

THE DETERMINATION OF PLATINUM IN ORES.

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The Determination of Platinum in Ores

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	Aperture
44	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  $\text{SnCl}_2$  and 3 M in HCl.

Lanthanum chloride solution - 6.45 g  $\text{La}_2\text{O}_3$  (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  $2.2 \pm 0.2$ . 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  $75^{\circ}\text{C}$ .



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.

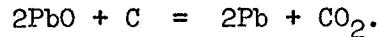
Classically lead has been used as the collector in fire assay procedures. However, the claim has been made that lead is not a particularly suitable collector, at least not for some of the more "insoluble" platinum metals such as iridium and osmium. These new collectors such as tin (9), copper (10), iron-nickel-copper (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.

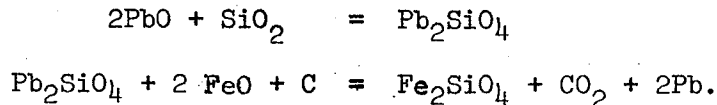
Materials commonly used for fluxing include litharge ( $\text{PbO}$ ), silica ( $\text{SiO}_2$ ), borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ), soda ( $\text{Na}_2\text{CO}_3$ ) and flour. The proportions of each material used will depend on the nature of the ore and the individual preference of the assayer. 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):

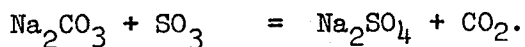
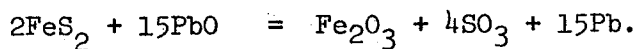


The lead droplets thus formed are homogeneously mixed with the charge, and a lead-platinum alloy formed by liquid-liquid extraction. Carbon dioxide is evolved and provides some measure of mixing between flux components, thereby increasing ease of extraction. As the temperature is raised, lead slowly 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.

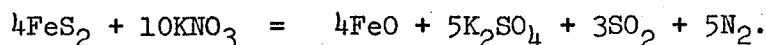
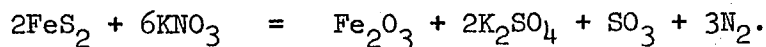
Lead may also be formed by litharge reacting with other components of the ore. In silicate ores, for example, the reaction may proceed with the initial formation of lead silicate, followed by reaction of the lead silicate with bases in the presence of a reducing agent:



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



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:



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.