

Assessing the Platinum Group Metal Content in Car Catalyst Recycling Materials by ICP-OES

Accurate determination of palladium, platinum, and rhodium using the Agilent 5800 VDV ICP-OES



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Introduction

Platinum group metals (PGMs)—palladium (Pd), platinum (Pt), rhodium (Rh), ruthenium (Ru), iridium (Ir), and osmium (Os)—are transition metals with similar physical and chemical properties. PGMs have various industrial uses due to their chemical inertness, corrosion resistance, and catalytic properties. The growing demand, high-cost, and limited availability of PGMs has led to alternative ways to mine or recover these elements from lower-grade ores, recycled materials, and catalytic converters (1).

For quality control (QC) purposes and to determine the commercial value of the metals, producers of PGMs from these alternative sources need to assess the concentration of the elements in the source materials. However, the quantitative analysis of PGMs in these sample-types can be challenging by atomic spectroscopy techniques. Low PGM concentrations are typically present, while the samples also contain high concentrations of other elements such as rare earth elements (REEs). Methods must take account of matrix effects arising from the samples, analytical interferences, and the potential for contamination during sample preparation.

Many car catalytic converters contain a PGM-based catalyst. To provide a large surface area for the treatment of exhaust gases, catalytic converters typically comprise a honeycomb-like structure of a ceramic or metal material. The core material is coated or fused with a combination and ratio of PGMs to suit the design (fuel-type and cubic capacity) of a particular engine. The high surface area of PGM-based catalysts facilitates the conversion of pollutants like carbon monoxide (CO) and nitrogen oxides (NO_x) in a vehicle's exhaust gases into less harmful substances. As spent (used) car catalysts are a potential source of PGMs, recycling processes have been developed that focus on recovering the valuable metals for re-use. A typical recycling workflow to prepare source material for PGM-extraction involves the following steps:

- Catalytic converters are sorted by car make, model, and date-range of manufacture. Materials with similar PGM content are then combined.
- The converters are cut open to retrieve the honeycomb material and the ceramic core on which the PGMs are coated.
- The ceramics are roasted to reduce the moisture content and eliminate any unburnt fuel residues (organic content up to 1–2%).
- The materials are then crushed to less than 150 microns.
- Ball milling is often employed to achieve finer particle sizes and to homogenize the materials.

Among the different techniques available to assess the PGM content in these materials, X-ray fluorescence (XRF) is often used before further refinement is carried out. While no additional sample preparation is needed for XRF analysis, the technique may lack the sensitivity needed for the analysis of low grade materials and only provides results for sets of pre-selected elements. To ensure a more accurate and precise analysis of PGMs, a more sensitive technique such as ICP-OES is often used.



Figure 1. Spent car catalysts (left) and partially milled material (right).

In this study, the Pd, Pt, and Rh content of recycled materials obtained from catalytic converters and blended ceramic cores like the ones shown in Figure 1 was measured using an Agilent 5800 Vertical Dual View (VDV) ICP-OES. The samples were prepared using a fast and cost-effective sodium peroxide fusion and aqua regia digestion method.

The 5800 VDV ICP-OES with Agilent ICP Expert Pro software includes several features and smart tools to ensure a robust and reliable method for the analysis of PGMs. The following hardware and software tools provide robustness, aid method development, ensure data quality, and optimize speed of analysis:

- The integrated six-port Advanced Valve System (AVS 6) switching valve maximizes sample throughput. It also minimizes the exposure of the ICP-OES sample introduction system to samples with a high total dissolved solids (TDS) content (2).
- IntelliQuant Screening assists method development by identifying and semi quantifying up to 70 elements in samples with varying matrices (3). IntelliQuant can also be used in routine quantitative analysis, providing a QC check on samples, to check for spectral interferences, and provide sample insight to ensure accuracy throughout the analysis.
- Early Maintenance Feedback (EMF) tracks instrument operational performance and alerts the user to any maintenance tasks (4).

Experimental

Samples

Six samples were provided as fine powders by a local car catalyst recycler. The four catalytic converter recycled materials were taken from two Japanese cars, an American car, and an American pickup truck. Two materials obtained from the blended ceramic cores of catalysts were also included in the study. The accuracy of the 5800 VDV ICP-OES method was assessed by analyzing NIST 2557 Used Auto Catalyst (Monolith) Standard Reference Material (SRM, Gaithersburg, MD, USA).

Sample preparation

Peroxide fusion to avoid the use of HF

Approximately 0.125 g of the fine powdered sample or SRM was weighed directly into a zirconium crucible followed by 1.50 g of Na₂O₂ (97%+ purity). The mixture was fused at a temperature just above the Na₂O₂ melting point for approximately 30 s. When cool, de-ionized (DI) water was added to solubilize the mixture. The solution was then transferred into a beaker fitted with a magnetic stir bar. The solution was acidified using a 20% aqua regia solution comprising 15 mL of concentrated HCl and 5 mL of concentrated HNO₃ and agitated for 30 min to ensure complete degassing of the solution. Finally, the sample was made up to 100 mL with DI water.

A fusion blank was prepared using the same Na₂O₂/aqua regia method but without adding any sample to the crucible.

Standards and spike solution

Calibration standards of Pd, Pt, and Rh at 1, 2, and 5 mg/L were prepared by adding a known amount of each of Agilent 1000 mg/L single element stock solutions to the fusion blank solution. For the spike recovery test of the PGMs at 0.5 ppm, 0.05 mL aliquots of 100 mg/L of Pd, Pt, and Rh were added to 10.00 mL of each sample (post digest).

Instrumentation

All measurements were performed using a 5800 VDV ICP-OES fitted with a SeaSpray glass concentric nebulizer, double-pass cyclonic spray chamber, and an Agilent Easy-fit fully demountable VDV torch with a high-solids 2.4 mm injector. Sample introduction was performed by the integrated AVS 6 and Agilent SPS 4 autosampler. The AVS 6 uses a high-speed positive displacement pump to rapidly fill the sample loop, speeding up the analysis and reducing argon consumption. The valve also reduces maintenance and cleaning requirements of the torch and nebulizer, as lower sample volume passes through the sample introduction system compared to conventional sampling.

Instrument and method parameters are given in Table 1 and the AVS 6 settings are given in Table 2.

Table 1. Agilent 5800 VDV ICP-OES instrument and method parameters.

Parameter	Setting
Read Time (s)	5
Replicates	3
Sample Uptake Delay (s)	0
Stabilization Time (s)	15
Pump Speed (rpm)	12
RF Power (kW)	1.40
Aux Flow (L/min)	1.8
Plasma Flow (L/min)	15.0
Nebulizer Flow (L/min)	0.75
Viewing Mode	Axial
Sample Pump Tubing	Solvaflex white-white
Waste Pump Tubing	Solvaflex Blue-blue
Background Correction	FACT

Table 2. Agilent AVS 6 switching valve system parameters.

Parameter	Setting
Sample Loop Size (mL)	1
Pump Rate - Uptake (mL/min)	22.5
Pump Rate - Inject (mL/min)	12
Valve Uptake Delay (s)	8
Bubble Inject Time (s)	0.5
Pre-emptive Rinse Time (s)	3
Rinse Time (s)	15

IntelliQuant Screening

To better understand the elemental content of the samples and to help with development of the quantitative method, each sample was quickly scanned using IntelliQuant Screening. A custom IntelliQuant calibration was prepared using the Agilent IntelliQuant calibration kit (p/n 5191-3932) in a 1.5% Na₂O₂/aqua-regia matrix.

The semiquantitative results can be presented visually to aid interpretation, including as a periodic table ‘heat map’, a pie chart, or a bar chart. Per the heat map shown in Figure 2, the semiquantitative data (reported in mg/L or %) revealed the presence Rh in one of the Japanese car catalyst samples, as well as other unexpected elements. It is likely that Zr and Hf are contaminants that leached from the crucible used during sample preparation, N and Cl are from the aqua regia used in digestion, and Si and Al are from the catalyst ceramic core. The presence of REEs including La, Ce, Pr, and Nd, which are often used as additives during the manufacture of modern catalytic converters, were also confirmed by IntelliQuant.

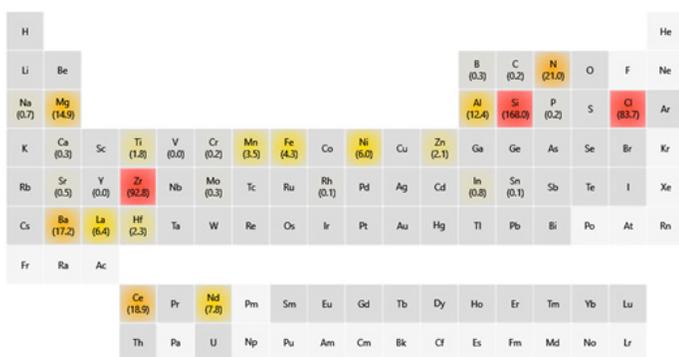


Figure 2. IntelliQuant heat map of the fusion solution of a Japanese car catalyst sample showing which elements are present in the sample, including Rh, and the semiquantitative concentrations in solution (mg/L, except for Na where the concentration is expressed in %).

Some of the ceramic material analyzed in this work comprised a special molybdenum (Mo)/cobalt (Co) formulation and both elements were reported in the IntelliQuant results. Lead (Pb) would only be found at a significant concentration in a material that predated the ban on Pb as a fuel additive. Other elemental contaminants are due to the unpredictable and complex matrix that is typical of recycling materials.

IntelliQuant uses smart algorithms to collect semiquantitative analysis data over multiple wavelengths for up to 70 elements in each of the car catalyst samples. The IntelliQuant Screening tool greatly helped to identify and confirm the presence of elements that could lead to spectral interferences, as discussed in the next section.

Background correction using FACT modeling

REE additives found in modern car catalyst samples lead to the generation of line-rich optical emission spectra and spectral interferences on Pd, Pt, and Rh, as summarized in Table 3. To correct for the interferences, the Agilent Fast Automated Curve-fitting Technique (FACT) background correction technique was used (5).

Table 3. Spectral interferences used in FACT modeling.

Element and Wavelength (nm)	Interferents
Pd 360.955	Zr, Hf, Ce, Mo, La, Nd, Co, Ni, Ti
Pt 214.424	Zr, Hf, Mo, La, Cd, Pr, Cr
Rh 343.488	Zr, Ce, Hf, Mo, Nd, Pr

FACT provides an alternative to Inter-Element Correction (IEC) and is most effective when an interferent partially overlaps the analyte peak. For low-level analysis of PGMs, REEs can add significant spectral content in the range of the Pd, Pt, and Rh analyte emission lines. FACT automatically models the relative contribution of the analyte, interferent or interferents, and background signals in the measured spectra, providing an accurate result for Pd, Pt, and Rh. FACT does not require knowledge of the precise concentration of any interferents, which is beneficial for routine applications.

The primary analytical line for Pd at 340.458 nm lies close to a strong Zr emission line. Since significant amounts of Zr and Hf leach from the crucible during the fusion process, this line is susceptible to the fusion process and the age of the crucible. Also, the presence of a strong Zr line negatively impacts the method detection limit (MDL) of Pd. The Pd 360.955 nm line was found to be a good compromise between selectivity and sensitivity. For the car catalyst samples, Ce 360.969 nm is the main spectral interference on Pd 360.955 nm. However, the interference can easily be corrected using FACT, as shown in Figure 3.

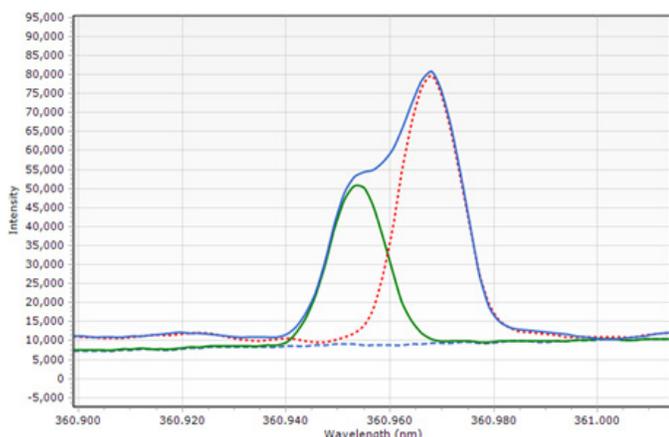


Figure 3. FACT model for correction of a Ce interference on Pd 360.955 nm (total signal shown by the solid blue line). The overall contribution of all interferents (red dashed line), predominantly Ce 360.969 nm in this case, is partly overlapping the Pd 360.955 nm (solid green) analyte line. The signal from the blank is shown by the light blue dashed line.

The Pt 214.424 nm line does not typically suffer from significant spectral interferences. The concentration of Pt found in car catalyst recycling materials ranges from tens to thousands of ppm (mg/kg), depending on the car make (as shown in Table 7). To ensure that the analytical method could analyze recycled materials that contained only trace levels of Pt, FACT correction was applied.

The primary analytical line for Rh at 343.488 nm is subject to a strong Zr spectral interference and other element-interferences (notably from Ce and Pr). These interferences are shown by a typical spectrum of Rh at 343.488 nm for a car catalyst recycling material (Figure 4). Spectral interferences originating from the different components overlap the Rh signal. Correcting these interferences using IEC would be challenging, because more than one element (notably Ce, Hf, and Zr), commonly found in car catalysts, contribute to the signal at 343.488 nm, i.e., the analytical line of Rh. Therefore, multiple IEC factors would be required to accurately quantify Rh, while this situation is easily managed using FACT modeling, as presented in this work.

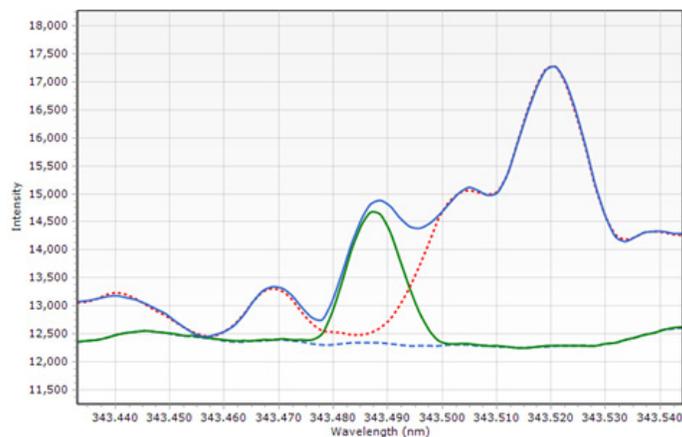


Figure 4. FACT model for correction of Zr, Ce, and Pr interferences on Rh (total signal shown by the solid blue line). The red dashed interference line is overlapping the Rh 343.488 nm (solid green) line. The signal from the blank is shown by the light blue dashed line.

Results and discussion

Method detection limits

To measure the MDLs of Pd, Pt, and Rh, other commonly found elements in the recycling materials such as Al, Ce, Co, Fe, La, Nd, Ni, and Pb were added to the fusion blank. The average concentration for each of these elements was estimated from the IntelliQuant Screening data obtained for all the samples. This strategy for determining the MDLs was found to be more representative of the complexity of real-life samples than using a fusion blank matrix solely spiked with Pd, Pt, and Rh. The MDLs and limits of quantification (LOQs) reported in Table 6 were calculated as 3 x standard deviation (sd) and 10 x sd of the spiked fusion blank, respectively. The limits are much lower than the cut-off grade of recycling materials that require a relatively high PGM content to be commercially viable.

SRM analysis

In addition to Pd, Pt, and Rh, the NIST 2557 SRM contains a large amount of Pb (1.39%), as it predates the ban on Pb as a fuel additive. Pb is known to deactivate the catalytic conversion process. The SRM does not contain appreciable amounts of REEs, other than Ce and La, nor special additives like Mo or Co, which are found in large amounts in some ceramic samples. Therefore, developing an ICP-OES method based solely on good recovery of this SRM would be an oversimplification of the challenge associated with quantifying PGMs in car catalyst recycling materials. However, the NIST 2557 Used Auto Catalyst SRM was included in this work to confirm the accuracy of the quantitative method using the 5800 VDV ICP-OES. The recoveries for Pd, Pt, and Rh were within $\pm 3\%$ of the certified value, as shown in Table 5, confirming the suitability of the method for the application.

Spike-recovery test

Spike recovery tests were performed to test for matrix effects. The Japanese car catalyst make #2 and American car catalyst samples were spiked at 400 mg/kg (+0.5 mg/L in the fused samples) and 240 mg/kg (+0.3 mg/L), respectively. The spiked amount of each element in each of the samples was recovered within $\pm 10\%$ for all three elements, as shown in Table 5. The results further confirm the accuracy of the method, despite the variation in composition between the samples.

Table 6. Recoveries of Pd, Pt, and Rh in the NIST Used Auto Catalyst SRM and spike recovery results for Pd, Pt, and Rh added to car catalyst recycling materials.

Element, Wavelength (nm)	MDL (mg/kg)	LOQ (mg/kg)	NIST 2557 Used Auto Catalyst			Japanese Car Catalyst Make #2			American Car Catalyst		
			Certified Value (mg/kg)	Measured Value (mg/kg)	Recovery %	Measured Value (mg/kg)	Measured Spiked Value (mg/kg)	Spike Recovery %	Measured Value (mg/kg)	Measured Spiked Value (mg/kg)	Spike Recovery %
Pd 360.955	6	22	233.2	240.2	103	164	554	97	227	468	100
Pt 214.424	5	15	1131	1115	99	2197	2613	104	57.6	315	107
Rh 343.488	3	9	135.1	133.2	99	504	913	102	139	396	107

Quantitative PGM analysis of recycled car catalysts

Linear calibration curves, with correlation coefficients >0.9999, were achieved for Pd, Pt, and Rh. Table 6 shows the quantitative results for the three PGMs from the analysis of the ceramic mix and car catalyst recycling materials. The relative proportions between all three precious metals varied significantly from sample-to-sample, and the level of PGMs in the car catalyst samples varied depending on the make of car. In all materials, the concentration of Pd ranged from trace level to 3131 mg/kg; Pt ranged from 46 to 2611 mg/kg; and Rh ranged from trace level to 599 mg/kg.

Table 6. PGM content of ceramic mixes and car catalyst recycling materials determined using the Agilent 5800 VDV ICP-OES.

Sample	Measured Concentration, mg/kg		
	Pd 360.955 nm	Pt 214.424 nm	Rh 343.488 nm
Industrial ceramic mix #1	< LOQ	46.8	< MDL
Industrial ceramic mix #2	3131	58.8	357
Japanese car catalyst make #1	204	92.5	139
Japanese car catalyst make #2	195	2611	599
American car catalyst	227	57.6	139
American pickup truck catalyst	146	934	448

IntelliQuant Screening carried out on the samples highlighted a great variability in the composition of the samples. With the aim of developing a method that is as robust as possible for the analysis of recycled materials, which comprise highly variable matrices, the presented work accommodates many interferences. However, it is possible that the method has not accounted for all potential interferences arising from the sample matrices of other recycled samples. If some interferences are not accounted for in the method, the accuracy of the PGM content in such materials could be affected. To ensure accurate data, it is recommended to scan the samples using IntelliQuant Screening to check the contents of specific samples before developing the quantitative method.

Long-term stability of the ICP-OES method

To assess the stability of the 5800 VDV ICP-OES, Pd, Pt, and Rh were measured in the actual sample digests. The sample digests typically contained 0.25 mg/L of Pd, 1.15 mg/L of Pt, and 0.20 mg/L of Rh (equivalent to 190, 925 and 170 mg/kg, respectively, in the original sample). The sample digests were measured throughout the continuous 90-minute acquisition against the same calibration curve. The sample-to-sample time was 62 s. The long-term stability curve (Figure 5) shows no signs of instrumental drift or carryover effects. The precision of the method was demonstrated by the relative standard deviation (%RSD) of below 1.4% for the repeated measurements of the three elements over 90 minutes.

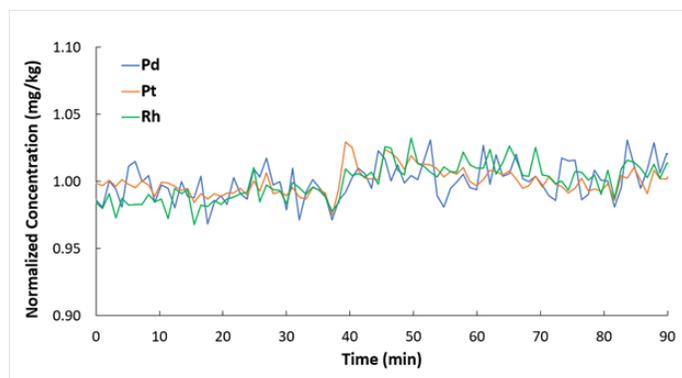


Figure 5. Repeated measurement of Pd, Pt, and Rh in the sample digests over a nonstop, 90-minute run without recalibration using the Agilent 5800 VDV ICP-OES.

Conclusion

The Agilent 5800 VDV ICP-OES demonstrated excellent accuracy and precision for the determination of Pd, Pt, and Rh in reclaimed PGM-source materials obtained from catalytic converters and blended ceramic cores. The samples were prepared within a few minutes using sodium peroxide fusion and aqua regia, avoiding the use of HF. The integrated AVS 6 sampling valve reduced the exposure of the ICP-OES sample introduction system to the high matrix samples, enhancing the robustness and analytical speed of the method.

IntelliQuant Screening of the samples highlighted a large variability in the elemental composition of the samples. Identifying many interferences helped to develop a robust method that was suitable for the unpredictable composition of recycled materials.

Combining the fast sample preparation procedure with the high-performance capabilities of the 5800 VDV ICP-OES enables the routine measurement of PGMs in recycling materials. The method is ideal for assessing the potential commercial value of recycled materials based on the concentration of PGMs. The data can be used to inform the viability of recovering PGMs for re-use.

References

1. Zientek, M.L., Loferski, P.J., Parks, H.L., Schulte, R.F., and Seal, R.R., II, Platinum-group elements, chap. N of Schulz, K.J., DeYoung, J.H., Jr., Seal, R.R., II, and Bradley, D.C., eds., Critical mineral resources of the United States—Economic and environmental geology and prospects for future supply: U.S. Geological Survey Professional Paper 1802, 2017, N1–N91, <https://doi.org/10.3133/pp1802N>
2. Reduce Costs and Boost Productivity with the Advanced Valve System (AVS) 6 or 7 Port Switching Valve System, Agilent publication, [5991-6863EN](#)
3. Agilent IntelliQuant Screening, Agilent publication, [5994-1518EN](#)
4. Early Maintenance Feedback for ICP-OES, Agilent publication, [5994-2164EN](#)
5. Real-time Spectral Correction of Complex Samples using FACT Spectral Deconvolution Software, Agilent publication, [5991-4837EN](#)

www.agilent.com/chem/5800icp-oes

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