Rapid Elemental Analysis of Trace and Minor Metals Using Enhanced Stabilised ICP

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Introduction

The Platinum Group Metals, or “PGMs” as they are sometimes referred to, are a collective of metals grouped together in the middle of the Periodic Table as below.

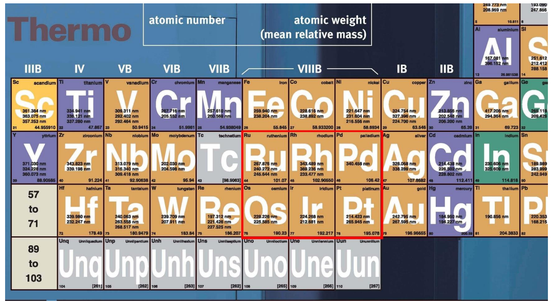


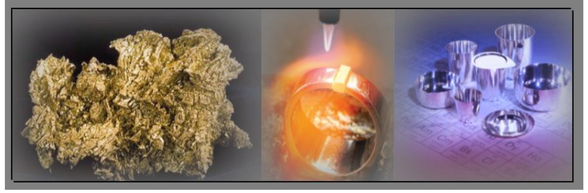
Figure 1. Periodic Table – Red Boxed Area shows PGM group

The six elements normally included in the group are all transition metals with some similar chemical and physical properties. Generally, this group is assumed to include Platinum, Palladium, Rhodium, Ruthenium, Iridium and Osmium; all have become valuable and extremely useful to Industry (and civilisation in general) because of their elemental properties, rarity and beauty.

The Platinum Group Metals have applications both exotic and mundane. The jewellery industry has been utilising the PGMs anti-corrosive properties to great effect since the mid-nineteenth century and producing hallmarked items in Britain since 1975. Many of the Industrial applications of the Platinum Group Metals utilise an alloy combination of two or more metals. A wide range of PGM alloy compositions are used in electronic applications including low voltage and low-energy contacts, thermocouples, furnace components and electrodes. The Chemical and Petrochemical industries use the PGM’s extraordinary catalytic properties for processes like refining crude oil, to produce a large number of synthetic organic chemicals and to produce substances such as chlorine and caustic chemicals(1).

Since 1979, the automotive industry has become the largest consumer of the Platinum Group Metals with the advent of the catalytic converters in car exhaust systems. The PGM’s are used as oxidation catalysts to reduce the potentially noxious emissions from exhausts.

FIGURE 2. Examples of Gold and Platinum Group Metals – Gold nugget (left) courtesy of the US Geological Survey, Palladium ring (centre) courtesy of Johnson Matthey Platinum Review 2007 and Platinum Laboratory crucibles (right) courtesy of Johnson Matthey



Precious Metal Occurrence and Pre-concentration Techniques

The Platinum Group Metals are customarily found in the presence of various base metals such as copper, nickel, chromium, iron and sulphur. Ordinarily, the concentration of total PGMs in ore will be in the grams per tonnne (ug/g) range of concentration, possibly rising into double figures. For this reason, ore analysis normally uses a pre-concentration and separation technique like a Fire Assay (fusion with fluxes) with lead or nickel sulphide collection to concentrate the PGMs prior to dissolution and analysis by instrumentation.

The resulting buttons are treated in entirely different ways. The lead button is heated to 950-1050^{0}C in a magnesite or bonemeal cupel (a porous, absorbent cup) with a flow of air passing over the cupel. The resultant lead oxides absorb into the cupel or sublimate into the exhaust at these temperatures. A small alloy prill containing the Au, Pt, Pd and Rh remains for weighing or further processing like digestion in acids. The nickel sulphide button, normally two since the slag is often refused, is ground up and reacted with dilute hydrochloric acid. The solids that are left contain the Pt, Pd, Rh, Au, Ru and Ir as suphides.

The pre-concentration techniques have almost no scope to distinguish between the individual PGMs. In addition, the PGMs can also alloy with other elements such as gold and silver in the fusion. For this reason, the lead collection Fire Assay for PGMs is used to give a total 3 PGMs plus gold figure (Pt, Pd, Rh + Au) or the final product from the Fire Assay – the prill, Pb or NiS button, depending on the Fire Assay type – is analysed by ICP, atomic absorption or spark emission.

Principle

The samples used for this particular analysis are a mixture of low to mid-grade PGMs and various base metals in high concentrations. The samples were kindly donated by a major world-wide PGM producer where they are used as in-house control standards. The samples have sufficiently high concentrations of PGMs so that no pre-concentration or separation was required. However, without the separation of base metals, it is necessary to use a high-resolution ICP with full wavelength coverage to make sure that there are no interferences.

Platinum Group Metals in samples such as these are commonly dissolved in an Aqua Regia digestion, either on a hotplate or using a microwave digestion system – the latter digestion was chosen as the most appropriate method. A 0.5g mass of sample was digested in a mixture of nitric and hydrochloric acids in a high pressure microwave digestion vessel. The sample solutions were analysed directly using a high-resolution iCAP 6500 ICP and appropriate standards. The iCAP 6500 Duo in axial mode was chosen as a suitable instrument for this work but the Radial version or, indeed, the iCAP 6300 model would also be well suited to the task since all of these models use the same high resolution spectrometer.

Method

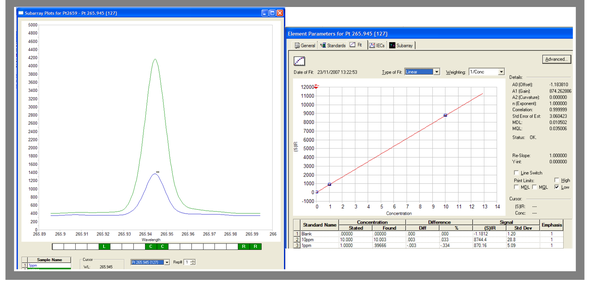
Reagents and Equipment

Nitric acid sg 1.42, Analar grade
Hydrochloric acid 35 % v/v, Analar grade
1000 ppm single element stock standards for each element
50ppm Yttrium stock solution made from 1000ppm stock diluted in deionised water
Microwave digestion system
100ml volumetric flasks

FIGURE 3. iCAP 6000 Series Duo and method parameters

Parameter	Setting
Plasma view	Duo
Nebulizer	Concentric
Torch center tube	2 mm ID
Mixing chamber	Glass Cyclonic
Sample pump winding	Orange-white Tygon
Drain Pump Winding	White-white Tygon
Integration time	15 seconds
Repeats per analysis	3
Sample uptake time	30 seconds
R.F. forward power	1150 watts
Coolant flow	12 l/min.
Auxiliary flow	0.5 l/min.
Nebulizer flow/Pressure	0.65 l/min/ 0.26 MPa

FIGURE 4. Pt 265.945nm peaks for standard and samples and Calibration for the same wavelength



Sample and Standard Preparation

Four 0.5g aliquots of each sample were weighed out into microwave digestion vessels. 10ml of AR grade Hydrochloric acid and 1ml of Nitric acid was added to each vessel. The vessels lids were inserted but not sealed and allowed to stand until the initial reaction had subsided slightly (10 mins). A generic digestion was used with a slow ramp to a temperature of 1800C and held there for 15 mins then allowed to cool down.

The vessels were unsealed and the solution was washed into a 100ml volumetric flask. An internal standard e.g. Y or Sc, may be added if required. The equivalent of 0.5ppm Y internal standard is all that is required for good performance but the internal standard intensity can be more closely matched to the intensities of the analytes if desired.

Standards were made up to the concentrations in Table 3 using 1000ppm stock solutions and deionised water. The standards were also matrix matched to the same acid concentration as the samples and may be matrix matched to major base metal components, if so required.

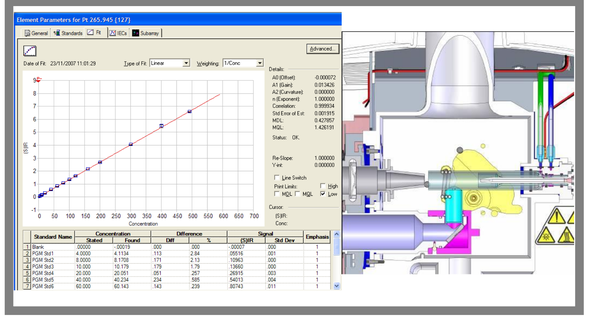
Method Development

The Platinum Group Metals Industry often utilise similar wavelengths for analysis comparison between laboratories. Wavelength selection was made from a larger subset of standard lines with help from the iCAP and iTEVA’s Fullframe capability which allows a snapshot of the spectrum. The Fullframe and the sub-arrays of the prospective element lines were used to check for interferences and suitability for the analysis. With judicious use of appropriate wavelengths, peak and background positions, it was found that the high-resolution and full wavelength coverage of the iCAP made inter-element correction factors for these particular samples unnecessary. The method was optimised for sample throughput by using the “Speed” mode as well as using 15 seconds integration time with three replicates.

Table 1: Results of individual elements and replicate samples

Element	Replicate 1 ppm	Replicate 2 ppm	Replicate 3 ppm	Average Measured ppm	Expected ppm
Au 267.595nm	67.0	70.6	70.0	69.2	67.9
Pd 340.458nm	784	813	849	815	817
Pt 265.945nm	1250	1383	1283	1305	1305
Rh 343.489nm	186	197	203	195	193
Ru 267.876nm	475	513	520	503	489

FIGURE 5. Pt 265.945 nm extended calibration graph – linear from 4ppm to 500ppm (left), diagram of the periscope of the Duo iCAP (right).



The high-resolution of the iCAP enabled analysis of samples containing high levels of base metals in the same solution. The sub-arrays examined (Platinum 265.945nm and Gold 267.595nm are shown in Figure 1), showed little problem with the measurements provided that the simultaneous background points were modified.

The method calibration line for Pt 265.945nm (Figure 4) shows that the wavelength is absolutely linear to at least 10ppm for this calibration. In fact, this particular wavelength on the iCAP is linear to much greater ranges. This capacity for excellent sensitivity without sacrificing on linearity at high concentrations is partly due to the excellent optical design for high sensitivity and partly due to the CID detector and it’s abilities to measure high intensities without saturating. The Platinum 265.945nm calibration above (Figure 5) shows the excellent linearity even when using standards ranging in concentration from 4ppm to 500ppm in radial mode.

Conclusions

The data shown in Table 5 demonstrates that the results are well within the PGM Producer’s in-house accuracy boundaries. The boundaries are based on sound statistical principles using 2 standard deviations of a mean. This mean was generated by repeated “Round Robin” analysis of these samples by numerous different laboratories in the same group of companies.

The simultaneous analysis of the PGM samples was comparatively simple with the high-resolution and full wavelength coverage capabilities of the iCAP. The results are excellent even though the plasma conditions were not specifically optimised with the Optimise Source feature on the iCAP 6500. Background and peak selection were simplified by dragging and dropping the measured regions in the sub-array.

The iCAP Duo shows it’s versatility by analysing samples with high concentrations of base metals while still achieving low detection limits and high accuracy. Either the Duo or the Radial versions of the iCAP offer the best analysis solution for PGMs analysis.

References

(1) http://minerals.usgs.gov/minerals/pubs/commodity/platinum/