Analysis of platinum group elements with the Thermo Scientific iCAP PRO Series ICP-OES

Author

Dhinesh Asogan,
Application Specialist,
Thermo Fisher Scientific,
Bremen, Germany

Keywords

Catalyst, Electronics, Jewelry, Metallurgy, Microwave digestion, PGE, Platinum group elements

Goal

To demonstrate the ability of the Thermo Scientific iCAP PRO XP ICP-OES to perform analysis of Platinum Group Element (PGE) analytes in high concentration metal matrices with excellent accuracy, where traditionally a radial instrument would be used.

Introduction

The platinum group elements, or PGEs as they are sometimes referred to, are a collective of metals grouped together in the middle of the periodic table. 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, iridium, ruthenium and osmium (see Figure 1); all have become valuable and extremely useful to industry (and civilization in general) because of their elemental properties, rarity and beauty.

A wide range of PGE alloy compositions are used in electronic applications such as low voltage and low-energy contacts, thermocouples, furnace components and electrodes. The chemical and petrochemical industries use the PGEs' extraordinary catalytic properties in a wide range of processes including refining crude oil to produce many synthetic organic chemicals.[1]

Thermo Fisher
SCIENTIFIC

Figure 1. The six Platinum Group Elements (PGEs). These can be further sub-divided into the Iridium-Platinum Group Elements (IPGEs: iridium, osmium and ruthenium), and the Palladium-Platinum Group Elements (PPGEs: rhodium, palladium and platinum).

Since 1979, the automotive industry has used PGEs as redox catalysts in catalytic converters to reduce the potentially noxious emissions from internal combustion engine exhausts. Within the catalytic converters, the PGEs are typically embedded on ceramic base supports along with various other metals to control side reactions, e.g. nickel is commonly added to the catalyst layer to prevent the production of hydrogen sulfide.

Instrumentation

A Thermo Scientific™ iCAP™ PRO XP Duo ICP-OES equipped with both the standard aqueous sample introduction kit and an internal standard addition kit was used for this work. Automated sample introduction was achieved using a Teledyne CETAC Technologies ASX-560 Autosampler. The instrument parameters used during analysis are shown in Table 1.

The Thermo Scientific iCAP PRO Series ICP-OES includes high-resolution Echelle optics and an improved, seventh generation Charge Injection Device (CID) detector. Advancements in CID technology allow a high sensitivity, lower noise, improved detection speed and better separation of spectral orders than any of its predecessors. All these performance improvements make it ideal for precise and accurate measurements of both high-grade and low-grade PGE samples.

Table 1. Instrument and method parameters.

Parameter	Setting	
Pump tubing	Sample	Tygon® orange/white
	Internal standard	Tygon® orange/blue
	Drain	Tygon® white/white
Pump speed	45 rpm	
Nebulizer	Glass concentric	
Nebulizer gas flow	0.65 L·min^{-1}	
Spray chamber	Glass cyclonic	
Auxiliary gas flow	0.5 L·min^{-1}	
Coolant gas flow	12 L·min^{-1}	
Center tube	2 mm	
RF power	1150 W	
Repeats	3	
Exposure time	Axial 10 s	
Uptake time	10 s @ 140 rpm (fast uptake)	
Wash time	20 s @ 140 rpm (fast wash)	
Stabilization time	10 s (uptake only)	

Sample preparation

The samples used for this application note are a mixture of low- to high-grade PGEs in the presence of various base metals in high concentrations. The samples were simulated, based on concentrations of PGEs and matrix elements from digested samples used in a previous study. The simulated sample concentrations were chosen to reflect a digestion of 0.25 g material into 100 mL acid (10% HCl/1% HNO_3, TraceMetal™ grade, Fisher Scientific, in deionized water). The pre-digestion sample composition is summarized in Table 2.
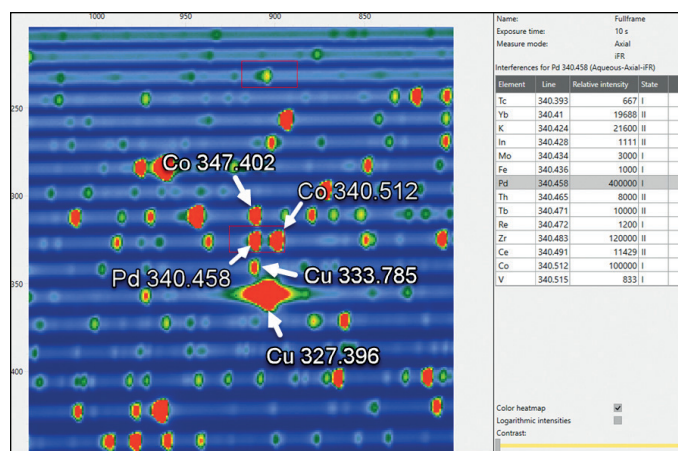
Table 2. Pre-digestion sample composition.

Element		Amount (%)
Matrix elements	Ni	40
	Cu	31
	Co	2.2
	Fe	2.8
	S	24
PG elements	Au	0.060
	Pd	0.080
	Pt	0.140
	Rh	0.020
	Ru	0.060

The samples have sufficiently high concentrations of PGEs 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-OES with full wavelength coverage to make sure that there are no interferences. Three replicate samples were produced to highlight the reproducibility of the iCAP PRO Series ICP-OES.
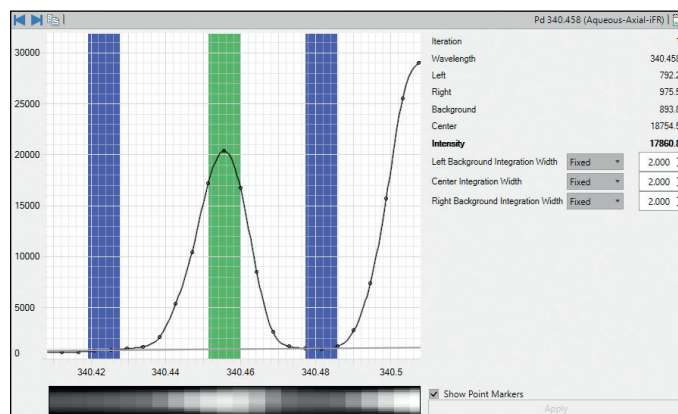
A matrix matched blank, low standard (1 mg·kg^{-1}) and high standard (10 mg·kg^{-1}) were made up for platinum, palladium, rhodium, gold and ruthenium using 1000 mg·kg^{-1} single element stock solutions (SPEX CertiPrep Group, Metuchen, US). An 8 mg·kg^{-1} yttrium internal standard was used for this experiment for maximum accuracy and precision; however, it is not normally required.

Method development and analysis

Wavelength selection was made from a subset of wavelengths using the Fullframe capability of the Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software, which allows a snapshot of the full spectrum to be viewed. A Fullframe was taken from the high standard, which, when combined with the individual subarrays of the prospective element wavelengths, shows that the iCAP PRO Series ICP-OES can achieve enough wavelength separation and coverage to make inter-element correction factors for these samples unnecessary. Palladium is shown in Figure 2 and Figure 3 as an example. All other elements measured in this application note do not have any potential interferences in close proximity like palladium does.

Figure 2. Section of a Fullframe exposure highlighting the Pd 340.458 nm line, showing full separation from the neighboring Co 340.512 nm matrix line within the same order, and full separation of matrix lines in adjacent orders (Co 347.402 nm, Cu 333.785 nm and Cu 327.396 nm).

Figure 3. Subarray for the Pd 340.458 nm line showing complete separation from the Co 340.512 nm line coming from the matrix. Selection areas for left and right baseline points are shown in blue, and the peak integration area is shown in green.

Results

The instrument was calibrated using the standards described and the samples were analyzed directly after. Initial sample weights and post-digestion volumes can be entered directly into the Qtegra ISDS Software to back-calculate measured concentrations in digests to original sample concentrations. Since the samples measured were simulated based on a digest of 0.25 g solid catalyst into 100 mL of acid, 0.25 g and 100 mL were entered into Qtegra ISDS Software as the Amount and Final Quantity, respectively.

Instrument Detection Limits (IDLs) are calculated directly in Qtegra ISDS Software from the standard deviations of the blank measurement and displayed for each calibration graph. Method Detection Limits (MDLs) were assessed by measuring 10 repeats of the blank solution, with Qtegra calculating concentrations accounting for sample dilution. The MDL is three times the standard deviation of these concentrations, and final MDLs reported are the average of three (separate) replicate assessments.

The analyzed data is summarized in Table 3. These results show that the iCAP PRO XP ICP-OES is capable of measuring low levels of PGEs within a highly concentrated matrix of base metals.

The calibration graph of the Pd 340.458 nm line, presented in Figure 4, shows the high correlation and linearity obtained in the analysis even though the samples contain high quantities of base metals. This calibration curve is representative of the linearity obtainable for the measured PGEs with the iCAP PRO XP Duo ICP-OES instrument.
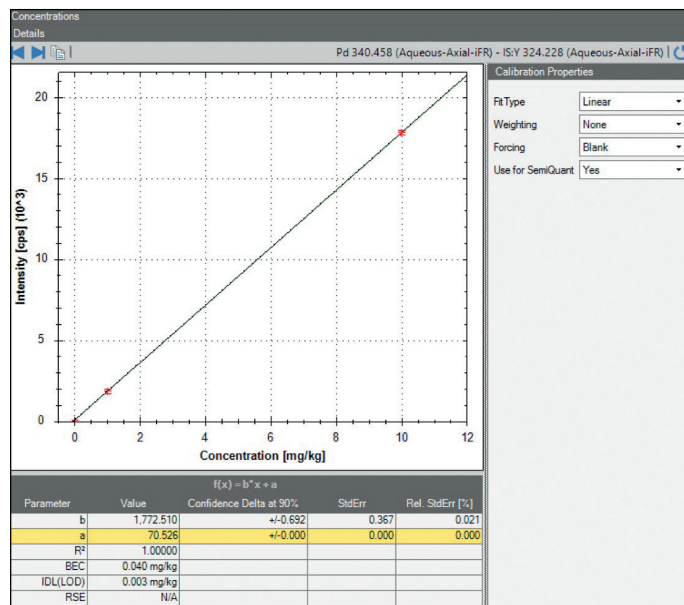

Figure 4. Calibration graph and details of calibration for Pd 340.458 nm.

The calibration curves and all relevant statistics of those calibrations can be checked by accessing the Calibration Details page on the Concentrations page of the LabBook in Qtegra ISDS Software. The calibration curve in Figure 4 shows that the wavelength is linear to at least 10 mg·kg^{-1} for this analysis, but this can be extended to much greater ranges.

The time taken to analyze each sample was 1 min 20 seconds, consistent throughout the entire LabBook. This means that the iCAP PRO XP Duo ICP-OES is capable of screening up to 45 samples per hour, or 360 samples in an 8-hour shift. With a discrete sample introduction system, the throughput achievable on the iCAP PRO XP Duo ICP-OES can be increased even further.

Table 3. Analysis results, instrument detection limits (IDLs), back-calculated concentrations, recoveries and method detection limits (MDLs) for the analysis of PGEs.

Element	Wavelength (nm)	Measured concentration (mg·kg^{-1})	IDL (mg·kg^{-1})	Expected original concentration (%)	Final calculated concentration (%)	Recovery (%)	MDL (%)
Au	267.595	1.537	0.003	0.060	0.061	101.7	0.00010
Pd	340.458	2.057	0.003	0.080	0.082	102.5	0.00014
Pt	265.945	3.499	0.010	0.140	0.140	100.0	0.00021
Rh	343.489	0.505	0.004	0.020	0.020	100.0	0.00009
Ru	267.876	1.521	0.003	0.060	0.061	101.7	0.00010

Conclusion

The data shown in Table 3 demonstrates that the simultaneous analysis of the PGEs within base metal samples was simple with the high resolution and full wavelength coverage capabilities of the Thermo Scientific iCAP PRO XP Duo ICP-OES. The results are excellent even though the plasma conditions were not specifically optimized with the Auto Tune features of the Qtegra ISDS Software. Background and peak selections were simplified using the graphical interface for the measured region subarrays in Qtegra ISDS Software.

The iCAP PRO XP Duo ICP-OES shows its versatility by analyzing samples with high concentrations of matrix metals while still achieving low detection limits and high accuracy. The iCAP PRO XP Duo ICP-OES has shown that it can perform excellently in high concentration matrices. This is due to its high matrix tolerance coming from a robust sample introduction design, and simple maintenance through an easy to remove and clean inner torch box.

Due to its high sample throughput capability, the iCAP PRO XP Duo ICP-OES can be used in manufacturing environments where speed is beneficial to keep processes running. The throughput can be extended further with the use of discrete sample introduction systems.

References

1. https://www.usgs.gov/centers/nmic/platinum-group-metals-statistics-and-information

Find out more at **thermofisher.com/ICP-OES**

Thermo Fisher
SCIENTIFIC