	Ag	Pt/Ag
1944	4703	0.4134	1896	4647	0.4080
2044	5226	0.3911	1964	4907	0.4002
2127	5068	0.4197	1954	5044	0.3874
2070	5087	0.4069	1955	5089	0.3842
2142	5049	0.4242	1967	4970	0.3958

Average ratio Side A: 0.4111±0.0160

Side B: 0.3951±0.0119

Side A: Top side of bead.

Side B: Side in contact with cupel.

Inter-element effects.

It is necessary to determine the influence of iridium, gold, rhodium and palladium on the platinum / silver intensity ratio, since these metals are present with platinum in most platinum bearing ores. Figure VII compares the positions of $L\alpha$ and $L\beta$ peaks obtained by individually counting evaporated platinum and gold solutions and iridium powder. Different amounts of each metal and different count times were used. Platinum, gold and iridium have similar excitation efficiencies and hence equal amounts of each metal would be expected to give peaks of equal intensity. If this was the case, analysis would be impossible since the L peaks of each metal would be unresolved. However, analysis of platinum in present ores should be possible because of the large excess of platinum compared to iridium and gold. To test this hypothesis, silver beads containing 100 μg platinum, 50 μg palladium, 10 μg rhodium, 10 μg gold, and 2 μg iridium were prepared by salting lead boats and cupelling as described previously. These numbers represent maximum values of each metal in the platinum ores analysed. The beads were counted in the usual manner and compared with standard 100 μg platinum beads. These results are shown in Table XVII. Comparison of absorption coefficients (A) indicate no interference from the other noble metals.

Iridium and rhodium are not fully soluble in molten silver, and hence are not uniformly distributed throughout the beads, but appear as black specks on the surface. Both sides of the beads containing these metals were counted, to determine if this had any effect on the

Figure VII. Comparison of $L\alpha$ and $L\beta$ peak positions for gold, platinum and iridium.

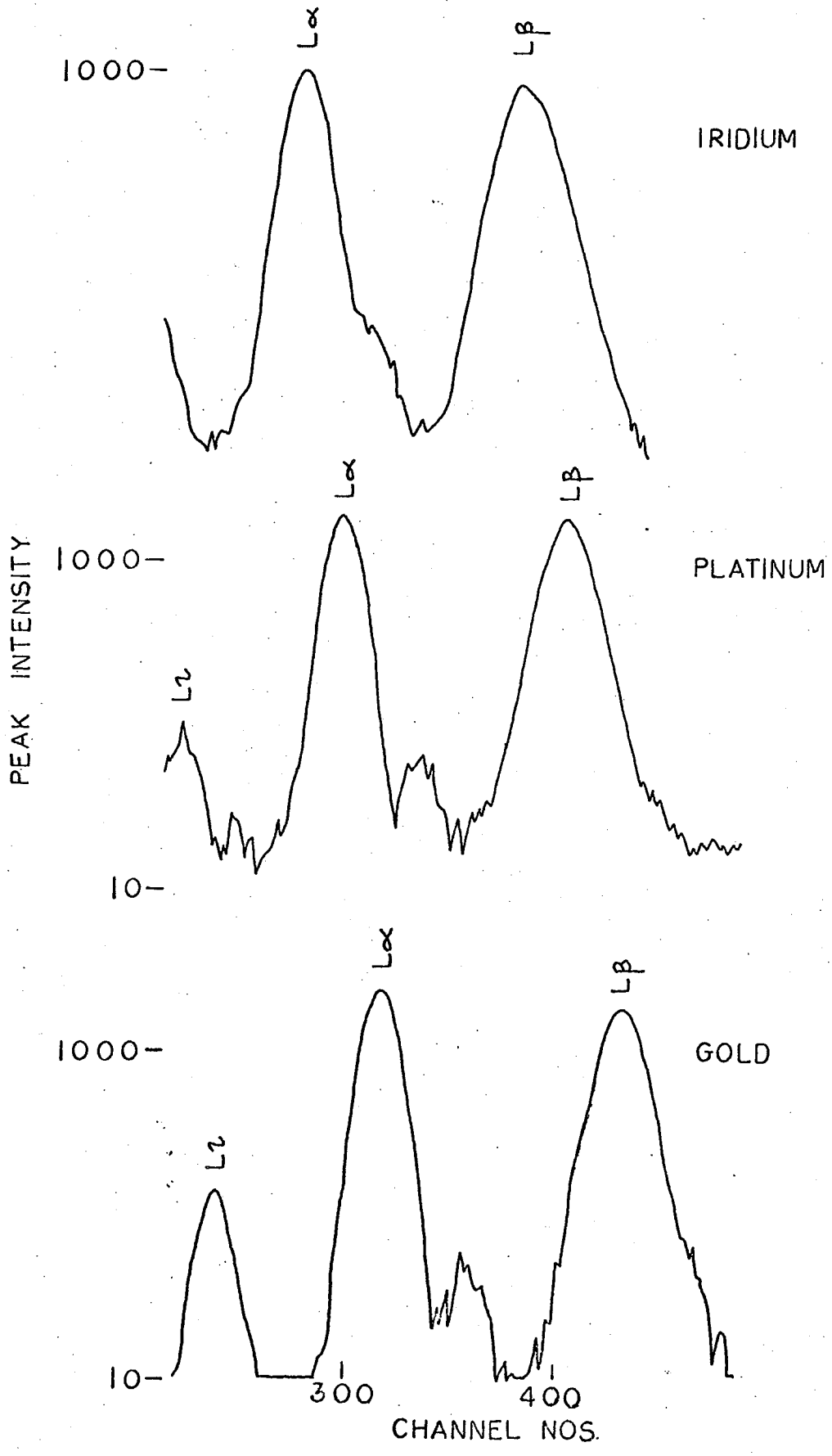

1000-
Lα
Lβ
IRIDIUM
1000-
Lα
Lβ
PLATINUM
Lγ
PEAK INTENSITY
10-
1000-
Lα
Lβ
GOLD
Lγ
10-
300
400
CHANNEL NOS.

Table XVII: Comparison of standard 100μg platinum beads with beads containing noble metal mixtures. (100μg Pt, 50μg Pd, 10μg Au, 10μg Rh and 2μg Ir).

Standard 100μg Pt beads					Beads containing noble metal mixtures				
	Net Peak Height Intensities Counts / 8 min.					Net Peak Height Intensities Counts / 8 min.			
% Pt	Pt	Ag	Pt/Ag	A	% Pt	Pt	Ag	Pt/Ag	A
0.886	944	10933 *	0.0863	0.0974	0.875	465	5439	0.0855	0.0977
0.939	476	5578	0.0853	0.0908	0.919	438(462)	5200(5100)	0.0874(0.0906)	0.0951(0.0986)
0.905	488	5194	0.0940	0.1039	0.892	452(459)	5010(5204)	0.0902(0.0882)	0.1011(0.0989)

* Counting time 16 minutes.

A= Intensity ratios divided by platinum concentration.

platinum / silver ratio. Results appear in parentheses in Table XVII.

Similarly, it was shown that palladium and rhodium Kα lines do not interfere with the AgKα line. This was expected because of the vast difference in the amounts of the elements present.

Thus, it has been demonstrated that by taking PtLα and AgKα peak heights, interference from the other noble metals is insignificant.

Analysis of ores.

Ores were sampled and fire assayed with flux A as described in previous sections. The float concentrate and ore USBM 31 were roasted for one hour at 700°C before fire assaying. Cupellation beads were prepared, flattened and counted in the usual way. The results of the ore analysis are shown in Table XVIII. The weights taken of the ores designated S4 and USBM 31 were such that a minimum of 40 μg platinum was determined. 1-2 g of the float concentrate was taken.

Conclusion.

X-ray fluorescence has been shown to be quantitative for platinum in the range studied. Acceptable results were obtained for ore S4 and the float concentrate. However, high results were obtained for ore USBM 31, as compared to previous analyses. Bead homogeneity was tested by counting the opposite side of each bead. The result of this analysis was 6.36 ± 0.60 ppm. This would seem to indicate homogeneity.

Table XVIII: Determination of platinum in ores by combined fire assay-x-ray fluorescence.

Ore designation:	Concentration of platinum (ppm).		
	S4	Float Concentrate	USBM 31
	5.45	90.8	5.19
	4.54	92.0	8.26
	6.02	80.3*	6.88
	6.32	89.0	6.74
	4.97	90.6	6.08
	5.59	92.6	6.23
	4.29		7.04
			6.01
Averages:	5.31±0.69	91.0±1.7	6.55±0.75

± - Values quoted at the 95% confidence level.

* Value rejected on statistical grounds.

Beads were also examined for lead. Lead peaks appear to the short wavelength side of platinum, and hence may excite the platinum peaks causing enhancement of the platinum - silver ratio. No evidence of lead was found. Also from experience with beads containing lead, more is usually present on the surface attached to the cupel, and so enhancement should be much higher on one side of the bead than on the other. This is not the case. Thus no satisfactory explanation can be given for the high results.

FLAMELESS ATOMIC ABSORPTION.

Introduction.

The theory and practice of atomic absorption is well established (53). When light of a characteristic frequency is passed through an atomic vapour containing neutral atoms in the ground state, energy is absorbed, provided the atoms resonate at the characteristic frequency. Atoms are excited to a higher energy level, but quickly return to the ground state, re-emitting energy at the same frequency. Neutral atoms are usually produced by nebulizing aqueous or organic solutions into a flame. Flames, however, suffer from several disadvantages. Nebulization efficiency is only approximately 15% for aqueous solutions, and atomization efficiency in the flame is extremely low. It is also difficult to maintain exact control over the chemical environment experienced by an analyte in the flame. A review by Kirkbright (54) lists the advantages and disadvantages of using flames for analytical work.

Some of the disadvantages of using flames may be removed by using non-flame cells. The chemical environment of a non-flame cell can be controlled by the use of an inert gas. Also the density of the atomic cloud is expected to be greater in the non-flame cell, since samples are not diluted by gases, burner design and rate of passage through the flame.

Non-flame devices for atom production include graphite furnaces, silica rods, graphite and tantalum filaments, cathode-sputtering

cells, d.c. arcs, r.f. and microwave plasmas and lasers. A comprehensive list of these flameless devices is given by Kirkbright (54). The most popular devices used today appear to be carbon rods and carbon tubes. These devices can attain temperatures as high as 3000°C in a matter of seconds. Heating may be done in cycles. During the drying cycle, the temperature is raised to the boiling point of the solvent. The dried sample is then ashed during the charring cycle. This removes any volatile components such as organics or low boiling inorganic substances. The sample is then atomized and the absorbance read at the wavelength of the analyte being measured. Thus selective volatilization is possible, considerably reducing chemical interferences in many cases. As a result, matrix effects are different from those in a flame. Only substances with boiling points equal to or in excess of the analyte are likely to cause interference. Other substances may be removed as described above.

L'vov (55,56) was the first to use a flameless device for analytical studies. Samples, both solutions and solids, were placed on a carbon electrode. The carbon electrode was then fitted into an electrically heated graphite tube and surrounded by argon gas. The graphite tube was lined with tantalum foil or pyrographite to prevent too rapid a diffusion of atomic vapour into the walls of the tube. In this way, absolute sensitivities were measured for some 37 elements, including noble metals.

Janouskova et al (57) studied the effect of some base metals and noble metals on 80 ng platinum in a 0.05 N hydrochloric acid medium, using the HGA-70 graphite furnace. Only ruthenium in a 5 fold excess

and strontium in a 50 fold excess were found to interfere. Various inorganic acids were tested and only 0.5N nitric acid found to interfere. The study was extended to the determination of platinum in reforming catalysts. Good agreement with a conventional flame method was reported.

Adriaessens and Knoop (58) studied optimum conditions for the flameless atomic absorption spectrometry of iridium, platinum and rhodium. Mutual interferences for binary systems in ratios up to 100:1 were not detected. Nitric acid was shown to have a more pronounced effect on platinum and rhodium absorbances than hydrochloric acid. Nitrogen and argon were compared as inert gases, and reduced sensitivity was obtained with nitrogen. It was also found that neither rhodium nor iridium gave signals at the platinum wavelength.

Rubeska and Stupar (59) used silica and ceramic absorption tubes for the determination of the noble metals. The tubes were either heated by a flame or placed in a furnace and heated electrically. Silver was found to cause serious interferences on noble metal absorbances, due to light scattering by silver-salt particles. This interference was eliminated by heating the tube in the electric furnace. It was stated that "direct determination of the noble metals after enrichment by cupellation is thus made possible by simply dissolving the silver beads in nitric acid." However, no results were produced to support this statement.

Pearton and Mallet (60) studied mutual interferences of the noble metals on a graphite tube in 4 per cent nitric acid, and

concluded that interferences are much more severe than those found in flames. Platinum absorbance was depressed by ruthenium (1Ru:1Pt ratio), rhodium (20Rh:1Pt) and iridium (30Ir:1Pt). Similar results were found in 4 per cent hydrochloric acid. Uranium, vanadium, lanthanum, copper and cadmium were tested as releasing agents to overcome these mutual interferences. Cadmium was considered the most effective.

Guerin (61) also studied the application of carbon rods for the determination of the noble metals. Mutual interference were found to be severe in some cases. Both rhodium and ruthenium depress the platinum absorbance by 10 per cent in a 100 fold excess. Copper reduced the depression due to rhodium but no other releasing effects were found. Only copper and nickel salts were tested as releasing agents. Uranium and vanadium caused depression of some individual noble metals when in a 1,000 fold excess, and so could not be tested as releasing agents. This is in marked contrast to flame techniques. Lead in a 1,000 fold excess did not interfere with the platinum absorbance.

As demonstrated above much work has been done on noble metals by flameless atomic absorption. However, most of the work has been concerned with studies of optimum conditions and interferences from various metals and inorganic acids. Very few practical applications have been reported.

Bratzel et al (62) determined gold and silver in geological and metallurgical samples in the parts per billion range using a

carbon rod atomizer. The gold and silver were leached from the samples by acids, and concentrated into organic phases by solvent extraction methods. This has the advantage of leaving potentially interfering species in the aqueous phase. The results showed good agreement with certified values obtained by a combination fire assay-flame atomic absorption procedure.

Having established the feasibility of using flameless atomization devices for the determination of noble metals, a procedure was developed for the determination of platinum in ores by a combined fire assay-flameless atomic absorption method.

Flameless atomic absorption of Platinum standards.

It was anticipated that ore samples would be the same as in previous flame atomic absorption work i.e. a 2 mg silver bead containing platinum dissolved in 0.5 ml concentrated nitric acid and made up to 10 ml with 50 per cent hydrochloric acid. The initial work was undertaken with this in mind.

Aqueous solutions of platinum were fired to determine the optimum concentration range. This was found to be 0.5-5.0 ppm for 50 µl injections. Slight curvature of the line was obtained at the higher concentrations. Instrumental conditions are shown in Table XIX.

Platinum solutions in 50 per cent hydrochloric acid were fired and found to be linear over the same range. However, peak heights had been depressed by approximately 50 per cent. These results were

Table XIX: Instrumental conditions and considerations for flameless atomic absorption.

Wavelength:	2659Å
Slit setting:	4
Lamp current:	28 mA
Drying time:	40 seconds
Charring " :	35 "
Atomization " :	15 "
Drying temperature:	100°C
Charring " :	1100°C
Atomisation " :	2600°C (10 volts)
Recorder fullscale:	1 Å
Recorder response:	1
Water flow:	3 litres/ minute
Argon flow:	3-5 arbitrary setting.
Sample volume:	50 µl
Chart speed:	51 mm/ minute

* Drying time and charring time were varied and the times listed are considered optimum.

Several graphite tubes were used in this work. They had all been used to some extent before platinum injections. Before each analysis, the tube was fired to maximum temperature for two to three seconds. Platinum solutions were then injected onto the tube. In all cases, consistent results were obtained immediately.

* Footnote

compared with the same solutions containing 2 mg silver per 10 ml of solution. Figure VIII shows the peak heights obtained from a 1 ppm platinum solution with and without silver. Silver depresses the platinum absorbance by three per cent. Increasing the silver concentration to 4 mg/ 10 ml indicated no further depression due to silver. Blanks containing only silver in 50 per cent hydrochloric acid were fired and no signal was obtained at the platinum wavelength.

Calibration curves for aqueous and 50 per cent hydrochloric acid solutions are shown in Figure IX. The lines for the 50 per cent acid solutions were drawn using the least squares method. At least four injections were used at each concentration. Peak heights were found to vary considerably from tube to tube, thus it was necessary to draw calibration curves for each analysis.

Acid effects on platinum absorbance.

The effects of the addition of sulfuric and phosphoric acids on the determination of platinum in hydrochloric acid were studied. In a similar study on silver, Mallet and Kellerman (63) found that the addition of these acids to nitric acid and hydrochloric acid solutions greatly improved precision for synthetic samples.

The addition of nitric acid to a silver bead containing platinum dissolves all the silver and some but not all of the platinum. This has been confirmed by this author in previous work on the fire assay of platinum. Thus, nitric acid was not used as a medium for platinum.

Figure VIII. Effect of silver on platinum determination by flameless atomic absorption:

A. 1 ppm platinum in 50% hydrochloric acid.

B. 1 ppm platinum + silver (2 mg/10 ml) in 50% hydrochloric acid.

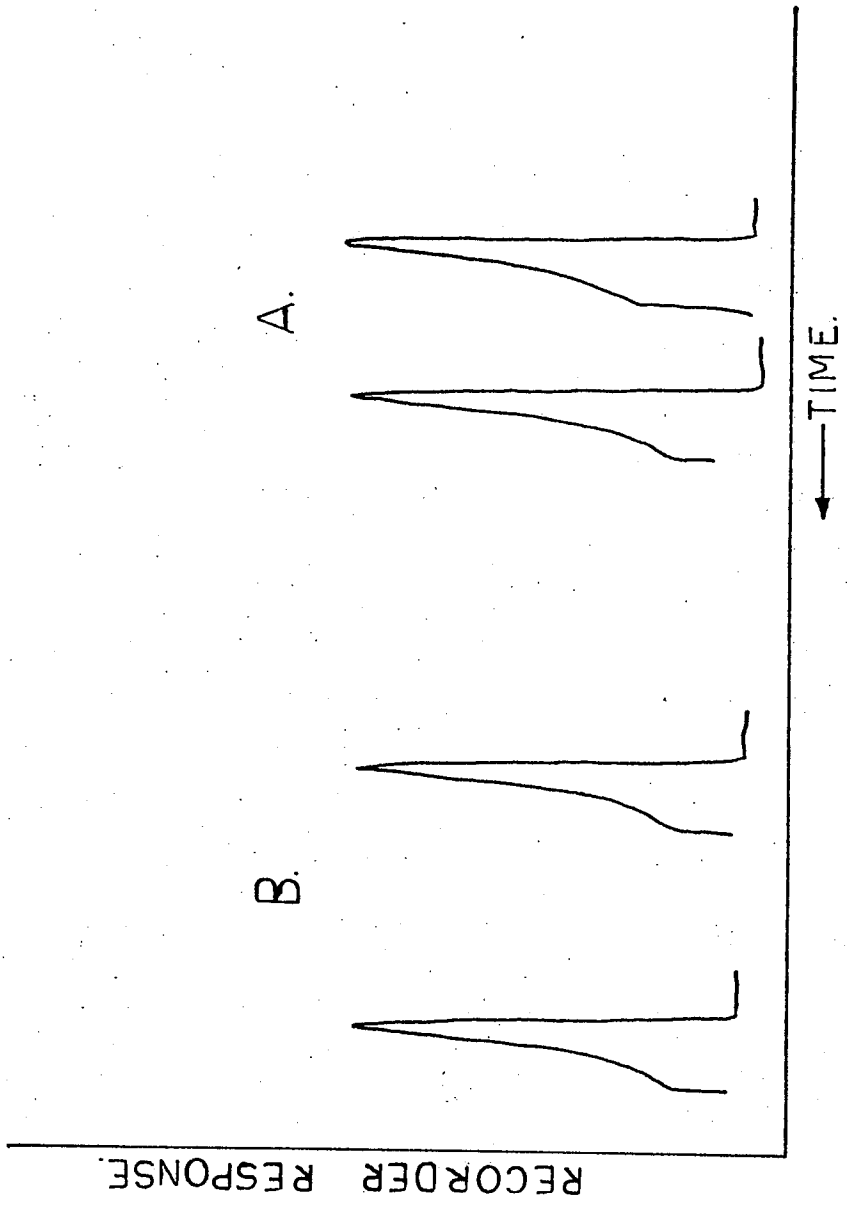
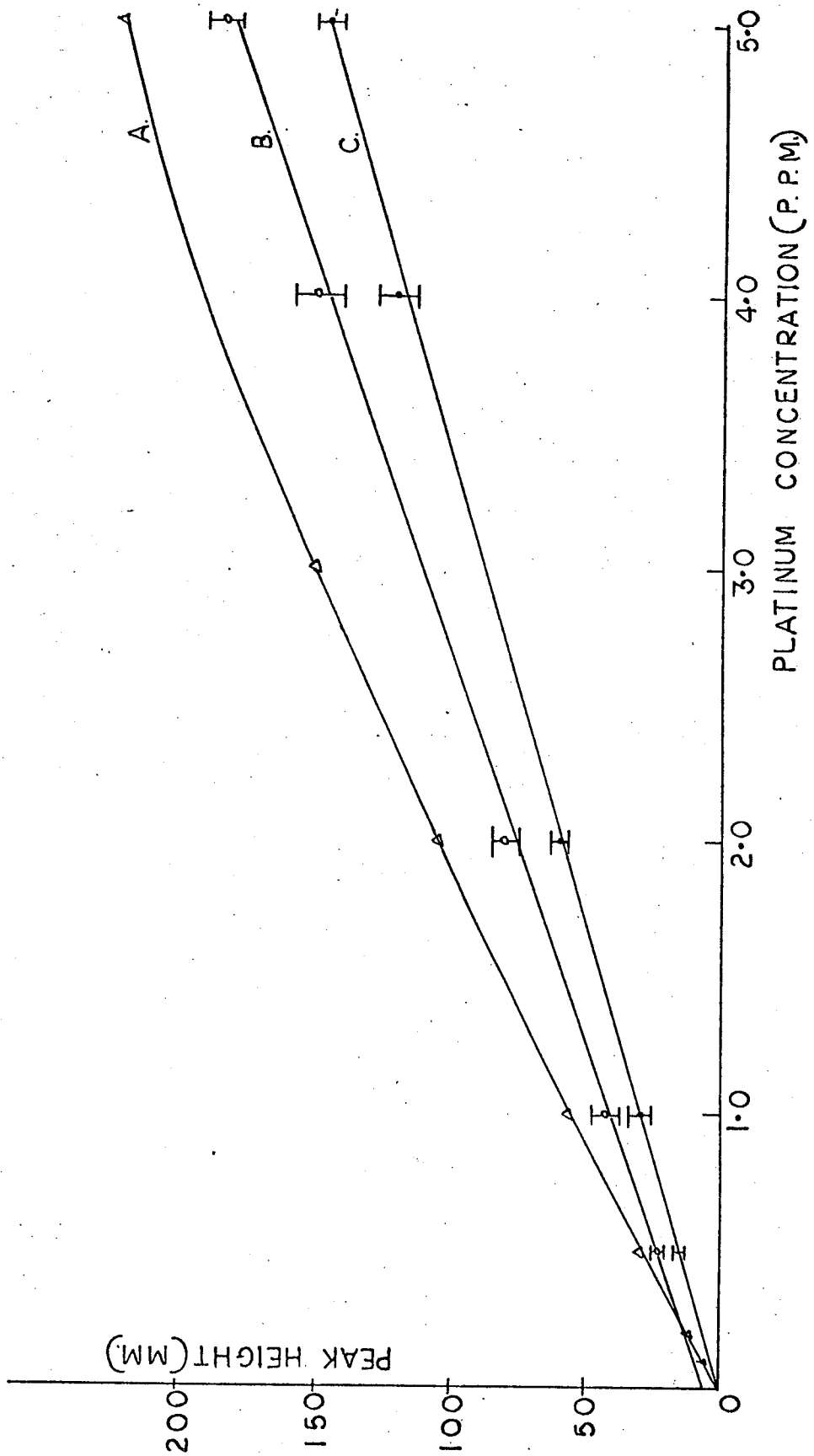

A.
B.
TIME.
RECORDER RESPONSE

Figure IX. Flameless atomic absorption calibration curve for aqueous and 50% hydrochloric acid solutions containing 0.5 - 5 ppm platinum.

A. H_2O - 5 m.v.

B. 50% HCl - 1% HNO_3 - 10 mg Ag/50 ml - 2 m.v.

C. 50% HCl - 1% HNO_3 - 10 mg Ag/50 ml - 5 m.v.


PEAK HEIGHT (MM.)
200
150
100
50
0
1·0
2·0
3·0
4·0
5·0
PLATINUM CONCENTRATION (P.P.M.)
A.
B.
C.

Sulfuric and phosphoric acids (10%v/v) were added to a 4 ppm platinum solution containing silver, nitric acid and hydrochloric acid as described previously. These solutions were fired and results shown in Table XX.

Each acid reduces both peak height and precision. This is especially marked in the case of sulfuric acid. Peak heights were initially consistent at 56 mm, but then became alternately short (~51mm) and then long (~68mm), accounting for the large coefficient of variation. Both acids emitted very dense fumes during volatilisation, and charring time had to be increased for phosphoric acid, to allow argon gas to clear the tube of these dense fumes.

As a consequence of these results, neither sulfuric nor phosphoric acids were added to platinum solutions.

Inter-element effects.

Mutual interferences between noble metals in flame and flameless atomic absorption have been well documented. Several explanations have been forwarded to account for these interferences using flameless devices, but none are as yet thoroughly satisfactory.

Pearton and Mallet (60) conclude that mechanical suppression is a possible reason for the depressant effects observed. Guerin (61) agreed with this conclusion. Aggett and West (64) account for the depression of gold by palladium as being due to vapour phase reactions. Enhancement effects according to Guerin (61) may be due to the

Table XX: Acid effects on platinum absorbance.

Acid medium	Peak Height *	Coefficient of variation (%).
50% HCl + 1% HNO_3	86.4	3.5
50% HCl + 1% HNO_3 + 10% H_3PO_4	81.6	3.6
50% HCl + 1% HNO_3 + 10% H_2SO_4	59.3	12.5

* Average of at least 11 measurements.

finer crystal size of the evaporated salt, although no relevant data has been found to confirm this.

All the interferences listed have been observed when the interferent is in a large excess, except for one example, that of ruthenium on platinum (1:1 ratio). However, in the platinum ores analysed, ruthenium is either absent or occurs to a much lesser extent than platinum. Also there is strong evidence to show that losses of ruthenium are high during the cupellation process (16), and thus the effect of this metal on platinum absorbance was not studied. For similar reasons, osmium was also not studied.

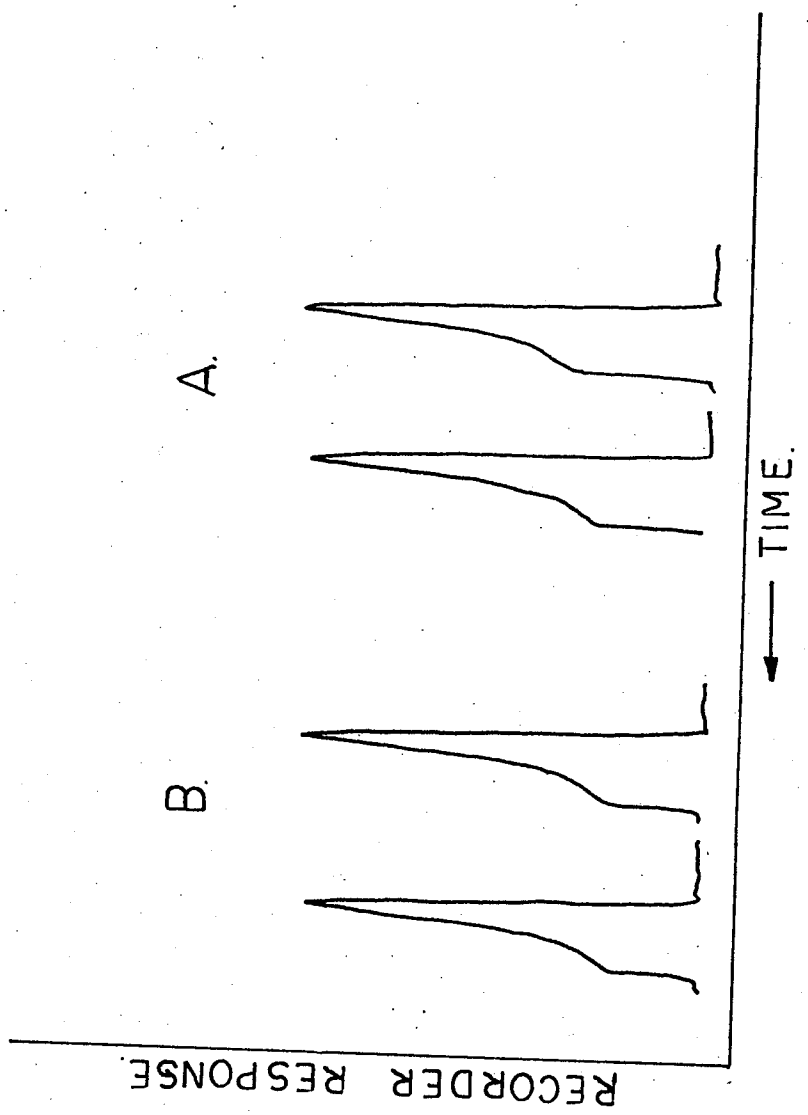
Solutions were prepared as described above containing 50 µg platinum, 25 µg palladium, 5 µg rhodium, 5 µg gold and 2 µg iridium. These solutions were fired in the usual way and results compared with a standard 50 µg platinum solution. Figure X shows this comparison. Peak heights are identical indicating no interference. Blanks containing the same concentrations of noble metals as above but not including platinum were fired. No signal was observed for platinum.

Base metal interference was not tested. The only base metal likely to be present in microgram quantities in a silver bead from cupellation is lead. Lead is more volatile than silver, and so it is expected that all the lead would be volatilized with silver during the charring cycle.

Figure X. Effect of noble metals on platinum determination by flameless atomic absorption:

A. Standard 50 μg platinum solution containing silver (2 mg/10 ml).

B. 50 μg platinum solution containing silver (2 mg/10 ml) + 25μg palladium, 5 μg gold, 5 μg rhodium and 2 μg iridium.


A.
B.
TIME.
RECORDER RESPONSE

Application to synthetic samples and ores.

The method was tested using synthetic samples prepared by salting lead boats and cupelling as described previously. In each case 2 mg of silver was used. Each bead was placed in a 10 ml volumetric flask and dissolved in 6 M hydrochloric acid in the usual manner. Samples and standards were then fired, such that two or three samples were fired between each standard. A standard graph was drawn using the least squares method, and used to calculate the recoveries of platinum shown in Table XXI.

The method was then extended to ores. Each ore was sampled as described in a previous section and the float concentrate and USBM 31 ore roasted at 700°C for one hour. The ores were fired assayed using flux A, after salting with 2 mg silver and the cupelled silver bead treated as above. In the case of the float concentrate, 20 mg silver beads were prepared. These beads were placed in 100 ml volumetric flasks and 5 ml concentrated nitric acid and 50 ml concentrated hydrochloric acid added. This was because 1-2 g of concentrate was sampled and a large dilution was necessary. The weights of the other ores taken were such that the concentration of platinum in the flasks were in the 1-4 ppm range. As for synthetic samples, ore samples and standards were fired such that two or three samples were fired between each standard. The ore samples were chosen at random for each firing. A calibration curve was again drawn using the least squares method. Ore analyses are shown in Table XXII.

Table XXI: Flameless atomic absorption of synthetic fire assay samples.

Platinum added (μg).	Platinum recovered (μg). [a]	Average recovery
10.0	9.7	
"	9.7	
"	10.2	
"	10.4	
"	10.7	10.1±0.5 μg(101.0±5.0%)
20.1	20.5	
"	21.7	
"	19.9	
"	19.7	20.5±1.3 μg(102.0±6.5%)
40.2	36.0	
"	38.2	
"	37.8	
"	39.0	
"	38.4	37.9±1.4 μg(94.3±3.5%)
50.2	44.0	
"	47.8	
"	46.1	
"	47.2	
"	48.0	46.6±2.0 μg(92.8±4.0%)

± Values quoted at the 95% confidence level.

(a) Average of at least 3 injections.

Table XXII: Determination of platinum in ores by combined fire assay-flameless atomic absorption.

Ore designation:	Concentration of platinum (ppm).(a)		
	S4	Float Concentrate	USBM 31
	5.43	77.0	4.56
	4.61 *	143.5*	4.25
	5.61	103.7*	5.04
	5.61	76.2	4.25
	5.50	68.2	4.88
	5.58	71.9	4.69
	5.46	78.4	4.28
	4.92	73.2	4.63
Averages:	5.44±0.22	74.2±4.0	4.57±0.28

* Values rejected on statistical grounds.

± Values quoted at the 95% confidence level.

(a) Average of at least 3 injections.

Conclusion.

Results obtained by flameless atomic absorption are in good agreement with previous analyses. Because interferences from noble metals were absent, and interference from silver only minimal no releasing agents were examined. This is in contrast to flame atomic absorption. Rhodium at the level tested caused serious depression of the platinum absorbance in an air-acetylene flame requiring the use of lanthanum as a releasing agent. The two extremely high results obtained for the float concentrate are perplexing, but could possibly be due to light scattering by silver salt particles.

WET EXTRACTION.

Introduction.

Wet extraction involves treatment of ores with reagents to obtain the noble metals in an aqueous medium. This has the advantage of converting the metals to forms which respond to separational techniques such as ion-exhange and chromatography. The usual wet extraction procedures are treatment with acids, or chlorination followed by an acid treatment. Ores should be ground as fine as possible to increase ease of extraction.

The industrial process for the dissolution of platinum involves treatment with aqua regia after concentration of the noble metals into a nickel matte (65). Gold is removed by reduction with ferrous sulfate followed by precipitation of platinum with ammonium chloride. The ammonium hexachloroplatinate formed is ignited to obtain the impure metal. Platinum is refined by dissolution and separation of base metals and iridium, rhodium and palladium as hydroxides by a bromate hydrolysis. Platinum is again precipitated with ammonium chloride, and the precipitate ignited at 1,000°C to obtain the pure metal.

In all wet extraction procedures, base metals accompany the noble metals into solution. Since noble metals are usually present in ores in trace quantities, the base metals to noble metals ratio is very large. Even in concentrates where the noble metal concentration has been upgraded, the ratio is still quite high. As it is extremely unlikely that accurate, precise results will be obtained by any method in the

presence of such an excess of base metals, because of interference effects, a separation of base metals prior to noble metal determination is essential. Methods for such a separation include liquid-liquid extraction, precipitation and ion-exchange.

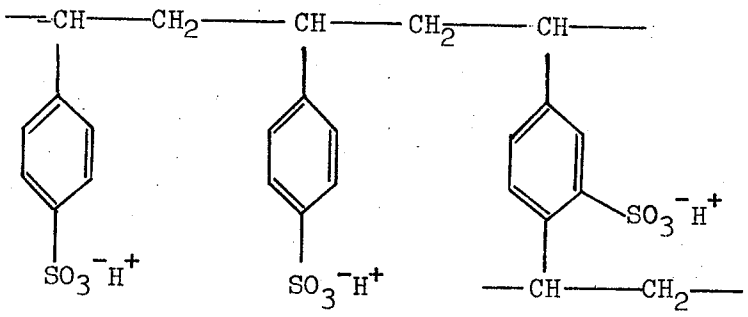
Having removed base metals, a solution is left containing the noble metals. Platinum may be determined in such a solution with or without separation of the other noble metals, depending on the ratios present. Methods of analysis without prior separation include emission spectroscopy, x-ray fluorescence and atomic absorption usually in the presence of releasing agents. However, on occasion, spectrophotometric or gravimetric methods of analysis are utilized, depending on the platinum concentration. Generally, these methods suffer from serious interferences from the other noble metals, and hence in these cases noble metal separation is a necessary pre-requisite to platinum determination. Separation techniques include precipitation, ion-exchange, chromatography and solvent extraction.

It was felt that ion-exchange removal of base metals, followed by chromatographic isolation of platinum would provide the most convenient and least time consuming methods of separation. All the methods mentioned above have been extensively reviewed by Beamish (66,67,68),

Ion-exchange removal of base metals.

Ion-exchange resins consist of a cross-linked polymer network containing ionized or ionizable groups. For exchange to take place at a reasonable speed the ion-exchanger must have an open structure which

is porous on the molecular scale. Most analytical work is done with ion-exchange resins based on polystyrene. Styrene is copolymerised with divinylbenzene to give spherical beads that are then treated chemically to introduce ionic groups. To make a strong acid cation exchanger, the polymer is sulfonated to give a structure as shown below:



Cross linking is expressed as the proportion of divinylbenzene in the monomer mix. Commonly a cross linking of 8 per cent is used for a sulfonic acid cation exchanger.

Typical reactions of a sulfonated cation exchanger are:

$$RzSO_3H + NaCl \rightleftharpoons RzSO_3Na + HCl$$

$$2RzSO_3Na + CaCl_2 \rightleftharpoons (RzSO_3)_2Ca + 2NaCl$$

Rz represents the non-mobile part of the ion exchange resin.

Strelow et al (69) measured distribution coefficients of base metals and noble metals in hydrochloric acid media on a strong acid ion-exchanger (Dowex 50W-X8). Distribution coefficients were very high for the base metals, whilst negligible adsorption was reported for platinum (IV). In a later study, Nelson et al (70) confirmed these findings,

reporting negligible adsorption for the noble metals in the range 0.2-9 M hydrochloric acid.

Separation is possible because base metals form cationic complexes, whereas the noble metals form stable anionic complexes.

Chromatographic isolation of platinum.

When discussing chromatographic or solvent extraction methods, mention should be made of the tri-n-butyl phosphate (TBP)/hydrochloric acid system, because of the ever increasing separations of the noble metals achieved in such a system. The positioning of the TBP and the method of contact with the hydrochloric acid phase determine whether the process is ion-exchange chromatography or solvent extraction. Distribution coefficients for the chlorocomplexes of platinum (II) and (IV), palladium (IV), iridium (IV) and gold (III) have been determined (71,72). Rhodium (III) and iridium (III) are not extracted into TBP.

Berg and Senn (72) believed two mechanisms were possible to explain the method of extraction. Using Pt(IV) as an example, these mechanisms may be outlined as follows:

(I) Extraction of an undissociated acid.

$$Pt^{4+} + 6Cl^{-} \rightleftharpoons PtCl_6^{2-}$$

$$PtCl_6^{2-} + 2H^{+} \rightleftharpoons H_2PtCl_6$$

$$H_2PtCl_{6(aq)} + n\ TBP_{(org)} \rightleftharpoons HPtCl_5 \cdot n\ TBP_{(org)} + HCl_{(aq)}.$$

(II) Extraction of a neutral complex.

$$Pt^{4+} + 4Cl^- \rightleftharpoons PtCl_4$$

$$PtCl_{4\,(aq)} + n\ TBP_{(org)} \rightleftharpoons PtCl_4 \cdot n\ TBP_{(org)}$$

Mechanism (I) was preferred because of the high stability of $PtCl_6^{2-}$ compared to $PtCl_4$, and because variations of distribution coefficients with hydrochloric acid concentration reflected more of a dependence than mechanism (II) indicated.

Bark et al (73) proposed a different mechanism, whereby TBP solvated protons ion-associated with chloride ions undergo ion exchange with the metal chlorocomplex.

$$TBP_{(org)} + HCl_{(aq)} \rightleftharpoons (TBPH^+Cl^-)_{(org)}$$

$$(n\ TBPH^+Cl^-)_{(org)} + PtCl_6^{2-} \rightleftharpoons PtCl_6^{2-}(TBPH^+)n_{(org)} + nCl^-_{(aq)}$$

Evidence for both schemes outlined above appear in the literature. Kulkarni and Sathe (74) reported extracted species of $HPtCl_5$ 3TBP in 4 M hydrochloric acid and $HPtCl_5 \cdot 2TBP$ in 6 M hydrochloric acid. Tuck (75) extracted gold (III) from 2 M hydrochloric acid as $HAuCl_4 \cdot 3$ TBP. Akaza et al (76) assumed the main extracted species to be $H(H_2O)_n\ TBP_6{}^+HPtCl_6{}^-$ in 3-4 M hydrochloric acid. However, this assumption appears to have been influenced by familiarity with the work of Bark et al.

It is known that very strong acids such as perchloric, sulfuric and hydrochloric are extracted mainly as $[H(H_2O)_4^+]$ [A (TBP-solvated)$^-$] ion pairs, whilst in moderate concentrations of acid the unionised form TBP . HA is extracted (77). Thus the mechanism proposed by Berg and Senn would appear to predominate at low concentrations of hydrochloric acid, and that proposed by Bark et al would predominate at high concentrations (> 7 M).

Using the TBP/hydrochloric acid system, separations of noble metals have been achieved by partition chromatography (78,79), reversed-phase partition chromatography (71,73,76), and solvent extraction (80).

In the solvent extraction procedure, platinum and palladium as iodide complexes (probably PtI_4^{2-} and PdI_4^{2-}) are separated from rhodium and iridium in a highly acidic medium. Under these conditions rhodium and iridium are not extracted, iridium (IV) possibly being reduced to iridium (III) by the iodide ion. The iodocomplexes of platinum and palladium are presumably extracted in an identical manner to the chlorocomplexes.

Proposed method of analysis.

After study of the literature it was decided to analyse the float concentrate and the ores by the methods briefly outlined below:

The float concentrate would be treated by acids, gold removed on a Porasil C column coated with TBP, followed by removal of base metals on a cation exchanger with subsequent determination of platinum by atomic

absorption in the presence of lanthanum.

Ores S4 and USBM 31 would be treated in an identical manner to the float concentrate, except that after passage through the cation exchanger, platinum would be isolated from the other noble metals on a TBP coated cellulose column and determined spectrophotometrically by tin (II) chloride.

Acid extraction was chosen in preference to chlorination, since the latter technique requires the use of furnaces, tubes and collection vessels, very inconvenient when a large number of samples is to be analysed. Acid extraction requires only beakers for ore digestion and less supervision would probably be required. Two methods of acid extraction were utilized.

A. Treatment of ores with three 25 ml portions of hydrofluoric acid, followed by three 25 ml portions of aqua regia, followed by three 25 ml portions of hydrochloric acid.

B. The above method but without any hydrofluoric acid treatments.

The removal of gold in the methods outlined above requires explanation. Pohlandt and Steele (79) in their study on the separation of the noble metals using a TBP coated cellulose column, showed that gold could be eluted along with platinum. This was probably due to reduction of gold on the column. Attempts to improve matters by the use of oxidising agents failed. Since gold (III) interferes with the tin (II) chloride determination of platinum (2) it must be removed prior to such determination. This is most conveniently done in 0.1 M hydrochloric acid on a TBP coated Porasil C column. It has been shown

that up to 20 mg of gold can be removed by 1 g of such material in the presence of base metals and noble metals (81).

Gold under certain conditions also exhibits erratic behaviour on cation exchange columns (82). It was felt by this author that such behaviour could affect the recovery of platinum and hence gold was removed prior to passage through the cation exchanger. This hypothesis is purely speculative and no results are produced to support it.

As will be described the chromatographic separation of platinum was not quantitative in the range studied and so an alternative method of separation was utilized.

The alternate method was the solvent extraction separation as described by Faye and Inman (80). This method was used without modification i.e. the separation of rhodium and iridium was included. Rhodium and iridium by themselves are not soluble in aqua regia, but there is ample evidence to show that, in the presence of the other noble metals, they are extracted (83,84).

It has been shown that gold (III) is extracted in TBP. Thus it is expected that gold would be carried through the procedure with platinum. Hence a prior separation of gold is also required using this method.

Evaluation of the method for analysis of float concentrate.

The procedure used for the determination of the float concentrate was evaluated using synthetic solutions containing both noble metals and base metals as their chlorocomplexes. A typical solution contained 2 g iron(III), 0.5 g copper(II), 0.5 g nickel(II), 240 μg platinum, 120 μg palladium, 80 μg gold, 40 μg rhodium and 40 μg iridium. Platinum was varied from 120 - 2,000 μg and the amounts of the other metals were increased or decreased in the same ratio as platinum. Base metal amounts were kept constant for all solutions.

Each synthetic solution prepared was diluted to 50 ml with 0.1 M hydrochloric acid and passed through the Porasil C column at the maximum rate of the column. The solution was collected in a 400 ml beaker, diluted to 300 ml with 0.1 M hydrochloric acid and passed through the cation exchange column at the rate of one drop per second. The exchanger was washed free of noble metals with 150-200 ml 0.1 M hydrochloric acid. The colourless eluate was collected in a 600 ml beaker and evaporated to dryness on a steam bath, after the addition of 25 ml concentrated hydrochloric acid.

After evaporation 2 ml concentrated hydrochloric acid, 15 ml perchloric acid and 5 ml concentrated nitric acid were added to the beaker.* The beaker was covered with a watch glass and the mixture gently boiled on a hot plate for approximately 15 minutes. This serves to destroy organic matter carried over from the cation exchanger, and also to remove ruthenium and osmium, if present, as tetroxides. After boiling the watch

* Mention should be made of the hazard present when working with hot concentrated perchloric acid. Evaporation of perchloric acid should be done in a stainless steel fume hood having provision for periodic flushing with water, or with a fume eradicator over the vessel (described in G.F. Smith Chemical Co. catalog).

glass was removed and the mixture slowly evaporated to dryness. Salts were then boiled with concentrated hydrochloric acid to convert the noble metals to their respective chlorocomplexes. The solution was evaporated to dryness, and the treatment with concentrated hydrochloric acid repeated twice more. Salts were finally dissolved in water, transferred to a 25 ml volumetric flask containing 5 ml lanthanum solution and analysed by atomic absorption. Samples were compared with standards prepared by adding the same amount of lanthanum to known concentrations of platinum diluted from a stock solution. Samples and standards were run in sequence, by aspirating a lower platinum standard first, followed by two samples and then a higher platinum standard. Blanks were run at each concentration of platinum determined. However, no platinum was detected in these blanks. Results are recorded in Table XXIII.

Analysis of float concentrate.

The above procedure was applied to the float concentrate. The concentrate was sampled in the usual way by making 1" squares and taking small portions from each square. Sample weights were varied from 3-7 g. Some samples were placed in Nalgene beakers and treated by method A, and some were placed in glass beakers and treated by method B. Samples were stirred at frequent intervals, whilst evaporating to dryness on a steam bath. After the last evaporation step, 25 ml of concentrated hydrochloric acid was added to each residue followed by an equal volume of water, and the solutions filtered through Whatman No. 42 paper into 200 ml

Table XXIII: Evaluation of wet procedure for the float concentrate.

Platinum added. (µg)	Platinum recovered. (µg)	Average recovery
120.5	116.8	
"	124.3	
"	123.0	
"	123.0	
"	112.5	
"	122.5	
"	116.3	
"	116.5	
"	124.0	119.9±3.3 µg(99.5±2.7%)
241.0	247.5	
"	243.2	
"	255.5	
"	234.3	
"	238.6	243.8±10.2 µg(101.2±4.2%)
482.0	479.0	
"	467.5	
"	479.0	
"	443.3 *	
"	470.5	
"	479.3	475.1±7.0 µg(98.6±1.5%)

Table XXIII (Cont'd).

Platinum added (μg).	Platinum recovered. (μg)	Average recovery
723.0	708.5	
"	711.4	
"	699.8	
"	711.4	
"	723.0	710.8±10.3 μg(98.3±1.4%)
1,004.0	992.0	
"	966.9	
"	980.9	
"	1,004.0	
"	975.9	983.9±17.9 μg(98.0±1.8%)
2,008.0	2,004.0	
"	2,038.2	
"	2,020.0	
"	2,004.0	
"	2,020.0	2,017.2±17.6 μg(100.5±0.9%)

* Values rejected on statistical grounds.

± Values quoted at the 95% confidence level.

beakers. Each residue was washed well with hot 1 M hydrochloric acid, and saved for fire assaying. Solutions were evaporated to dryness on a steam bath, and then dissolved in 50 ml 0.1 M hydrochloric acid and subjected to the same treatment as described for synthetic solutions. Prior to passage through the Porasil C column, each solution was filtered through Whatman No. 42 paper, since it was invariably found that traces of residue came through the first filtration. These residues were combined with previous residues for fire assaying. During evaporation of the eluates from the cation exchange column, a white precipitate settled out at low volume in each beaker. These precipitates were filtered off, dried, mixed thoroughly and prepared in pellet form in a boric acid matrix and examined by x-ray fluorescence. Silicon was the only element found to be present.

Salts, after conversion to chlorocomplexes with concentrated hydrochloric acid, were dissolved in water and filtered through Whatman 541 paper into 25 ml volumetric flasks containing lanthanum, and analysed by atomic absorption. Filtration removes all but traces of dissolved silica.

Results of these analyses shown in Table XXIV are low when compared with previous analyses. Residues were fire assayed with flux A, taking into account the silica content of the residues and the carbon content of the filter papers. The 2 mg silver beads obtained were analysed by atomic absorption as described by the method of Van Loon (30). These results are also shown in Table XXIV.

To determine if sulfur in the matrix was the cause of incomplete attack by acids, several concentrate samples were weighed into porcelain

Table XXIV: Determination of platinum in float concentrate by methods A and B before roasting.

A. AQUA REGIA

Acid extraction (ppm Pt).	Acid extraction & fire assay (ppm Pt).
67.8	79.1
64.1	75.8
63.1	75.9
67.8	79.8
66.4	77.2
lost	lost

B. HF

Acid extraction (ppm Pt).	Acid extraction & fire assay (ppm Pt).
62.2	lost
66.8	86.1
61.2	84.9
59.6	86.4
63.3	83.6
59.6	78.5

dishes and roasted in a furnace at 700°C for one hour. These samples were treated with acids as described under methods A and B, and put through the complete analytical procedure, as in outlined in Figure XI. Results of these analyses are shown in Table XXV. Residues were again fire assayed, and platinum determined by atomic absorption. No platinum was found in residues from hydrofluoric acid treatments, but small amounts were found in the residues from the aqua regia treatment. Consequently method A was the method chosen for future wet extractions. Several more samples of float concentrate were analysed and a complete statement of results is given in Table XXVIII.

Chromatographic isolation of platinum.

A solution containing 200 µg platinum and 100 µg palladium as their chlorocomplexes was evaporated to dryness, great care being taken not to overheat the residue formed. The residue was dissolved in 2 ml 5N hydrochloric acid, and with a plunger in position resting on top of the column bed, this solution was transferred to the cellulose column. The beaker was washed once with 1 ml of 5N hydrochloric acid and washing continued with small amounts of 1:1 TBP/toluene mixture. The plunger was slowly removed and the solution allowed to enter the cellulose column. Elution was carried out with the TBP/toluene mixture at a rate of 2 ml per minute. Effective separation of platinum and palladium was achieved. Platinum was completely eluted between 30-65 ml and palladium between 90-150 ml. Tin (II) chloride was used to test aliquots being eluted from the column.

Figure XI. Schematic diagram of wet procedure for analysis of float concentrate.

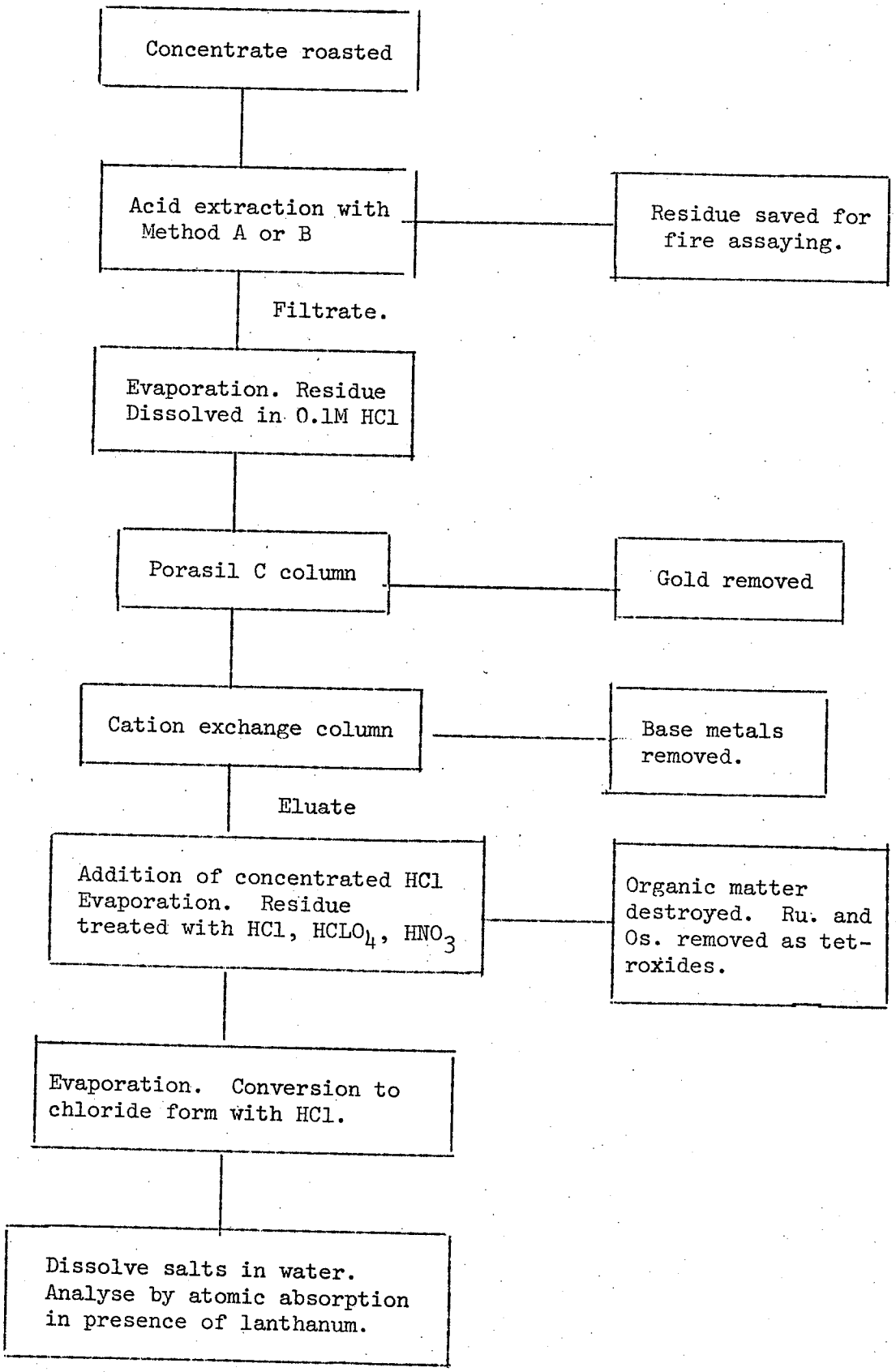

Concentrate roasted
Acid extraction with Method A or B
Residue saved for fire assaying.
Filtrate.
Evaporation. Residue Dissolved in 0.1M HCl
Porasil C column
Gold removed
Cation exchange column
Base metals removed.
Eluate
Addition of concentrated HCl Evaporation. Residue treated with HCl, $HCLO_4$, HNO_3
Organic matter destroyed. Ru. and Os. removed as tetroxides.
Evaporation. Conversion to chloride form with HCl.
Dissolve salts in water. Analyse by atomic absorption in presence of lanthanum.

Table XXV: Determination of platinum in float concentrate by methods A and B after roasting.

HF (ppm Pt).	AQUA REGIA (ppm Pt).	AQUA REGIA + FIRE ASSAY (ppm Pt).
80.1	80.2	82.4
82.3	73.5	76.4
82.4	74.3	77.3
84.6	71.7	74.4
81.9	77.3	80.4

Solutions containing 200 µg platinum, 100 µg palladium, 20 µg rhodium and 20 µg iridium were evaporated to dryness, dissolved in 2 ml 5N hydrochloric acid and added to the cellulose column as described above. The first 30 ml of organic eluate was discarded and the next 35 ml collected in a 50 ml graduated clinder. The contents of the graduated cylinder were transferred to a 125 ml separatory funnel and platinum extracted by shaking with 50 ml water for 30 seconds. The water was then run off through Whatman 541 paper into a 200 ml beaker. Extraction was repeated twice more with 50 ml aliquots of water, and the aqueous extracts combined. The combined extracts were then evaporated to dryness in the presence of a few millilitres of concentrated hydrochloric acid. The residue was dissolved in water, transferred to a 25 ml volumetric flask containing 2.5 ml concentrated hydrochloric acid and 5 ml tin (II) chloride, and platinum determined spectrophotometrically using 1 cm cells. Recovery for platinum at this level was 95 per cent.

A second solution was passed down the same column and while good separation was still achieved, recovery was lower. It was observed that the flow rate of the column had decreased to 1ml per minute. Passage of a solution through the column a third time produced similar results. Recovery of platinum was again lowered and the flow rate had decreased to 0.5 ml per minute.

The above studies were repeated using solutions containing 20 µg platinum, 10 µg palladium, 2 µg rhodium and 2 µg iridium. The best recovery obtained for platinum at this level was 85 per cent.

Column parameters such as length, flow rate, strength of acid and amount of TBP used were changed in an attempt to improve on recovery but with no success. Consequently, chromatographic studies were terminated at this point in favor of solvent extraction.

Recovery of platinum at the 200 μg level agrees well with that obtained by Pohlandt and Steele (71) using a Porasil C column coated with TBP. However, it appears that no work has been done at lower levels of platinum and so comparisons with this work cannot be made. Pohlandt et al (79) report "double-band" formation for platinum on prolonged heating, after evaporation to dryness. Presumably the double bands are due to Pt (II) and Pt(IV). As already stated, great care was exercised in the evaporation step, beakers being removed from the steam bath just at the moment of dryness or a few moments earlier. Nevertheless, at such low concentrations of platinum, reduction of Pt(IV) to Pt(II) may be possible. In their procedure, Pohlandt et al (79) recommended adding sodium sulfite, primarily to precipitate gold. It was shown that an excess of sodium sulfite did not have undesirable effects and actually increased resolution for platinum and palladium. In another study, Pohlandt and Steele (71) demonstrated different distribution coefficients for Pt (II) and Pt (IV) in a TBP/HCl system using Kel-F powder for batch extractions. In elution studies with a TBP coated Porasil C column, 90 per cent of the platinum was eluted as Pt (II) and 10 per cent as Pt (IV) under oxidising conditions, in 5 N hydrochloric acid solution. Under these conditions, complete separation of platinum and iridium could not be achieved. However, under reducing

conditions in the presence of an excess of sodium sulfite, complete separation was possible, platinum being eluted as Pt (II).

A solution containing 200 μg platinum was evaporated to dryness and the residue dissolved in 2 ml of 5 N hydrochloric acid. Ten milligrams of sodium sulfite was added, and the solution added to the cellulose column as described above. The eluate was tested with tin (II) chloride and as before platinum was eluted between 30 - 65 ml. This procedure was repeated for solutions containing 20 μg platinum, 10 μg palladium, 2 μg rhodium and 2 μg iridium. The eluate portion containing platinum was treated as described above and platinum was determined spectrophotometrically with tin (II) chloride using 4 cm cells. Of four solutions tested recovery varied from 67 - 140 per cent. Thus, results obtained were far more erratic in the presence of sodium sulfite than in its absence, and formation of "double-bands" does not appear to be responsible for low recovery of platinum at the 20 μg level.

Analysis of ores.

As before the method used for analysis of ores was evaluated using synthetic solutions containing base metals and noble metals. Initially, however, the solvent extraction procedure was evaluated using a solution containing only platinum, palladium, rhodium and iridium. Platinum was varied from 20 - 120 μg and the ratios of the other noble metals were the same as described for the float concentrate.

I. Evaluation of solvent extraction procedure.

A sample solution containing the noble metals as their chlorocomplexes was evaporated to dryness on a steam bath. Salts were dissolved in 10 ml of 6 M hydrochloric acid and transferred to a 60 ml separatory funnel with an additional 10 ml of acid. The solution was shaken with 5 ml of an aqueous 4 per cent (w/v) solution of sodium iodide and the mixture allowed to stand for at least 10 minutes. Platinum and palladium iodocomplexes were extracted with two 15 ml portions of the TBP/hexane solution, and the extracts combined and saved for further treatment. The aqueous layer was washed with 10 ml hexane to remove organic traces, and the hexane portion added to the TBP/hexane extracts. The aqueous layer containing rhodium and iridium was discarded.

The combined TBP/hexane extracts were shaken with three separate 10 ml portions of concentrated nitric acid for 30 seconds each. Nitric acid extracts were placed in a separatory funnel, diluted with an equal volume of water, and washed with 10 ml hexane to remove as much TBP as possible. The nitric acid solution was run off into a 200 ml beaker and evaporated to dryness on a steam bath, after the addition of 1 ml of a 5 per cent solution of sodium chloride. Platinum and palladium were converted to their chlorocomplexes by repeated evaporation with 2 - 3 ml of concentrated hydrochloric acid. Two millilitres of buffer solution and 10 ml of water were added to the beaker, and the solution warmed to dissolve the salts. After cooling to room temperature, 1 ml of a 0.5 per cent alcoholic solution of p-nitrosodimethylaniline was

added, and the solution transferred to a 60 ml separatory funnel with a minimum quantity of water. The red palladium-p-nitrosodimethylaniline complex was extracted with two 15 ml portions of chloroform. The aqueous layer containing platinum was filtered through a Whatman 541 paper into a 200 ml beaker. Approximately 2 ml concentrated sulfuric acid and 5 ml perchloric acid were added and the solution evaporated to fumes of sulfur trioxide. The solution was cooled and 5 ml concentrated hydrochloric acid very carefully added. Platinum was converted to the chlorocomplex by boiling, and boiling continued until 2-3 ml of solution were left in the beaker. The solution was quickly cooled by immersion of the beaker in cold water, and added to a 25 ml volumetric flask containing 5 ml tin (II) chloride. Platinum was determined spectrophotometrically using 4 cm cells. Results are recorded in Table XXVI.

II. Evaluation of Porasil C, cation exchanger and solvent-extraction.

Solutions were prepared containing 2 g iron, 0.5 g copper, 0.5 g nickel and the noble metals including gold in the ratios already quoted. These solutions were passed through the Porasil C and cation exchange columns and after treatment to remove organics, the remaining noble metals were converted to their chlorocomplexes by repeated evaporations with concentrated hydrochloric acid. Platinum was then isolated by the solvent extraction procedure described above and determined spectrophotometrically with tin (II) chloride. Results are shown in Table XXVII.

Table XXVI: Evaluation of the solvent extraction procedure.

Platinum added (μg).	Platinum recovered (μg)	Average recovery
20.1	19.8	
"	20.6	
"	20.4	
"	20.3	
"	18.7 *	
"	20.4	
"	19.3	20.1±0.5 μg(100.0±2.5%)
40.2	41.4	
"	40.2	
"	39.4	
"	36.7	
"	35.9	
"	35.9	38.3±2.5 μg(95.3±6.2%)
100.5	101.3	
"	102.1	101.7±5.1 μg(101.2±5.1%)
201.0	192.5	
"	197.4	
"	203.0	197.6±13.1 μg(98.3±6.5%)

* Value rejected on statistical grounds.

± Values quoted at the 95% confidence level.

Table XXVII: Evaluation of Porasil C, cation exchange and solvent extraction procedure.

Platinum added (μg)	Platinum recovered (μg)	Average recovery
20.1	19.4	
"	21.2	
"	22.4 *	
"	19.2	
"	19.2	
"	20.1	19.8±1.1 μg (98.5±5.5%)
40.2	43.0	
"	40.7	
"	41.9	
"	34.0 *	
"	38.2	
"	39.7	40.7±2.3 μg (101.2±5.7%)
100.5	97.3	
"	98.8	
"	93.1 *	
"	98.0	
"	101.0	
"	100.9	99.2±2.1 μg (98.7±2.1%)
201.0	204.4	
"	201.6	
"	205.4	
"	202.8	
"	188.9 *	
"	208.2	204.5±3.2 μg (101.7±1.6%)

* Values rejected on statistical grounds.

± Values quoted at the 95% confidence level.

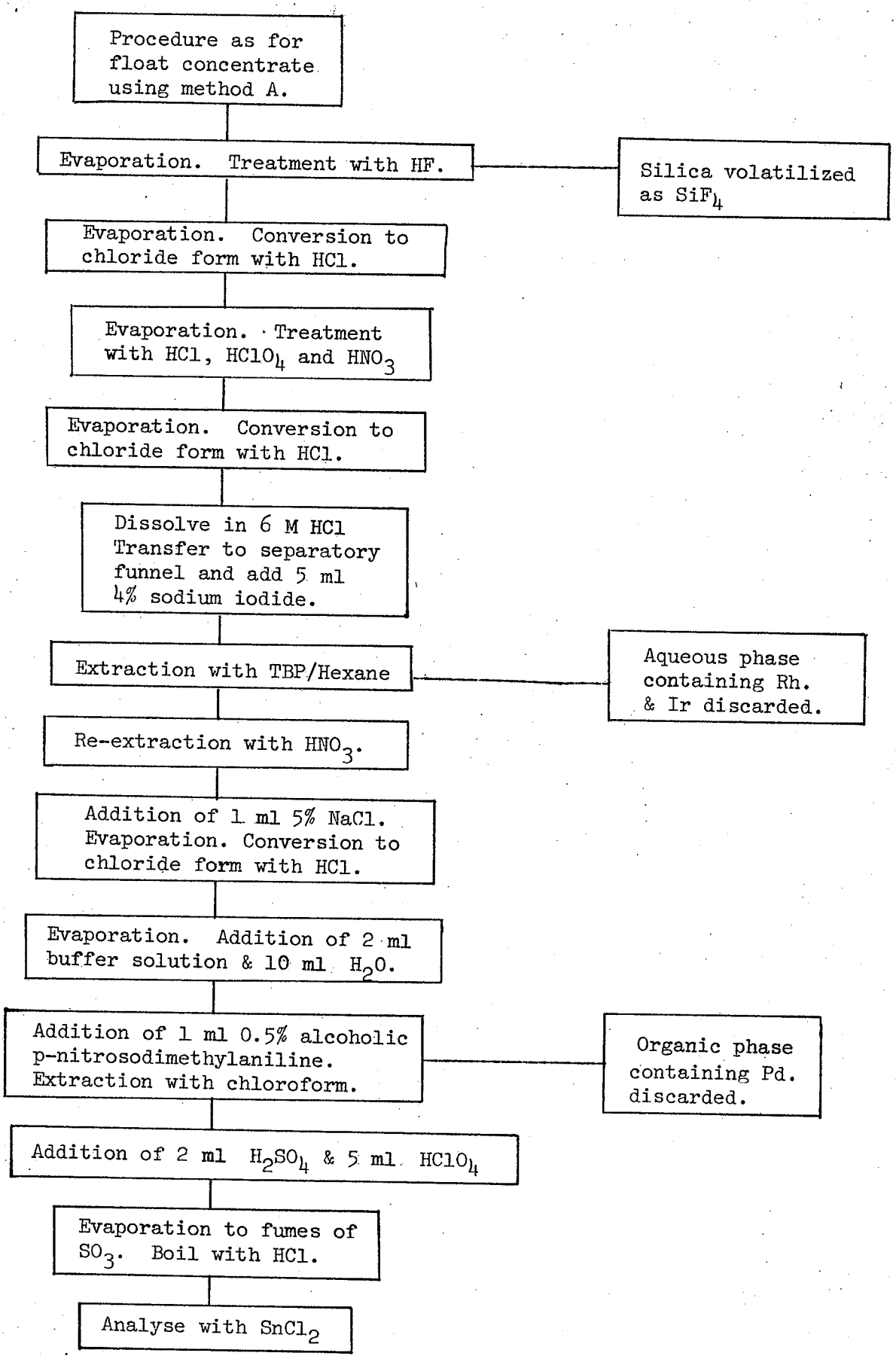
III. Analysis of ores S4 and USBM 31.

Initial results for these ores were low and therefore all samples to be analysed were roasted at 700°C for one hour before acid extraction. Ore samples weighing between 5-10 g were treated using method A. The full analytical procedure is given in schematic form in Figure XII. The solutions were treated in an identical manner to that already described for synthetic solutions. Ore residues were saved for fire assaying.

On evaporation of the solutions after passage through the cation exchange column, a white precipitate settled out at low volume - 50-100 ml in each beaker, and the solutions became very green in colour. This was especially pronounced in the case of the USBM 31 samples. The precipitates were filtered off and identified as silica by x-ray fluorescence. Repeated filtrations of aqueous solutions failed to remove all the silica, and so an additional evaporation step with 3-4 ml of hydrofluoric acid was included in the analytical scheme.

The green solid obtained on evaporation to dryness was identified as containing chromium by diphenyl carbazide and confirmation was obtained by atomic absorption. Also, on boiling with perchloric acid, the solutions turned red, and a red solid precipitated out on cooling. This is further evidence of chromium (65). Chromium (III) is oxidised to chromium (VI) which is precipitated in cold perchloric acid. On evaporation of the perchloric acid and addition of concentrated hydrochloric acid, chromium (VI) is reduced to chromium (III)

Figure XII. Schematic diagram of wet procedure for analysis of ores S4 and USBM 31.


Procedure as for float concentrate using method A.
Evaporation. Treatment with HF.
Silica volatilized as SiF_4
Evaporation. Conversion to chloride form with HCl.
Evaporation. Treatment with HCl, $HClO_4$ and HNO_3
Evaporation. Conversion to chloride form with HCl.
Dissolve in 6 M HCl Transfer to separatory funnel and add 5 ml 4% sodium iodide.
Extraction with TBP/Hexane
Aqueous phase containing Rh. & Ir discarded.
Re-extraction with HNO_3.
Addition of 1 ml 5% NaCl. Evaporation. Conversion to chloride form with HCl.
Evaporation. Addition of 2 ml buffer solution & 10 ml H_2O.
Addition of 1 ml 0.5% alcoholic p-nitrosodimethylaniline. Extraction with chloroform.
Organic phase containing Pd. discarded.
Addition of 2 ml H_2SO_4 & 5 ml $HClO_4$
Evaporation to fumes of SO_3. Boil with HCl.
Analyse with $SnCl_2$

and a green colour is once again obtained. Repeated passes of 0.1 M hydrochloric acid solutions through the cation exchange column failed to remove any of this green colour. However, the presence of chromium in the +3 oxidation state was not considered detrimental, since it is known that chromium in this state is not extracted into TBP (85), and so is not likely to cause any interference in the determination of platinum. Hence solutions were analysed for platinum without any further attempts at removal of chromium, and results are shown in Table XXVIII. Results were initially low for USBM 31 samples and ore residues were fire assayed. The silver beads obtained were dissolved in aqua regia, and the solutions evaporated to dryness. Residues were treated several times with concentrated hydrochloric acid and finally dissolved in 0.1 M hydrochloric acid. This precipitates silver and lead if present. The precipitates were filtered off and the solutions then analysed for platinum by the scheme outlined in Figure XII except that the small cation exchange column was used. No platinum was found for S4 but considerable platinum was recovered for USBM 31.

Two USBM 31 ore samples were boiled with perchloric acid for three hours, prior to treatment with method A. It was thought that platinum may be trapped in a chromium matrix, resulting in low recoveries. Perchloric acid is frequently used for dissolution of chromium ores (65). However, low results were obtained and ore residues still had to be fire assayed for complete recovery.

To determine if platinum was quantitatively extracted into the TBP/hexane phase in the presence of chromium, the aqueous filtrates

from several extractions were combined and subjected to fire assay using flux A. The solutions obtained after dissolution of silver beads were passed through the small cation exchange column and put through the solvent extraction procedure. No platinum was found.

Analyses of USBM 31 ore were obtained independently of the solvent extraction procedure by atomic absorption of solutions after passage through the cation exchanger. Chromium is known to cause interference in the atomic absorption determination of platinum, when present in a ratio of 50:1 (Cr:Pt), even in the presence of releasing agents (33). Thus, it was deemed necessary to try and remove as much of the chromium as possible before analysis. This was achieved by addding concentrated hydrochloric acid in 2-3 ml aliquots, to hot solutions of perchloric acid, and volatilising chromium as chromyl chloride (86). This was repeated several times until no more chromyl chloride was evolved in the addition of hydrochloric acid. It was assumed that platinum was not volatile under such conditions. Noble metals were converted to their chlorocomplexes by repeated evaporations with concentrated hydrochloric acid, dissolved in water and transferred to 10 ml volumetric flasks containing 2 ml lanthanum solution. Ore residues were fire assayed and analysed for platinum by the scheme outlined in Figure XII. Twice as much ore as was normally taken was used for this analysis. Recoveries by acid extraction were still low, and results quoted in Table XXVIII also include fire assay of the residues.

Table XXVIII: Determination of platinum in ores by wet extraction.

Ore designation:	Concentration of platinum (ppm). S4	Float concentrate	USBM 31
	5.09	80.1	5.78[a]
	5.19	82.3	5.92
	4.51 *	82.4	4.20
	5.15	84.6*	5.40
	5.37	81.9	5.30
	5.11	80.2	5.14
	5.30	81.8	3.92
		81.2	4.90[b]
		79.8	4.28
		79.1	4.21
		80.2	5.35
Average:	5.20 ± 0.12	80.9 ± 0.8	4.95 ± 0.46

a) Spectrophotometric analysis.

b) Atomic absorption analysis.

± Values quoted at the 95% confidence level.
* Values rejected on statistical grounds.

Conclusion.

Wet extraction provides an independent method for evaluating fire assay procedure, and is especially useful when fire assay values are in doubt. While this method is time consuming, it requires less knowledge of ore composition than is needed for fire assay. However, it is sometimes necessary to fire assay residues for the highest accuracy. The above work has demonstrated the importance of roasting ores containing sulfur prior to acid extraction. The higher values obtained by method A are interpreted as hydrofluoric acid being able to penetrate the sulfur lattice which may still be present after roasting. Chromium which is eluted from the cation exchange column with the noble metals has been shown not to interfere in the solvent extraction procedure.

Summary.

Fire assay and wet extraction methods were evaluated for both milligram and microgram quantities of platinum. Recoveries were found to be quantitative for both methods. The main loss of platinum in the fire assay process was found to be to the crucible walls. Cupellation losses were shown to be negligible.

Results obtained in the analysis of each ore and the precision obtained by each method are shown in Table XXIX. These results are compared with values obtained independently as described in Table VI. Good agreement is demonstrated for each ore when compared with previous analyses except for x-ray fluorescence of the float concentrate and USBM 31 and flameless atomic absorption of the float concentrate.

The Student "t" test was used to determine if there was any difference in the averages obtained by the different procedures for each ore. Results obtained for ore S4 are not statistically different at the 95 per cent confidence level, although this is only barely so for flameless atomic absorption and wet extraction. For the float concentrate and ore USBM 31, flame atomic absorption and emission spectrographic results are the same at the 95 per cent confidence level and these results are the same as the wet extraction results at the 99 per cent confidence level. Results by x-ray fluorescence and flameless atomic absorption for the float concentrate and USBM 31 are respectively high and low, although the flameless atomic

Table XXIX: A comparison of the accuracy and precision found in each method for the determination of platinum in ores.

Ore designation	S4				Float Concentrate				USBM 31			
Method of analysis	Average (ppm)	σ	No. of Values	C.V. %	Average (ppm)	σ	No. of Values	C.V. %	Average (ppm)	σ	No. of Values	C.V. %
Fire assay & Flame Atomic Absorption	5.26	0.20	10	3.8	79.5	0.9	10	1.2	5.52	0.31	8	5.6
Fire assay & Emission Spectroscopy	5.43	0.49	8	9.0	77.1	5.0	7	6.5	4.98	0.73	7	14.6
Fire assay & X-ray Fluorescence	5.31	0.69	7	13.0	91.0	1.7	5	1.9	6.55	0.75	8	11.5
Fire assay & Flameless Atomic Absorption	5.44	0.22	7	4.0	74.2	4.0	6	5.4	4.57	0.28	8	6.1
Wet Extraction	5.20	0.12	6	2.3	80.9	0.8	10	1.0	4.95	0.46	11	9.3
Independent Analysis.	5.23				82.6				4.9		8	

σ = standard deviation at the 95% confidence level.

C.V.= Coefficient of variation.

absorption result for USBM 31 shows no statistical difference from the results obtained by emission spectroscopy and wet extraction at the 95 per cent confidence level. The reason for these high and low values is not readily apparent especially in light of the excellent agreement obtained by both methods in the analysis of ore S4.

Several generalizations may be made as regards the precision obtained by each technique. Emission spectroscopy and x-ray fluorescence generally yield the lowest precision. This is due in part to the difficulty in preparing standards whose platinum content is known to a high degree of accuracy. Precision for ores S4 and USBM 31 - of which approximately equal amounts were taken - is fairly constant except for analysis by wet extraction and spectrophotometry. The large difference may be attributed to the nature of the ores. Recovery of platinum was complete for ore S4 by wet extraction, but ore USBM 31 required fire assay of the residue after acid extraction to effect complete recovery. Flameless atomic absorption shows very comparable precision to flame atomic absorption for ores S4 and USBM 31. The most precise method was wet extraction followed by spectrophotometric analysis of ore S4. However, wet extraction procedures are very time consuming and certainly no advantage was gained in accuracy over fire assay. If platinum is present in large enough concentration then fire assay followed by flame atomic absorption is the preferred method of analysis. It may be fortuitous that ores chosen for this study were amenable to fire assay, whereas in theory, dissolution of any ore should be accomplished by wet procedures. The results indi-

cate however, that when ores are known to be amenable to fire assay, this method may be used on a routine basis. Wet extraction need only be used as a check or when fire assay values are in doubt.

The precision obtained in this work by flame atomic absorption, emission spectroscopy and spectrophotometry compares favorably with that obtained in the previous analyses of USBM 31 (Table VI). It can be seen that although emission spectroscopy can be as precise as the other two methods, precision tends to be more variable, and the figure obtained for precision in this work is approximately equal to an average value of the four results from Table VI.

For low values of platinum, flameless atomic absorption and emission spectroscopy have been shown to offer feasible alternatives to spectrophotometric determination, when highest accuracy and precision are not required. Emission spectroscopy may be made more precise by using smaller bead weights, resulting in smaller dilutions and more platinum being applied to the electrode for the same sample volume. X-ray fluorescence offers the advantage that samples are not destroyed and potentially variable photographic processes are eliminated. Precision may be increased by longer counting times or by using a crystal spectrometer and obtaining higher count rates in a shorter time. Sensitivity may also be increased by the use of higher energy x-ray tubes.

To the author's knowledge this is the first time evaluation of flameless atomic absorption, emission spectrographic and x-ray fluorescence techniques has been compared for analysis of platinum in ores. Using these methods, palladium, gold, rhodium and iridium in the ratios tested have been found not to interfere with the determination of platinum.

Appendix A.

Least squares method.

Application of the least squares method to the collected data gave the following equation for the line:

$$y = 0.0990(\pm 0.0013)x + 0.0000.$$

Thus, it is seen that the line passes through the origin. This is to be expected since a blank correction has already been applied. Because of this the equation of the line was simply taken as:

$$y = 0.0990(\pm 0.0013)x.$$

Because errors in counting statistics are larger at the 0.2% Pt level than at the 4% level, a weighted regression was also used to calculate the equation of the line. The weighted form was taken as a reciprocal of the variance of the number of counts. This yielded the same equation as above.

The standard deviation of the line Sy was calculated as:

$$Sy = \left[\frac{\sum (y-y')^2}{n-1} \right]^{\frac{1}{2}}$$

where y = measured value

y' = calculated value

n = number of samples

Thus Sy = 0.00755.

Appendix B.

"t" test for significance.

To determine if there is a significant difference between the average ratios of sides A and B of the beads tested, the following equations were used:

$$t = \frac{\bar{X}_A - \bar{X}_B}{S\bar{x}} \qquad \text{----------(1)}$$

$$S\bar{x} = s\left[\frac{N_A + N_B}{N_A N_B}\right]^{\frac{1}{2}} \qquad \text{----------(2)}$$

$$s = \left[\frac{\sum(X_A - \bar{X}_A)^2 + \sum(X_B - \bar{X}_B)^2}{N_A + N_B - 2}\right]^{\frac{1}{2}} \qquad \text{------(3)}$$

where $\bar{X}_A$ = Average ratio of side A.

$\bar{X}_B$ = Average ratio of side B.

$S\bar{x}$ = Estimated standard deviation of the difference between means.

s = Standard deviation of a single determination in the two groups.

$N_A + N_B$ = Number of counts = 5.

$(X-\bar{X})^2$ = Represents the sum of the squares of the deviation in each group.

The experimental "t" found is compared with the values of "t" tabulated for given probabilities at specified degrees of freedom. If the experimental value is less than the tabulated value, then there is no difference statistically.

Experimental values of "t" for 50.2 μg and 480.3 μg platinum samples are 0.52 and 0.82, respectively at the 95 per cent confidence level. The tabulated value of "t" for both samples is 2.31. This indicates homogeneity for both beads.

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