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Accurate and Precise Determination of Platinum in Solution by ICPES

It is widely recognised that Wendt and Fassel (1) and Greenfield *et al.* (2) were the first to describe the technique of inductively coupled plasma emission spectrometry as a means of analysis. The technique has a number of acronyms, with ICPES being favoured over ICP-OES (where the O stands for optical) and ICP-AES (where the A stands for atomic). In the forty or so years since the inception of the technique, ICPES instrumentation has developed in sophistication and usability and is now to be found in most laboratories where simultaneous compositional analysis of a number of elements is required.

Application for Elemental Analysis

In recent years, the ICPES technique has been increasingly used as the method of choice for the quantitative determination of many metals, including platinum and the other platinum group metals (pgms). The reference methods remain in the domain of classical gravimetry, where precision in the order of 0.1% relative standard deviation (RSD) can be achieved. However, gravimetric methods are relatively slow and require complex sequential chemical separations before an element can be determined. In complex samples this degrades the optimum precision and accuracy obtainable. ICPES is capable of achieving precision of < 1% RSD with fast simultaneous determination of each of the elements present. To achieve the best precision and accuracy in determining Pt and the other pgms in samples, several factors must be considered.

Nature of the Sample

Samples for Pt analysis are almost invariably in solid form when received by the laboratory. Pt loadings may range from low mg kg^{-1} (for example in emission control catalysts) to high percentage levels (for example in fuel cell catalysts). The subject of dissolution of the pgms for analysis has been covered in many other texts by many other authors (see, for example, (3)). To achieve optimum precision and accuracy in determination, the Pt concentration in the solution presented should fall in the range 10 to 1000 mg l^{-1}, with not more than 50 g l^{-1} in total of dissolved solids.

Sample Introduction

The sample is introduced into the plasma *via* nebulisation. In this process, a fine spray of the sample is carried to the plasma by the injector gas. In the experience of laboratories analysing Pt solutions, the concentric-type nebulisers give good precision when coupled with a tortuous path for the nebulised spray. The classical 'double pass' type and newer 'Twister cyclonic' nebulisers have both found utility within leading Pt assay laboratories. A range of concentric glass nebulisers are available on the open market, for example (4). The sample is delivered to the nebuliser by a peristaltic pump. Where poor precision and accuracy occur in ICPES determination, they are often attributable to the sample introduction system. In most expert laboratories the standard set-up consists of humidified injector gas, and a 30 rpm eight-roller peristaltic pump delivering the sample at a rate of 1 ml min^{-1} to a glass concentric nebuliser in a double pass spray chamber.

Calibration

ICPES is often quoted as having a wide linear response range, covering five to seven orders of magnitude in concentration. Nevertheless, a good calibration strategy is still important in achieving ultimate accuracy and precision. Common practice is to limit the concentration range to 10 to 1000 mg l^{-1} *via* manipulation of the sample dissolution and dilution strategy. Under these circumstances a good match of the calibration solutions with the samples can be achieved.

Matching the major base metal composition of the sample solution in the calibration solutions requires some planning, but can still allow simultaneous analysis of each of the sample constituents. Importantly, acid concentrations in solution should be matched between samples, standards and solutions used for flushing between intermediate samples.

For ultimate accuracy and precision, a weight-based approach to solution preparation over standard volumetric glassware has begun to find favour. Good traceability and reliable calculation can be achieved through integration of laboratory balances, with instrumental systems reducing errors attributable to manual transcription and data entry (5).

Spectrometers, Detectors and Lines

One major improvement in ICPES technology of the last fifteen years has been the introduction of solid-state detector systems. The low cost of the detector elements has allowed true simultaneous measurement of peak and background intensities. Line selection is the subject of much discussion in the standard texts. However, for Pt, the leading laboratories will select Pt lines at wavelengths of 265.9, 214.4, 299.8, 306.4 and 203.6 nm.

Internal Standardisation

While internal standards can partially correct for matrix differences between sample and standard, their best use is in precision improvement. In common use are yttrium (321.7 nm), scandium (357.6 nm) and indium (451.1 or 303.9 nm). Measuring the ratios of intensities for the analyte and internal standard filters out imprecision caused by noise at mid-range frequencies (~ 1 kHz). An accurate match of the signal counting parameters is necessary to achieve the best performance.

In the final analysis, optimising the analytical method according to the above parameters offers routine Pt determinations of high accuracy and precision.

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