

FINAL ANALYSIS

The Role of Inductively Coupled Plasma-Optical Emission Spectrometry in Determining the Fineness of Precious Metals

Accurate precious metal analysis is routinely carried out to determine the precious metal content in a wide variety of different materials. This is particularly important for fineness determination for the hallmarking of precious metals for jewellery use (see **Figure 1**). The precious metal concentration in different materials can vary from parts per million (ppm) or lower in car catalyst or powdered ore samples, to virtually 100% in jewellery alloys or bullion bars. This article considers the benefits of analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES).

The wide range of sample types in which precious metals occur require that a variety of classical and instrumental methods, or combinations of the two, be used in precious metal testing. In the last six decades more than 400 methods have been published for the analysis of precious metals (1, 2). Even an experienced analytical chemist may hesitate to choose the most suitable procedure for separation and determination of precious metals in a material of unknown

composition. There can be a temptation to accept the more recently published procedure as being superior to those which are well tried and tested.

Analysing Precious Metal Content

It is estimated that less than 10% of all precious metal determinations can be performed by strictly instrumental techniques. Probably no more than 30% of all determinations are carried out by strictly classical chemical methods. Hence a large portion of the analytical workload must be handled by a combination of chemical and instrumental approaches, which as a result become strongly interdependent. Fire assay and smelting based techniques (**Figure 2**) are the earliest analytical procedures recorded in human history, and remain essential pretreatment steps for a large variety of samples.

To determine whether an analytical method can achieve the required performance for fineness determination, the method must be tested by frequent repetition, ideally with the same sample.



Fig. 1. Hallmark of platinum jewellery (left to right): sponsor's mark, standard mark, traditional fineness mark, assay office mark and date letter



Fig. 2. The precious metal samples are withdrawn from the furnace after the cupellation process has been fully completed

The International Organization for Standardization (ISO) technical committee 'TC 174: Jewellery' and the corresponding European Committee for Standardization technical committee 'CEN/TC 283: Precious metals – Applications in jewellery and associated products' are pursuing the standardisation of jewellery testing at an international level.

Some important analytical standards established to date are listed in **Table I**.

Table I

ISO Standards for the Determination of Precious Metals in Jewellery Alloys

ISO Standard	Title
ISO 11427:1993	Determination of silver in silver jewellery alloys – Volumetric (potentiometric) method using potassium bromide
ISO 11426:1999	Determination of gold in gold jewellery alloys – Cupellation method (fire assay)
ISO 11210:1995	Determination of platinum in platinum jewellery alloys – Gravimetric method after precipitation of diammonium hexachloroplatinate
ISO 11489:1995	Determination of platinum in platinum jewellery alloys – Gravimetric determination by reduction with mercury(I) chloride
ISO 11490:1995	Determination of palladium in palladium jewellery alloys – Gravimetric determination with dimethylglyoxime
ISO 11494:2008	Jewellery – Determination of platinum in platinum jewellery alloys – Inductively coupled plasma (ICP) solution-spectrometric method using yttrium as internal standard element
ISO 11495:2008	Jewellery – Determination of palladium in palladium jewellery alloys – Inductively coupled plasma (ICP) solution-spectrometric method using yttrium as internal standard element

Inductively Coupled Plasma-Optical Emission Spectrometry

The Birmingham Assay Office uses ICP-OES extensively. It is one of the best techniques available for the analysis of the platinum group metals (pgms): platinum, palladium, rhodium, iridium and ruthenium, as well as base metals such as copper, zinc and nickel, being accurate to 1 ppm. The technique is destructive but it does accurately determine both major and trace elements.

Using this technique, a small sample is accurately weighed and dissolved in an appropriate acidic matrix (**Figure 3**) then subjected to temperatures (plasma) high enough to cause excitation of the sample atoms. Once the atoms or ions are in their excited states, they



Fig. 3. Sample preparation for ICP-OES. The chemist is checking for the presence of undissolved sample in the volumetric flask, before subjecting the solution to instrumental analysis

decay to lower stable states by releasing energy. Light is emitted at a specific wavelength by each element present and these emission lines are measured and used to determine the concentrations of the elements of interest.

The high precision of ICP methods is due to the stability of intensity quotients of emission lines, essentially of gold (267.6 nm), platinum (265.9 nm), palladium (340.5 nm) and the internal standard element yttrium (371.02 nm). If the precious metal and yttrium lines are measured simultaneously, a reproducibility in results of at least 0.01% can be achieved.

Comparison with Classical Methods

Classical methods such as gravimetry have maintained their importance and set the standard for the accuracy of instrumental methods. In order to be approved by the ISO as an alternative analytical technique for determining the fineness of precious metal alloys, ICP methods would be required to achieve at least the same level of repeatability as gravimetric methods. In addition it is especially crucial that interference-free direct measurement of the precious metal can be achieved. This is, of course, necessary for the optimisation of ICP-OES.

Over a period of time it has been recognised that ICP-OES can be applied for a wide variety of precious metal alloys. The method is more easily and economically carried out than gravimetry, and can also be faster, as it can be used for multiple element determinations at the same time. It gives results with acceptable precision and its chemical selectivity is higher than for gravimetry. Above all, it attains a reproducibility and accuracy comparable with those of gravimetry.

Conclusion

ICP-OES is now routinely employed by several commercial laboratories for the analysis of pgm-containing powder and ore samples, after fire assay with nickel sulfide as the collector. It is common practice for the analysis of some non-metallic materials, such as car catalyst samples, to use a combination of both

chemical (gravimetric) and instrumental approaches. The precision and accuracy of ICP methods make them highly suitable for fineness determination of precious metals for hallmarking.

Anybody interested in the analytical chemistry of precious metals would do well to study the excellent reference works by Beamish and Van Loon (1), Beamish (3), Bugbee (4) and Smith (5, 6).

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