

Improved Accuracy in the Analysis of Precious Metals by ICP-OES

Andy Smith

(Johnson Matthey, UK)

Jol Desmarchelier

(Glass Expansion, Australia)

Introduction

This study investigates the intensity variations and measurement accuracy of precious metals at different spray chamber temperatures, compared with a conventional spray chamber at ambient temperature. The aim of the exercise was to investigate the feasibility of analysing precious metal solutions using ICP techniques to replicate the high level of accuracy and precision obtained using conventional wet chemical techniques.

The investigation was carried out using an IsoMist Programmable Temperature Spray Chamber connected to a Varian Vista Radial ICP-OES as shown in Figure 1. Figure 1 also shows the Capricorn Argon Humidifier, which is used to help prevent salt build-up inside the sample introduction system when running samples having a high concentration of dissolved solids. The IsoMist allows the user to control the temperature of the spray chamber, whether it be for cooling or heating, to finely tune the conditions for optimal sample introduction and ensure long term stability of the signal. Therefore, any change in laboratory temperature is not reflected in the results. The IsoMist also has a number of other benefits depending on the type of sample matrix. For example; setting the IsoMist at low temperatures reduces the solvent load on the plasma and facilitates the analysis of highly-volatile organic samples that, under normal laboratory conditions, tend to promote plasma instability, or in some cases completely extinguish the plasma. Thus, even highly volatile solvents like naphtha can be run undiluted if the IsoMist temperature is set at -10°C . Another advantage is that when samples are very limited in volume, they can be analyzed at very low uptake rates with a heated spray chamber without the ensuing loss in detection limits as would be realized on a conventional spray chamber without temperature control.

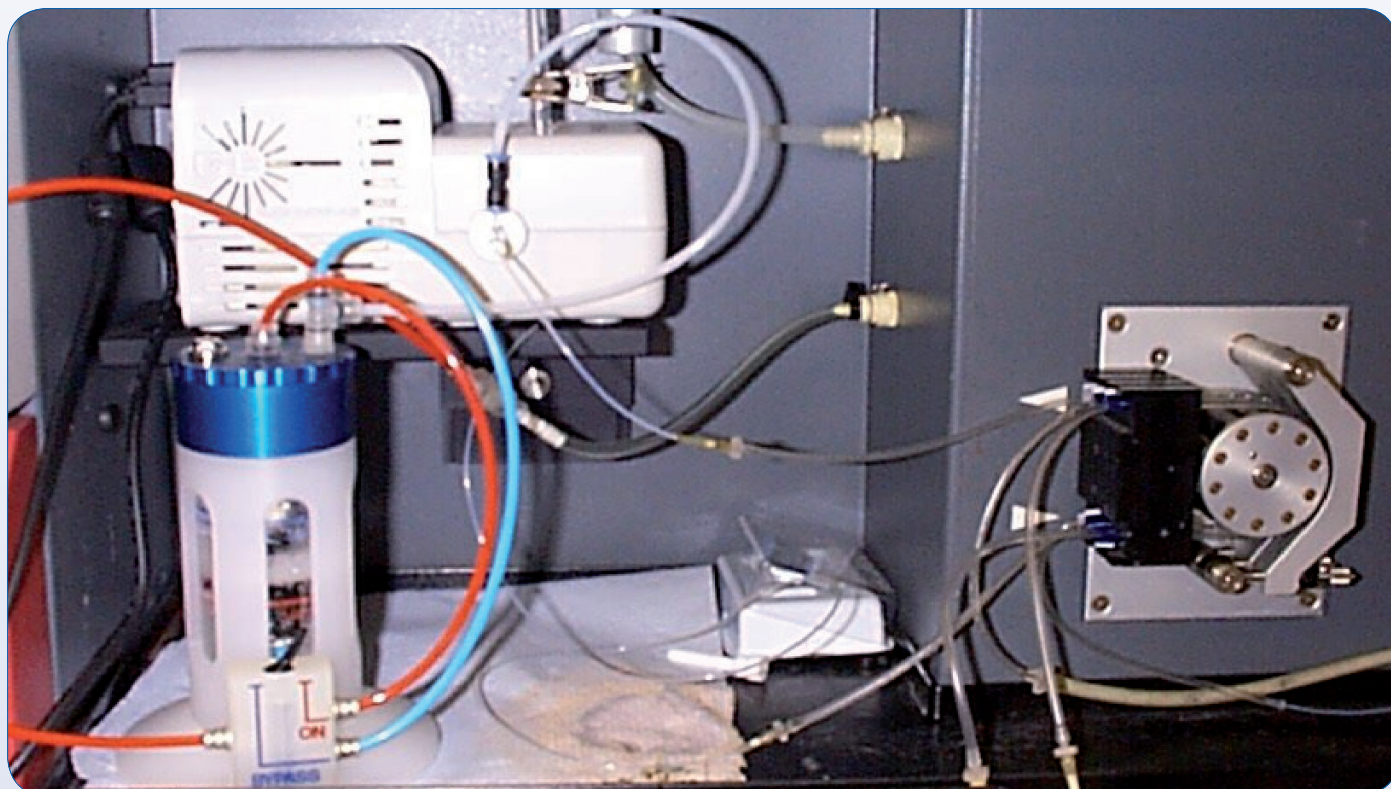


Figure 1: Experimental setup for the Varian Vista Radial ICP-OES with a Glass Expansion IsoMist Programmable Temperature Spray Chamber and the Capricorn Argon Humidifier attached.

Results for Aqueous Solutions

In this study, the IsoMist was used to precisely control the spray chamber conditions during the analysis of various precious metal elements in solution to investigate the effect of temperature on precious metal signal intensities and analytical accuracy. The elements analysed included: gold [Au]; iridium [Ir]; palladium [Pd]; platinum [Pt]; rhodium [Rh]; and ruthenium [Ru]. Figure 2 shows the average signal intensity [n = 10] of various precious metals at specified spray chamber temperatures using the IsoMist.

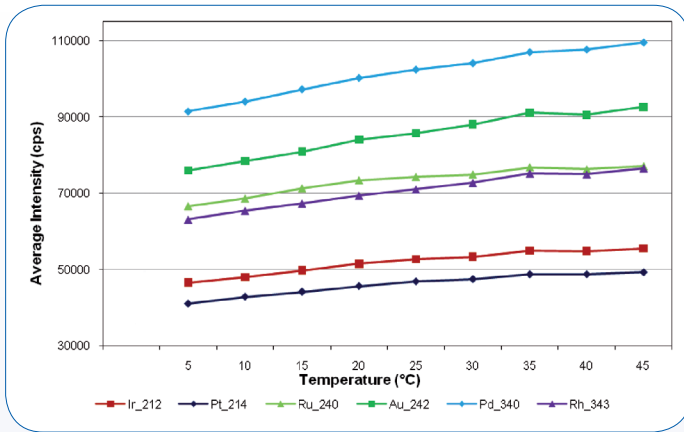


Figure 2: Graph of signal intensity versus spray chamber temperature for several precious metals.

In order to gauge the effect of temperature on the accuracy of the precious metal measurements, a solution of platinum was analysed at a range of temperatures and compared to the concentration determined gravimetrically. The results shown in Figure 3 show that, at higher spray chamber temperatures, the ICP determinations of the platinum concentration are closer to the gravimetric or true value. Again this demonstrates that the IsoMist enhances the sample introduction environment to help provide the conditions necessary for accurate and reproducible platinum measurements.

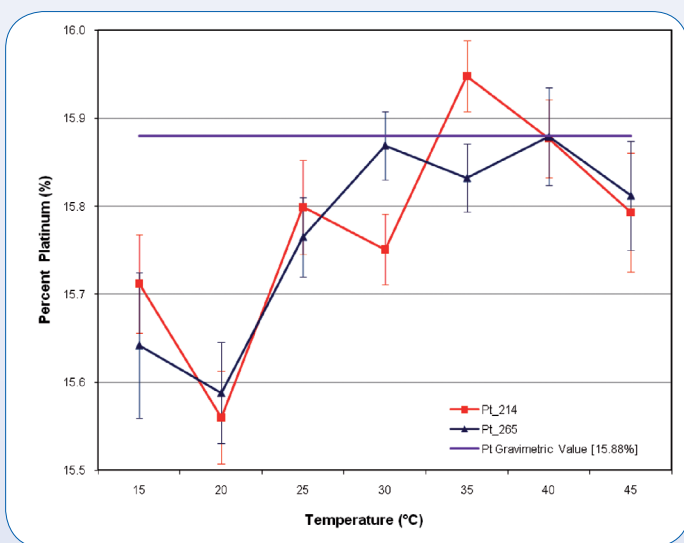


Figure 3: Plot of average ICP measurement of the percentage of platinum in solution [n = 10] versus temperature. The error bars are 1σ.

At higher temperatures the data is more accurate according to Figure 3; both platinum wavelengths measured by ICP are closest to the wet chemistry gravimetric figure when the IsoMist is at 40°C. But what is the effect of the IsoMist on the precision of the measurements? Figure 4 shows the frequency distribution of the RSD (%) for each of the elements analysed with a conventional spray chamber and those analysed with an IsoMist set at 30°C. A higher proportion of low RSD values implies that the data is more “precise”. Although the data set is small there is an indication that the IsoMist has improved the accuracy and precision of precious metal measurements.

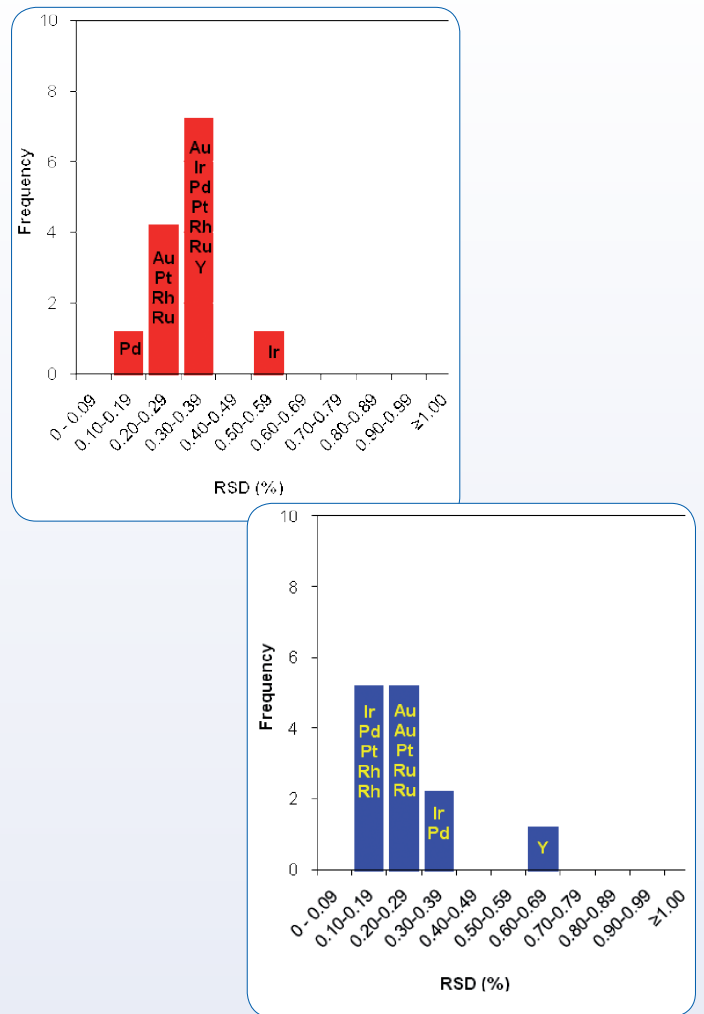


Figure 4: Frequency histogram of RSDs of precious metal measurements [n = 10] taken with a conventional spray chamber [left figure] and those measurements taken using an IsoMist set at 30°C [right figure]. A higher proportion of measurements in the lower bins suggests high precision.

Results for Organic Solutions

The ability of the ICP analyst to control the temperature of the spray chamber improves their ability to analyse elements in matrices that would otherwise require further chemical treatment and the potential loss of analyte, for example, the analysis of ruthenium in an organic solvent matrix. The organic solvent matrix is common with pharmaceutical samples as these are analysed with liquid chromatographic techniques using organic solvents as the carrier. Conventional methods would involve wet oxidising the sample in a mixture of nitric and sulphuric acid to remove the organic solvent, however there is the possibility of ruthenium loss during the oxidation process. Another potential method would be to dry ash the sample, but loss of ruthenium occurs with the volatile species; and then there is the problem of dissolving ruthenium metal which can only be done in alkali hypochlorite solutions. The fused alkali dissolution process results in a solution containing sodium salts which unfortunately inhibits the detection limits.

It is possible to directly measure precious metals in an organic matrix using the IsoMist set at low temperature. In this experiment the spray chamber was set to temperatures between -10°C and $+10^{\circ}\text{C}$ in order to minimise the amount of vapour going into the plasma and two solvents, methanol and isopropanol, containing various precious metals, were analysed. Note that, if a methanol matrix is run at temperatures above 10°C , then the plasma is extinguished and, for an isopropanol matrix, the plasma is extinguished at temperatures above 15°C . Additional steps were also taken to reduce plasma loading such as increasing the power and argon flow rates, as well as using smaller diameter peristaltic pump tubing.

Table 1 shows the plasma conditions used with the organic solutions compared with those for the aqueous solutions. The results for methanol and isopropanol are shown in Figures 5 and 6. Figure 5 shows that there is a general decrease in intensity as the temperature is increased. This is most likely to be due to an increase in the plasma loading. Figure 6 indicates that, as the temperature is increased from -10°C , there is an initial increase in intensity due to increased sample transport but, above zero, plasma loading becomes the dominant factor and the intensity decreases.

These results clearly demonstrate that the IsoMist facilitates the measurement of analytes in volatile organic solvents at temperatures below 15°C .

| | Organic | Aqueous |
|-------------------------------|--------------------|------------------|
| Power (W) | 1600 | 1300 |
| Plasma flow (L/min) | 19.5 | 15.0 |
| Auxiliary flow (L/min) | 2.25 | 1.50 |
| Nebuliser flow (L/min) | 0.60 | 0.60 |
| Integration time (s) | 10.0 | 10.0 |
| Pump tubing [ID mm] | black-black [0.76] | grey-grey [1.30] |
| Waste tubing [ID mm] | red-red [1.14] | blue-blue [1.65] |
| Injector diameter (mm) | 1.5 | 1.8 |
| Pump rate (rpm) | 25 | 15 |
| Sample uptake (mL/min) | 1.0 | 1.5 |

Table 1: Plasma conditions for the analysis of precious metals in an organic matrix compared with those for aqueous solutions.

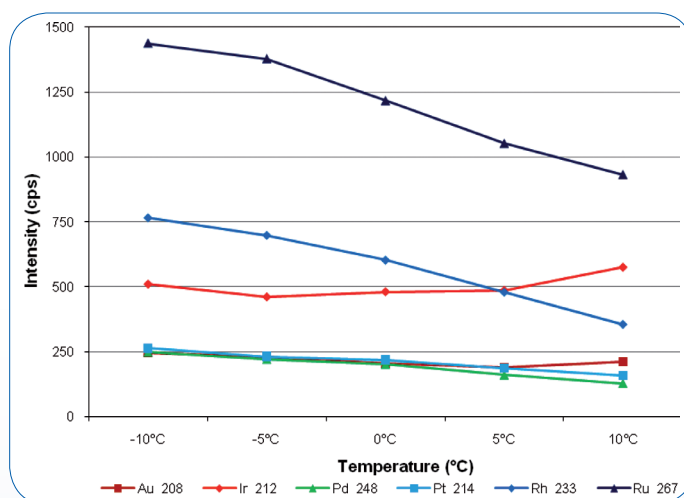


Figure 5: Average [$n = 5$] intensity of various precious metals in a methanol matrix versus temperature. All species shown are ionic. Note that at spray chamber temperatures above 10°C the plasma was extinguished.

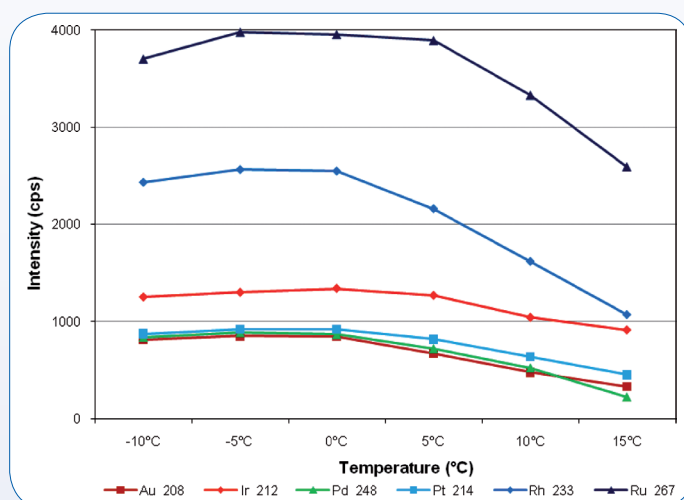


Figure 6: Average [$n = 5$] intensity of various precious metals in an isopropanol matrix versus temperature. All species shown are ionic. Note that at spray chamber temperatures above 15°C the plasma was extinguished.

Conclusion

The benefits of the IsoMist for the analysis of precious metals are:

- (1) control of the temperature of the spray chamber to enhance signal intensity;
- (2) reduced signal instability and improved measurement accuracy and precision;
- (3) direct analysis of elements in organic solvents at temperatures below 15°C .