APPLICATION NOTE

Determination of Platinum, Palladium, and Rhodium in Spent Automotive Catalytic Converters

Using Niton handheld XRF Analyzers

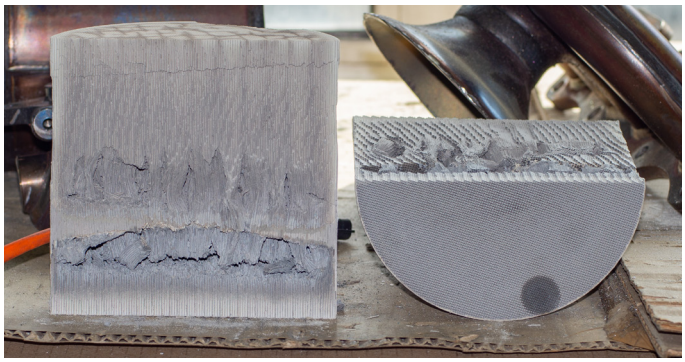
Introduction

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 respectively 215, 308, and 31.2 tons. About 32% of the total Pt, 85% of the total Pd, and 90% of the 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 at the 2020 cumulative average price of fine metals a total value of about $12 Billion.

Depending on supply, demand, and speculation, prices of Pt, Pd, and Rh have been fluctuating strongly over the last 15 years (see figure 1). These fluctuations, as well as tightening of emission regulation, had a direct incidence on the compositions of the catalysts which themselves had a strong influence on the demand. Because of a deficit in the supply, the prices of Pd and Rh have spiked in 2020-2021.

The value in terms of PGM composition of a single catalytical 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:

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



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

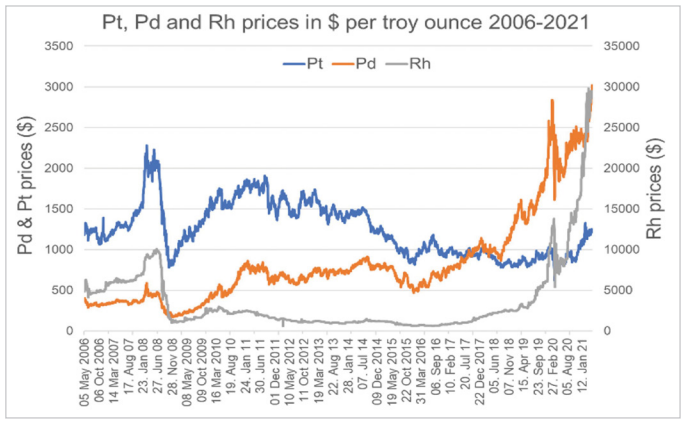


Figure 1: Pt, Pd, and Rh prices 2006-2021[2]

To maximize profit and avoid considerable financial losses, it is invaluable to be able to determine accurately and in real-time the contents of Pt, Pd, and Rh in spent automotive catalytical converters.

ThermoFisher SCIENTIFIC

Thermo Scientific™ Niton™ Handheld XRF Analyzers

We offer an entire range of handheld XRF analyzers to accurately quantify Pt, Pd, and Rh in automotive catalytical 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 allowing for optimum beam conditions, provide more precise and accurate results for PGMs
- The XL3t 951 and 981 GOLDD+ are the high-end models equipped with a 50kV tube and a high performance, large-area silicon drift detector. These analyzers offer the best precision and accuracy. The XL3t 951 and 981 GOLDD+ also detect light elements such as magnesium, aluminum, silicon, and phosphorous and are more sensitive to detect low levels of PGMs, while enhancing productivity with 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 for the analysis of the spent materials which nowadays show unprecedented variability in their composition. Measuring rare earth elements, as well as zirconium, lead, and other elements potentially present at high levels in spent catalysts is a key consideration in obtaining accurate results for Pt, Pd, and Rh.

Sample Preparation

The collected catalysts with ceramic substrate undergo a de-canning operation which is the extraction of the ceramic with honeycomb structure from the steel case. Automotive catalyst material is made of either a ceramic substrate or a metallic substrate. The ceramic substrate is 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 and then the metallic parts are separated using

Model	XL2 501	XL3t 501/801	XL3t 951/981 GOLDD+
			
Tube max voltage[1]	45 kV	50 kV	50 kV
Detector technology[2]	Si-PIN	Si-PIN	SDD
Optimum number of beams for PGMs / total number of beams[3]	1 for PGMs/1	2 for PGMs/3	2 for PGMs/4
Typical total measurement time	80 seconds	120 seconds	60 seconds
Limits of detection (3σ)[4]	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
Accuracy[5]	★★	★★★	★★★
Precision[6]	★	★★	★★★
Sensitivity[7]	★	★★	★★★
Productivity[8]	★	★★	★★★

1. Higher voltage provides better precision and accuracy for elements such as Pd, Rh, and rare earth elements **2.** Silicon drift detector (SDD) technology allows the collection of higher count rates and thus improves precision, sensitivity, and enables light element detection vs. Silicon-positive-intrinsic-negative (Si-PIN) technology. **3.** More beam conditions with different filters optimizes measuring conditions and means better precision and sensitivity for analytical lines with different energies. **4.** The limits of detection are given for cordierite and depend on the testing time, the interferences/matrix, and the level of statistical confidence **5.** Indicates the degree of closeness to the true value **6.** Indicates how repeatable and reproducible a measurement is. **7.** Indicates the ability to detect small amounts of PGMs. **8.** Economic productivity: sample throughput and economic recovery of Pt, Pd, and Rh.

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

magnets and winnowing from the wash coat powder containing precious metals. Because of this enrichment, the PGM content of wash coats from metallic catalytical converters is generally much higher than for converters made of ceramics. In both cases the materials are pulverized to typically less than 250 µm particle size and loaded in XRF cups for analysis and placed in a test stand.

Results

The results for the analysis of 3 commercially available reference materials are given in table 1. The values of Pt, Pd, and Rh, measured with a Niton XL3t 951 GOLDD+ analyzer, agree very well with the certified values.

Figures 2 through 4 show the correlation curves between lab results (fire assay+ICP) vs. measured concentrations with the Niton XL3t 951 GOLDD+. For all the elements determined in 130 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 value was 4.4% for Pt, 2.8 % for Pd, and 3.8% for Rh. These results demonstrate the robustness of the analysis against considerable matrix changes and

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

Materials/ Elements	Niton value (ppm)	Certified value (ppm)
NIST SRM 2557		
Pt	1110 ± 20 (2σ)	1131 ± 11
Pd	230 ± 10 (2σ)	233.2 ± 1.9
Rh	130 ± 10 (2σ)	135.1 ± 1.9
NIST SRM 2556		
Pt	690 ± 30 (2σ)	697.4 ± 2.3
Pd	310 ± 10 (2σ)	326 ± 1.6
Rh	40 ± 10 (2σ)	51.2 ± 0.5
BAM ERM-504		
Pt	1720 ± 60 (2σ)	1777 ± 15
Pd	290 ± 10 (2σ)	279 ± 6
Rh	330 ± 20 (2σ)	338 ± 4

sometimes very high concentrations found in the 130 samples for relevant concomitant elements like cerium, lanthanum, zirconium, lead, iron, or chromium.

Proficiency Test

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

Conclusion

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

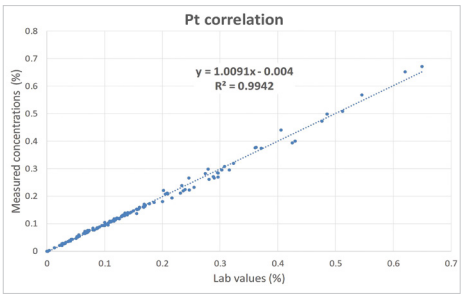


Figure 2: Correlation curve for Pt

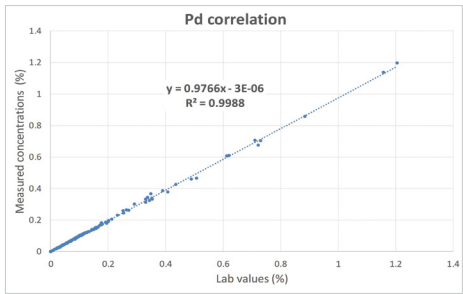


Figure 3: Correlation curve for Pd

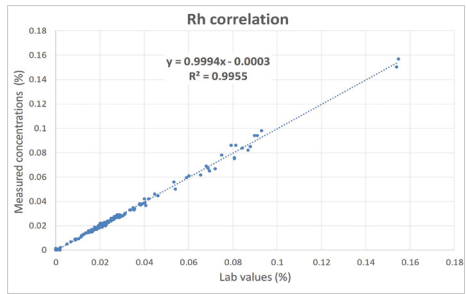


Figure 4: Correlation curve for Rh

The main benefits of using Niton 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

Table 2: Results of the proficiency test

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

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