

## Precious metals

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### **Abstract**

Platinum group elements (PGM's) are discussed and the problem involved with their accurate determination considered. Analysis is the central theme but other related aspects such as geology, concentration processes and uses are covered. The assay/analytical laboratory is required to measure concentrations from ppb to 99.99% of elements in ores, concentrates, plant intermediates and finished products for any and every impurity. Because of the high intrinsic cost of the metal, the highest accuracy and precision are demanded.

### **1. INTRODUCTION**

The agenda for my presentation is as follows:

- (a) Occurrence/Geology
- (b) Treatment Routes
- (c) Analytical Procedures
- (d) Analytical Instrumentation
- (e) Quality Assurance
- (f) Uses

The theme of the presentation is the analysis of the PGMs in the various materials associated with their concentration and refining. I will highlight the difficulties which the analyst must overcome which are due to:

- (i) The very wide analyte concentration range from ppb to >99,99%.
- (ii) The close similarity of the chemistry of the PGMs.
- (iii) The very large number of associated base metal elements which are 'carried along' in the recovery processes to a greater or lesser degree. These must then be analysed on their own account or create difficulties in the analyses of the PGMs.
- (iv) The intrinsic value of the PGMs requires very high levels of precision and accuracy and, therefore, the use of sophisticated quality assurance procedures.
- (v) Certain individuals are allergic to the soluble salts of platinum. Although rarely a major problem, except in platinum refineries, the potential hazard cannot be disregarded: preventive measures should be encouraged.

## 2. OCCURRENCE/GEOLOGY

The major sources of the PGMs are in the Republic of South Africa, Canada and the C.I.S. They are all primary deposits, usually associated with ultrabasic rock formations, and often with copper and nickel sulphide deposits. The South African sources, which constitute at least 80% of known world reserves, are in the Bushveld Igneous Complex (BIC) of the Transvaal. The PGMs are concentrated in reefs, such as the Merensky, UG-2 and Platreef. They occur as native grains or in mineral species such as sperrylite ( $\text{PtAs}_2$ ), cooperite  $\text{Pt(AsS)}_2$ , bragite ( $\text{Pt,Pd,NiS}$ ), stibiopalladanite ( $\text{Pd}_3\text{Sb}$ ), laurite ( $\text{Ru,OsS}_2$ ) and osmiridium ( $\text{Os,Ir}$ ).

Other elements of commercial value are copper, nickel and cobalt. But the mineralogical complexity of the reefs are such that up to 25 additional elements are analysed for on a routine basis.

The geographical locations of mining operations on the BIC are shown in Figure 1.

## 3. TREATMENT ROUTES

A typical treatment route for PGMs is as follows:

### FEED → CONCENTRATE → MATTE → REFINERY FEED → FINISHED METALS

The PGMs are either present in the ores as sulphides or they are closely associated with base metal sulphides within a silicate matrix. The initial stage of the recovery of these metals is a metallurgical flotation recovery process for sulphide minerals. In this process, the ore from the mining operation is ground to a fine powder and, in the form of a pulp, is contacted with various chemical reagents. The pulp is pumped to agitated tanks, into the bottom of which large volumes of air are introduced. The chemical reagents induce the sulphide minerals to 'float' on the resulting air bubbles to the top of the tank where they overflow. The unwanted silicate gangue minerals sink to the bottom of the tanks where they can be separately removed. This process produces a concentrate of the minerals of interest which has a PGM content one or two orders of magnitude higher than the ore. There are, however, still major quantities of silicate minerals within the concentrate.

The sulphides are separated from the silicates by smelting the concentrate in electric furnaces at temperatures in excess of  $1200^\circ\text{C}$ . When the concentrate is molten, the high density of the sulphides allows them to sink to the bottom of the furnace, while the silicates form a separate upper layer. The two layers are then removed from the furnace through separate tapping holes at appropriate heights from the furnace floor.

The PGMs are now contained in what is known as a matte, which in the South African situation is essentially a copper nickel sulphide containing low levels of iron and cobalt and, still, minor amounts of the PGMs.

The matte is further treated in a refinery, where firstly the base metals are removed and separated in hydrometallurgical processes and a PGM concentrate is produced. This PGM concentrate, which contains significant concentrations of base metals, is dissolved in an oxidising acid. The PGMs are then separated from each other and the remaining base metals by hydrometallurgical processes to produce finished metals with purities normally in excess of 99,9%.

The matrices requiring analyses are therefore: silicate, matte, PGM concentrates, liquors, residues and pure metals. The concentrations go from the ppb level to greater than 99,9%. The problems, therefore range from analysing the PGMs as trace constituents in base metal matrices, to analysing base metals as trace constituents in pure PGMs.

The intrinsic value of the PGMs is such that the analyses are routinely reported to two decimal places even in the low ppb range. The analyst has developed the methods and the skills to achieve this level of accuracy.

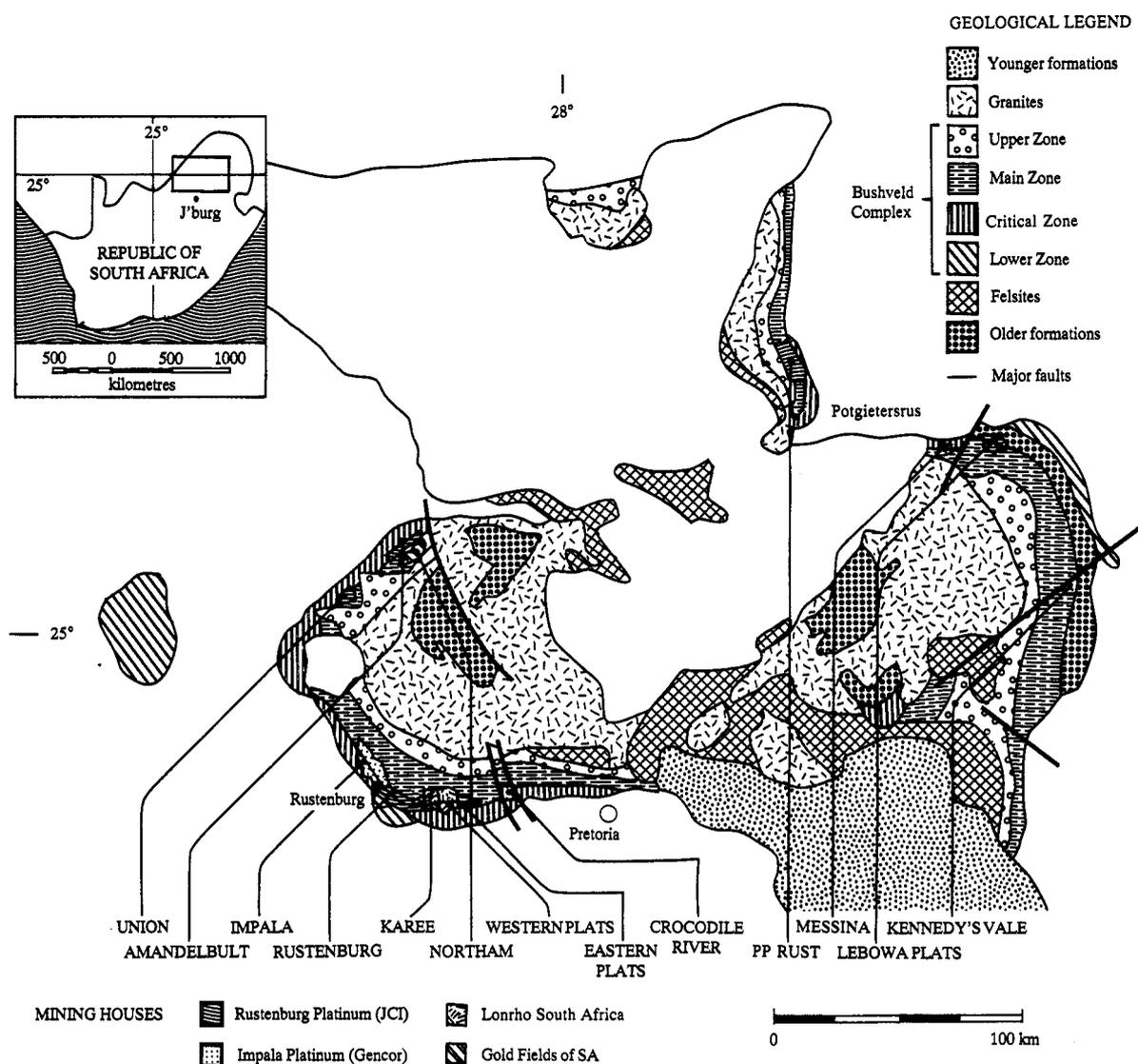


Fig. 1 GEOLOGY AND PLATINUM MINES OF THE BUSHVELD COMPLEX IN SOUTH AFRICA

#### 4. ANALYTICAL PROCEDURES

Because of the low concentration levels of economic interest, a necessary first step in many analytical procedures is the concentration of the PGMs into matrices which lend themselves to further treatment. Two such procedures are collection into lead (normal fire assay) or nickel sulphide.

Traditionally, the lead is removed by cupellation and the total PGMs + Au in the resulting prill are determined by weighing the prill. An alternative procedure is to dissolve the prill and determine Pt, Pd, Rh and Au by AA or ICP.

Unfortunately, varying amounts of all the PGMs are lost during the cupellation process. Within a laboratory these losses are reproducible and can therefore be compensated for by using correction factors. This is becoming increasingly recognised as a non-ideal situation. A recent innovation is the analysis of the lead button directly by instrumental procedures such as SAFT (Spark Analysis for Traces).

In the nickel sulphide procedure, the base metal sulphides are removed by leaching with hydrochloric acid to leave a PGM residue. This is dissolved and the PGMs determined by a variety of techniques, usually instrumental.

The last sentence highlights the help and the hindrance of the nobility of the PGMs. The 'help' is that under these conditions they are not soluble in hydrochloric acid and can therefore be easily separated from the base metal matrix. The 'hindrance' is then ensuring the complete dissolution of the PGM residue.

Three approaches are most often used:

- (a) Aqua regia leaching followed by fusion of any residue by sodium peroxide.
- (b) Direct fusion with sodium peroxide.
- (c) Pressure leaching in a sealed glass-tube using an 'oxidising' acid media.

The latter technique has the advantage of not introducing large amounts of sodium into the analytical system.

### 5. ANALYTICAL INSTRUMENTATION

Prior to the development of modern instrumental procedures, the chemical similarity of the PGMs provided the major analytical problems. Essentially the analyst was forced to separate cleanly the individual PGMs from each other, which is not an easy task. Each element was then determined gravimetrically usually as the metal, or spectrophotometrically. It was not unusual for a full suite of analyses to take more than two weeks.

The advent of AA and XRF, which eliminated the need to separate the PGMs from each other, significantly reduced analytical turn-around times. Even so, interelement and mineralogical effects can severely affect the accuracy of even these techniques. Releasing agents such as uranium and copper/lanthanum have fortunately removed most of the interelement effects in AA and measurement of solutions the mineralogical ones in XRF. Although the placing of highly corrosive liquors into an XRF is not a method of choice.

ICP-OES has further simplified the analyses of the PGMs because of its simultaneous multi-element capability, relative freedom from interferences and large dynamic range. ICP-MS has the added advantage of sensitivity in the ppb range.

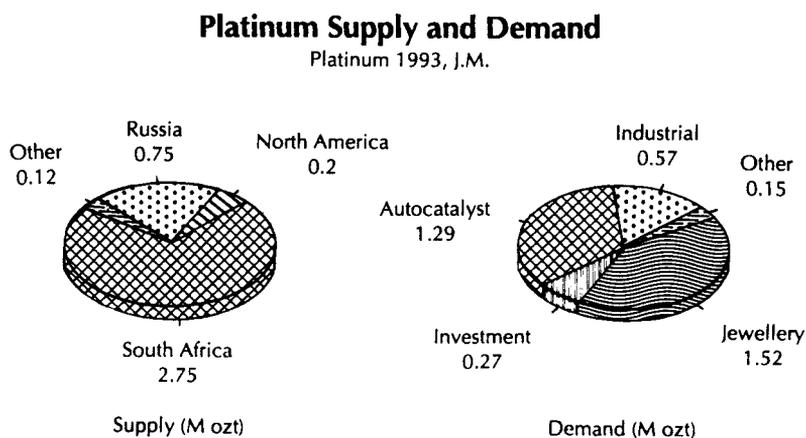


Figure 2.

## Palladium Supply and Demand

Platinum 1993, J.M.

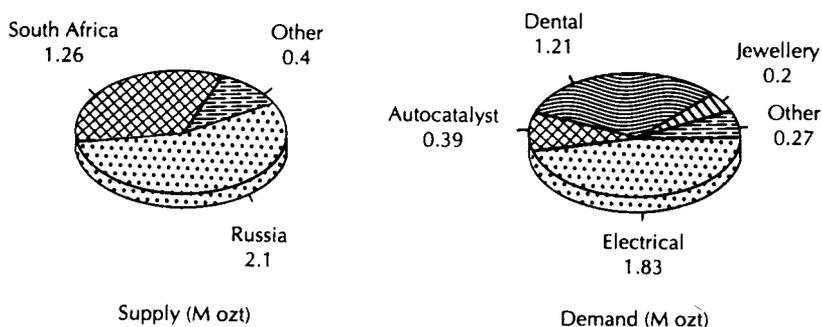


Figure 3.

## Rhodium Supply and Demand

Platinum 1993, J.M.

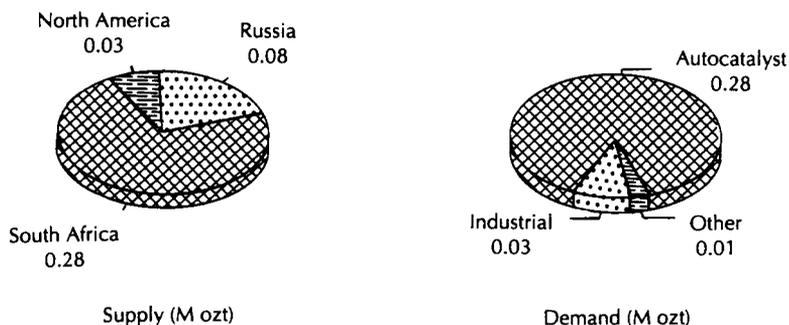


Figure 4.

Recent additions to the analyst's armoury of instrumental weapons are ion chromatography, used for the determinations of ionic species, SAFT and AZTEC. SAFT is a spark source spectrographic procedure which has been especially developed to accurately analyse trace constituents in metal matrices. It is being used to analyse PGMs in the lead produced from the fire assay collection. AZTEC is a highly sensitive EDS-XRF system which can analyse down to the low ppm range.

### 6. QUALITY ASSURANCE

As mentioned previously, the determination of the PGMs must be accurate and the precision levels must be low. Typical RSD levels are 3 - 5% in the low ppm range and analytical biases greater than half of one standard deviation must be identified quickly.

Widespread use is therefore made of Shewhart and Cusum graphs. A number of reference materials with known contents are also a vital requirement.

### 7. USES

The catalytic and noble properties of the PGMs have formed the basis for their industrial uses.

The individual PGMs, either alone, or in mixtures, have been used for many years in the petroleum refining and fertiliser industries. Recent major uses are in car exhaust catalytic converters. Their noble property enables them to withstand the extremely aggressive conditions found in these systems.

A major outlet for platinum in recent years has been as jewellery, especially in Japan. A minor, in terms of consumption, but extremely important use is in the anti-cancer drug, Cisplatin.

A future major use for palladium will be in fuel cells for the production of 'clean' electricity.

The supply and demand situation for platinum, palladium and rhodium are given in Figures 2, 3 and 4 respectively.

**Acknowledgements**

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