Application note

Elemental analysis

Determination of platinum, palladium, and rhodium in spent automotive catalytic converters

Introduction

Highly variable compositions and volatile prices of platinum group metals (PGMs) such as platinum (Pt), palladium (Pd), and rhodium (Rh) are, more than ever, important factors in the purchase, trading, and recycling of spent catalytic converters. In 2020, the demand for Pt, Pd, and Rh totaled 215, 308, and 31.2 tons. About 32% of total Pt, 85% of total Pd, and 90% of total Rh were consumed by the automotive catalyst industry[1]. The same year 33.7 tons of Pt, 41.2 tons of Pd, and 7.3 tons of Rh[1] were recovered from recycling activities, mainly from spent catalytic converters, representing about $12 billion of the cumulative average price of fine metals in 2020.

Depending on supply, demand, and speculation, Pt, Pd, and Rh prices have fluctuated strongly over the last 15 years (see figure 1). These fluctuations and the tightening of emission legislation directly affected the compositions of the catalysts, which themselves had a strong influence on the demand. Because of a supply deficit, Pd, and Rh prices spiked during 2020-2021.

The value of the PGM composition of a single catalytic converter can vary from less than $100 to more than $1000. When traded, these materials are often ground into a powder and blended; hence it is crucial for traders and recyclers to be able to:

The physical recycling begins with decanning, or the removal of the shell and extraction of the honeycomb-shaped material inside the catalytic converter.

- Identify single catalytic converters or blends containing high levels of PGMs
- Pay or get paid a fair price
- Catch fraudulently blended and adulterated material

It is invaluable to determine the contents of Pt, Pd, and Rh of spent automotive catalytic converters accurately in real-time to maximize profit and avoid considerable financial loss.

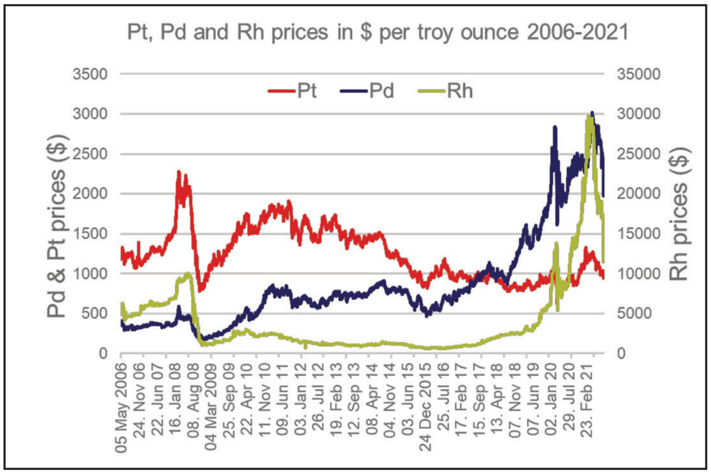

Figure 1: Pt, Pd and Rh prices 2006-2021 (Data collected from [2])

Thermo Scientific™ Niton™ Handheld XRF Analyzers

We offer an entire range of handheld XRF analyzers to accurately quantify Pt, Pd, and Rh in automotive catalytic converters:

- The Niton XL2 501 analyzer offers great value for money while maintaining a high level of performance for PGMs
- The Niton XL3t 501 and 801 analyzers, our mid-range models equipped with 50 kV and a filter changer, allow for optimum beam conditions and provide more precise and accurate results for PGMs
- The Niton XL3t 951 and 981 GOLDD+ analyzers are high-end models equipped with a 50kV tube and a large silicon drift detector. The Niton XL3t 951 and 981 GOLDD+ analyzers also detect light elements such as magnesium, aluminum, or silicon and have increased sensitivity to detect low levels of PGMs.
- The Niton XL5 Plus analyzer is the top of the line model with state-of-the-art hardware including an extra-large silicon drift detector and a 5W tube offering ultimate sensitivity. Productivity is further enhanced due to shorter measurement time.

The pre-calibrated Automotive Catalyst Mode uses a fundamental parameter approach (FP), an algorithm that corrects using theoretical constants for the influence of all elements contained in the sample. FP is suitable in analyzing the spent materials that, nowadays, show unprecedented variability in their composition. Measuring rare earth elements and zirconium, lead, and other elements potentially present at high levels in spent catalysts is a critical point in obtaining accurate results for Pt, Pd, and Rh.




Models	XL2 501	XL3t 501/801	XL3t 951/981 GOLDD+	XL5 Plus
Tube Max Power[1]	2W	2W	2W	5W
Tube max voltage[2]	45 kV	50 kV	50 kV	50 kV
Detector technology[3]	Si-PIN	Si-PIN	Large SDD	Extra-Large SDD
Number of beams for PGMs / total number of beams[4]	1 for PGMs/1	2 for PGMs/3	2 for PGMs/4	2 for PGMs/4
Typical total measurement time	80 seconds	120 seconds	60 seconds	30 seconds
Limits of detection (3σ) @ typical measurement time [5]	Pt: 20 ppm Pd: 13ppm Rh: 13 ppm	Pt: 16 ppm Pd: 7 ppm Rh: 6 ppm	Pt: 10 ppm Pd: 5 ppm Rh: 5 ppm	Pt: 9 ppm Pd: 3 ppm Rh: 3 ppm
Accuracy[6]	★★	★★★	★★★★	★★★★
Precision[7]	★	★★	★★★	★★★★
Sensitivity[8]	★	★★	★★★	★★★★
Productivity[9]	★	★★	★★★	★★★★

1.Higher power provides better precision and allows shorter measurements at constant precision. Sensitivity is improved also. 2.Higher voltage obtains better precision and accuracy for element such as Pd, Rh, and rare earth elements. 3. Silicon drift detector (SDD) technology collects higher count rate and improves precision, sensitivity, and enable light element detection vs. Silicon-positive-intrinsic-negative (Si-PIN) technology. 4. More beam conditions with different filters mean better precision and sensitivity for lines with different energies. 5. The limits of detection depend on the testing time, the interferences/matrix, the level of statistical confidence. 6. Indicates the degree of closeness to the true value. 7. Indicates how repeatable and reproducible a measurement is. 8. Indicates the ability to detect small amounts of PGMs. 9. Economic productivity: sample throughput and economic recovery of Pt, Pd, and Rh

Sample preparation

The collected catalysts with ceramic substrate undergo a decanning operation, which is the extraction of the ceramic with honeycomb structure from the steel case. Automotive catalyst material is made of a ceramic substrate, mostly cordierite coated with a PGM-containing wash coat. Therefore, the entire ceramic is sorted, crushed, milled, and often blended with other catalysts. In contrast, converters with a metallic substrate are first shredded or milled; then, the metallic parts are separated using magnets and winnowing from the wash coat powder containing precious metals. Because of this enrichment, the PGM content of wash coats from metallic catalytic converters is mostly much higher than for converters made of ceramics. In both cases, the materials are pulverized to typically less than 250 µm particle size, loaded in XRF cups for analysis, and placed in a test stand.

Materials are pulverized to a maximum 250um and loaded in XRF sample cups or sample bags for analysis

Table 1: Typical results of analysis for a commercially available automotive catalyst certified reference material

Materials/Elements	Niton value (ppm)	Certified value (ppm)
BAM ERM-504a		
Pt	1495 ± 41 (2σ)	1414 ± 15
Pd	1583 ± 19 (2σ)	1596 ± 6
Rh	210 ± 8 (2σ)	210 ± 4

Results

The results for the analysis of one commercially available reference material are given in Table 1. The values of Pt, Pd, and Rh measured with the Niton XL5 Plus analyzer agree very well with certified values.

Figures 2 through 4 show the correlation curves between lab results (fire assay+ICP) vs. measured concentrations with the Niton XL5 Plus analyzer. For all the elements determined in 120 samples, there is an excellent linear correlation over a wide range of concentration between lab and measured values: both the slopes and the coefficients of determination R^2 are close to 1. The average relative difference between laboratory and measured values was 5.0 % for Pt, 3.9 % for Pd, and 2.9 % for Rh. These results demonstrate the robustness of the analysis against considerable matrix changes and sometimes very high concentrations found in the 120 samples for relevant concomitant elements like cerium, lanthanum, zirconium, lead, iron, or chromium.

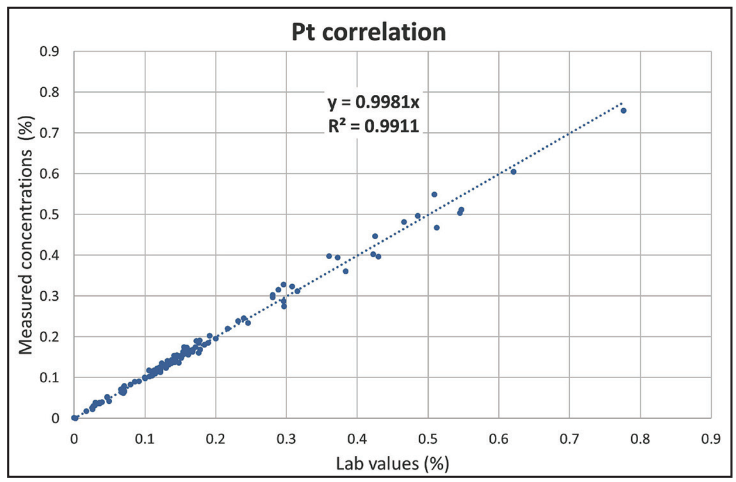

Figure 2: Correlation curve for Pt

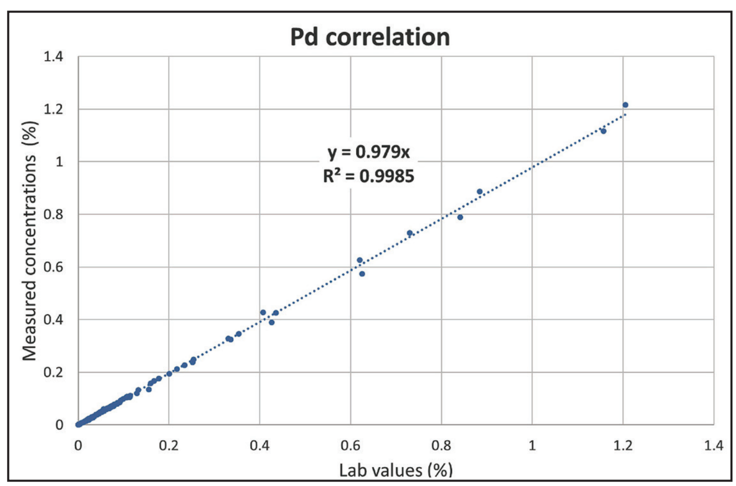

Figure 3: Correlation curve for Pd

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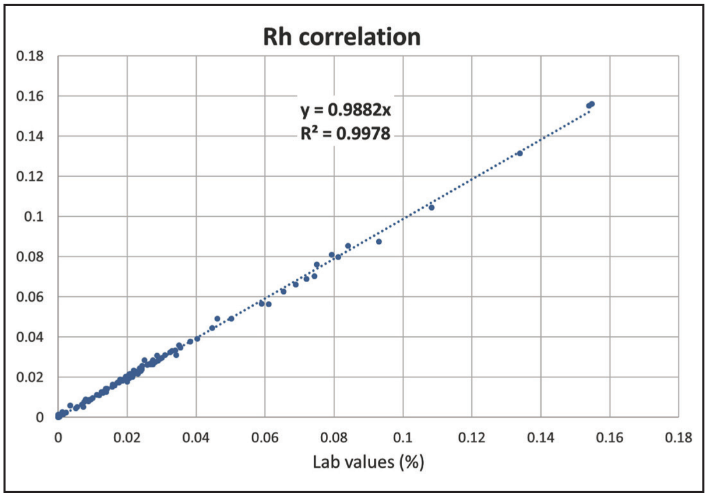

Figure 4: Correlation curve for Rh

Proficiency test

Thermo Fisher participated as a laboratory in a proficiency test organized by the well-established XRF company Fluxana [3] to analyze two samples FLX-CRM 132 and FLX-CRM 133, under lab code #9. The results are shown in Table 2 and the report issued by Fluxana [4], which again demonstrates the excellent accuracy of the analysis obtained using the Thermo Fisher Niton XL3t 980 analyzer (same instrument as XL3t 951/981).

Table 2: Results of the proficiency test

	Mean Niton XL3t 980 Value ± sd (ppm)	Certified Value ± uncertainty (ppm)
FLX-CRM 132		
Pd	1668±18	1673±27
Pt	1758±16	1770±73
Rh	284±6	295±12
FLX-CRM 133		
Pd	1062±10	1075±40
Pt	460±4	465±28
Rh	232±4	242±18

Conclusion

Ceramic catalytic converters from gasoline or diesel engines, wash coats from metallic converters, and blends of materials are all analyzed accurately using Niton handheld XRF analyzers. Niton XRF analyzers are the ideal tool for dependable analysis for people and companies trading and recycling spent automotive catalytic converters.

- The main benefits of using Niton XRF analyzers are:
- Excellent accuracy proven over many years of operation
- Real-time analysis
- Ease of use vs. lab analysis requiring special know-how
- Fast return on investment and low cost of ownership

References

1. Johnson Matthey, Pgm market report February 2021 http://www.platinum.matthey.com/
2. http://www.platinum.matthey.com/
3. https://fluxana.com/products/reference-materials/proficiency-tests
4. https://fluxana.com/images/products/Ringversuch/FINAL_Report_RV_2017_01.pdf

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