

All That Glisters is Not Au/Ag/Pt/Pd/Ru/Rh/Ir/Et Al

The Art and Science of a Precious Metal Laboratory

By David Court, Laboratory Manager, Alex Stewart Assayers

The precious metals trade is diverse, and this is no less true when we look into the analysis of the metals and minerals involved. The chemistry of precious metals can be both complex and intriguing, and often chemists will build an enviable knowledge and understanding after years of working in laboratories.

Over recent years, higher metal prices, efficient lines of communication and the advance of technology into laboratories has had a positive effect on the analyst, and there has been a need for laboratories' performance to keep up to pace. Quality and reliability of assay results are the most important factors due to the fact that exchange splitting limits* on all metals – and especially precious metals – have tightened, necessitating that assay results be precise and accurate. Any delay can be costly to all parties involved.

The analysis of precious metals covers a wide spectrum, from poor-grade materials containing only parts per million (ppm) to metals of 99.999% purity.

Our laboratory reflects this: the diverse range of precious-metal-bearing materials that we assay includes sweeps, jewellery scrap, resins, catalysts, bullion, doré, electronic scrap, solutions, conductor pastes, concentrates and residues, in addition to the

occasional non-standard specialized alloys /products.

Assaying of such materials involves different analytical techniques according to the particular criteria of each sample, including the base carrier (the substrate of the material) and precious metal contained.

To establish the composition of the sample, it is often necessary to carry out a preliminary fact-finding assay or trial. Once the matrix of the material is known, the chemist can make a judgment and choose the most appropriate assaying method to be applied. This approach is essential, and highly skilled chemists complement any decision within a modern laboratory equipped with reliable instrumentation.

This preliminary assay is especially significant in the assaying of the platinum group metals (pgms), as the ratio of the precious metals contained in the sample will dictate the analytical procedure.

Even the most modern and up-to-date techniques are dependent on the representative sample for analysis being true and homogeneous. The extreme importance attached to obtaining a sample that accurately represents the total original material cannot be stressed too strongly – errors made during the sampling process cannot be corrected in the course of analysis. The sample must be in a state that will support the expected accuracy and precision of the method and instrumentation.

In addition to the preliminary fact-finding assays previously mentioned, preparation of the material or sample may be required prior to commencing the actual analysis. Some samples received in the laboratory

will have already been prepared and be in a suitable condition for analysis, the first stage invariably being moisture determination. However, laboratories will also receive materials in various shapes and in conditions ranging from natural state to partially prepared – for example electronic scrap, ores, catalysts and production residues that will require extensive sample preparation. This may involve melting, matting, milling, screening, leaching and drying before the sample is suitably prepared and ready for assaying.

Techniques used for precious metal analysis may include:

- Fire Assay
- Inductively Coupled Plasma Optical Emission and Mass Spectrometry (ICP OES and ICP MS)
- X-Ray Fluorescence Spectrometry (XRF)
- Gravimetric Analysis
- Microwave Digestion.

A description of some of these principles and techniques follows.



Recovered gold

All photos courtesy Alex Stewart Assayers

*Exchange splitting limits: Splitting limits are specified in the contract between the seller of the material and the buyer. If the difference between the assay obtained by the buyer and that obtained by the seller is within the specified limit, the two parties agree to split the difference. If the difference is outside those parameters, the matter then goes to umpire – an independent assayer – which is also named in the contract.

Fire Assay

Fire assaying, a technique that has been used throughout the world for centuries – it is recorded as long ago as the ancient Egyptians – is still the most generally accepted method of analysis for gold and platinum group elements. It has stood the test of time due to some distinct advantages, notably large sample weights and separation of the precious metal from the base carrier, which reduces interference.

Fire assaying is used for the determination of gold, silver and pgms in all types of materials, ranging from bullion, jewellery and ores to concentrates and electronic scrap. The methods have been modernised, and aligning this technique alongside the latest instrumentation can provide the most accurate results.

In principle the weighed sample is fused at a temperature in excess of 1000 degrees Celsius in a flux made up of various constituents, the purpose of which is to reduce the metal oxide constituent (usually lead, but it could also be nickel, copper or tin from its oxide to the metal).

In the smelting, a slag phase is also created, which will aid the removal of base metals and gangue materials (sand, rock and other impurities) from the metal button, which then collects the precious metal and sinks to the bottom of the crucible. When fusion is complete, the crucible contents are poured into a cast-iron mould and the button containing the precious metals and the slag are separated. The slag is washed again with additional flux to ensure complete collection of the precious metal, and is discarded.

Depending on the metal oxide used as the collector in the flux, different chemical processes take place.

If lead is used, the next stage is to remove the lead, through a technique known as cupellation, wherein the button is placed on a cupel (a porous pot made from magnesium oxide) in a muffle furnace with good airflow at a temperature of approximately 950 degrees Celsius. The cupel has an affinity for lead oxide, and acts as a filter, absorbing the lead oxide as it forms from the molten lead. This process leaves the precious metal bead on the



Fire assay fusion furnace

cupel, which can be weighed accurately to obtain total precious metal weight. This bead is then treated further using nitric acid to determine the metals in the bead, usually silver, gold (gravimetrically), platinum and palladium (ICP).

In the assay of doré, the bullion samples are weighed and placed directly into lead foil and cupellated (they do not have to undergo fusion as they are already free from significant base metals). The beads can be weighed using accurate balances capable of weighing to seven decimal places. Parting in nitric acid separates the silver and gold from each other – the silver is dissolved and the gold remains as the metal, which is dried and annealed and weighed to calculate the percentage in the sample. Various corrections are necessary, made using standards of pure metal alongside the assays.

The noble metals are analysed more frequently by nickel collection. This technique uses nickel oxide as the collector, and it is possible to determine a range of metals in one

procedure, namely platinum, palladium, rhodium, iridium and ruthenium. This method does not use cupellation to separate the collected precious metals, but instead dissolves the pulverised precious metals, but instead dissolves the pulverised nickel button in acid. The nickel is removed by filtration, the remaining residue of precious metals is treated and the final determination of the solutions is made using instrumentation such as ICP.

ICP OES: Inductively Coupled Plasma Optical Emission Spectrometry

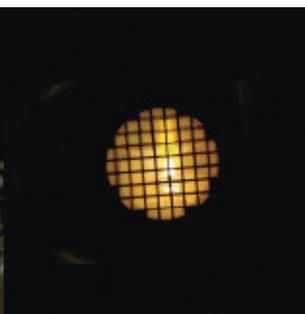
ICP spectrometry analyses solutions of samples of known weights into known volumes by the most appropriate preparation method for the type of sample. The resulting solution from direct dissolution of the sample or from parting of the precious metal beads from fire assay is then analysed directly on an ICP spectrometer. This method requires comparative standards and reference samples and has the advantage that it can measure a range of elements simultaneously.

Opening the fusion furnace

Pouring fire assay fuse

Inductively coupled plasma

Buttons prepared for cupellation





XRF automatic sample changer

Solutions being analysed by ICP

Seven-decimal-place micro balance with platinum basket used for gold bullion assay

Gold cornet weighed on balance

ICP spectrometry is an excellent method for measuring pgms in solution. It is an emission technique, which requires the sample to pass through a nebuliser to create a fine mist. This is then swept into the plasma via a spray chamber and a torch. The plasma itself is a high-energy source that causes the atoms and ions within the sample to absorb energy and reach higher energy states. They then revert to their normal energy states in the cooler part of the plasma, thus giving off energy in the form of light, which is then measured by the spectrometer.

The great benefit of ICP is that linear calibrations can be obtained over orders of magnitude not possible by other comparable techniques. This, coupled with the fact that modern spectrometers use CCD (charge coupled device) detectors to measure light over the whole spectrum range, means that fast multiple-element-wavelength determinations can be made from just one solution containing ppm levels up to higher concentrations.

ICP as a technique does have a number of interferences, which the analyst needs to be aware of. Matrix interferences can be overcome by making sure that the samples and standards have the same acid strength and alloy base.

An internal standard should also be added to the solutions – pgm elements have both atomic and ionic wavelengths, which can

behave differently in the plasma, so an internal standard should match these characteristics.

Matrix effects can also affect the background of a spectrum, therefore suitable background correction should also be applied to each elemental wavelength being measured. Inter-element interferences can be problematic and need to be overcome (they are reduced using correction factors).

Pgm samples are run with calibration check standards, reference materials and drift-correction software to ensure the high quality of the analysis reported from the ICP instruments.

XRF: X-Ray Fluorescence Spectrometry

XRF is an excellent method for the qualitative and quantitative determination of the major and important trace elements in many materials.

During x-ray fluorescence analysis, the sample material is irradiated with x-rays, which excite secondary x-ray fluorescence. The secondary x-ray has characteristic wavelengths produced by the elements of the sample material. The separation of individual wavelengths of the fluorescent x-ray emission is done by Bragg diffraction from crystals of particular lattice spacings. Through measurement of these characteristic wavelengths, the qualitative composition of the sample can be determined.

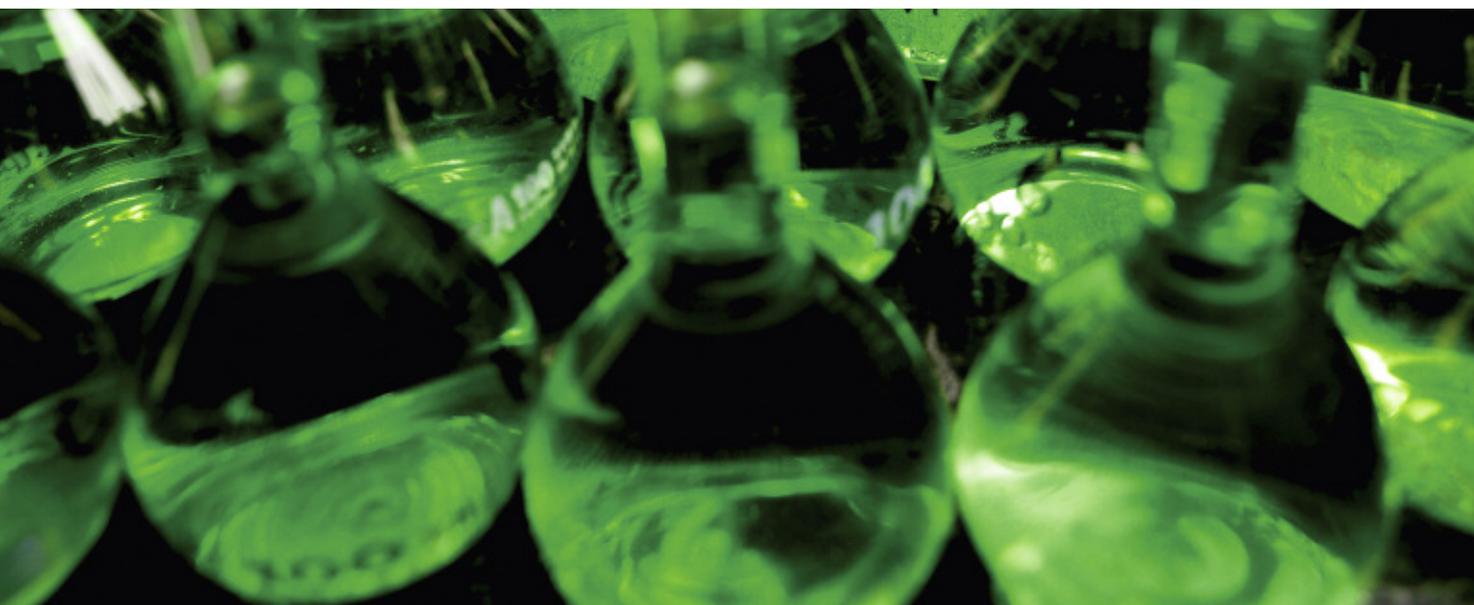
The intensity of the fluorescent radiation allows the determination of the element concentrations in the sample. In quantitative analysis, intensities are compared with standards of known composition.

The advantages of XRF in comparison with wet chemical methods are the accurate analysis of samples that contain minerals, e.g. zircon, that are difficult to dissolve and samples that contain elements that are unstable or volatile in solution.

XRF is a non-destructive technique and can be used to identify and determine the concentrations of elements present in solid, powdered and liquid samples. It's also capable of measuring all elements from trace levels up to 100% while carrying out accurate, reproducible analyses at very high speed.

In practice, samples should be presented to the spectrometer in homogeneous reproducible form. Metals may be ground or milled to give a flat surface. Powders are reduced to a controlled particle size and pressed into pellets for convenience of handling. Fusing with a suitable flux, producing a glass-like bead, is a valuable technique to eliminate errors with materials that exhibit varying mineralogical composition or are difficult to present in other forms. Liquids and loose powders are simply supported on a plastic membrane in the base of suitable sample cups.

Solutions prepared for AA (Atomic Absorption)



Gravimetric Analysis

Gravimetric methods are used routinely in laboratories worldwide – probably the most familiar being the gravimetric assay for gold and silver previously described. Gravimetric methods for pgms are a little more complex, and are gradually being replaced by instrumental techniques in commercial laboratories.

One example is the treatment of the solution from parting. After removal of the gold and silver, the palladium can be determined gravimetrically by precipitation using dimethylglyoxime (DMG). The method was used extensively in laboratories prior to the growth of instrumentation and is still used today as an alternative or support to instrumentation.

There are many classical gravimetric techniques for determining the noble metals; these invariably involves the separation of the individual metals using reduction or precipitation, sometimes taking many hours /days to complete. The skills and experience of the precious metal chemist are paramount when using these methods.

Often in analysing bullion material containing different levels and ratios of platinum, palladium, rhodium and iridium by wet chemistry, the samples may not be readily soluble in any particular acids and, even if left for days in acid with heating, will show no signs of dissolution. Not so long ago, these samples would have given the chemist some serious problems, but as mentioned earlier we now have microwave digestion to assist in the analysis. This technique dissolves the sample in laboratory microwave equipment using heat and pressure, and in considerably less time. Once in solution, the analysis can then proceed using the appropriate instrumentation or gravimetric technique.

As mentioned, this is only a brief insight into a few of the operational aspects of a modern laboratory, and there are many other techniques and instruments in daily use. Technological advancements will continue and, naturally, commercial methods and procedures will utilise these to keep up with the unrelenting pace whilst still offering markets reliable independent service. ■



David Court

joined the independent analysis and supervision company Alex Stewart Assayers in 1978, the

year of its founding. In the 30 years since, he has been involved in myriad projects, including the setting up of a specialist gold assay laboratory in Dubai. Today he is responsible for the laboratory operations at the head office in Knowsley, Liverpool.

Additional background information for this article was provided by Andrew Smith, Precious Metals Business Development Manager, Alex Stewart (Assayers) Ltd.