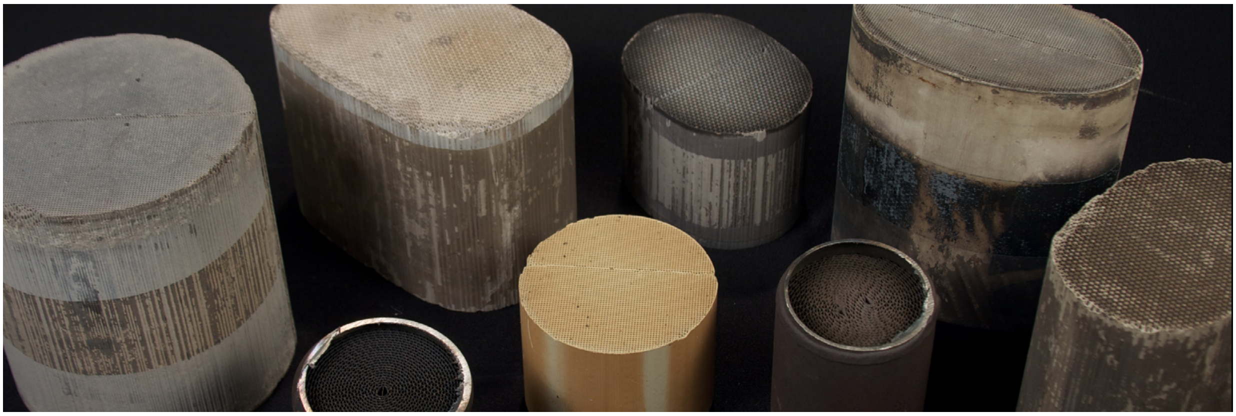
Determination of Platinum, Palladium, and Rhodium in Spent Automotive Catalytic Converters with Thermo Scientific Niton XL3t Series Analyzers



Introduction

More than ever, highly variable compositions and volatile prices of platinum (Pt), palladium (Pd), and rhodium (Rh) are important factors in the purchase and recycling of spent catalytic converters. In 2010, the global sales of Pt, Pd, and Rh totaled, respectively, 245, 299, and 27.2 tons. About 46% of the total Pt, 57% of the total Pd, and 77% of the total Rh were consumed by the automotive catalyst industry. That same year, 33.7 tons of Pt, 41.2 tons of Pd, and 7.3 tons of Rh were recovered from the recycling of spent catalytic converters [1], representing a total value of $3 billion at the 2010 cumulative average price of fine metals.

Depending on the supply, the demand, and speculation, the price of these three elements has fluctuated strongly over the last 20 years (see Figure 1). These fluctuations, as well as the tightening of emission legislation, have had a direct correlation on the composition of the catalysts, which themselves have had a strong influence on the demand.

The average concentration and the ratio of Pt and Rh were more or less constant 20 years ago [2], so a simple weighting was sufficient to arrive at a good estimation of the precious metal content. Currently, the composition, which depends on the cubic capacity of the engine and the type of fuel used, varies dramatically. The formulation can consist of only Pt, or various ratios of Pt-Pd-Rh, Pt-Rh, and Pd-Rh [2]. Today's recycled catalytic converters come from cars manufactured, on average, 10 to 15 years ago [3]. Further, the amounts of recoverable Pt, Pd, and Rh in each can range from 1-2 grams for a small car to 12-15 grams for a big truck in the US. The corresponding value in precious metals ranges from $25 to a few hundred dollars per vehicle [4]. Moreover, the trade of ground-up material sold as catalysts can be very dangerous because of possible alterations, which can mean inclusion of lead or spent nickel-cadmium batteries.

To avoid considerable financial losses, there is a definite advantage in having the ability to determine quickly and accurately the contents of Pt, Pd, and Rh in spent catalytic converters at the collector's site or in the refineries. Thermo Scientific Niton XL3t x-ray fluorescence (XRF) Series analyzers are the ideal instruments for achieving this objective.

Thermo Scientific Niton XL3t and Niton XL3t GOLDD+ Handheld XRF Analyzers

Our advanced, Niton® XL3t Series analyzers were the first handheld XRF instruments equipped with a

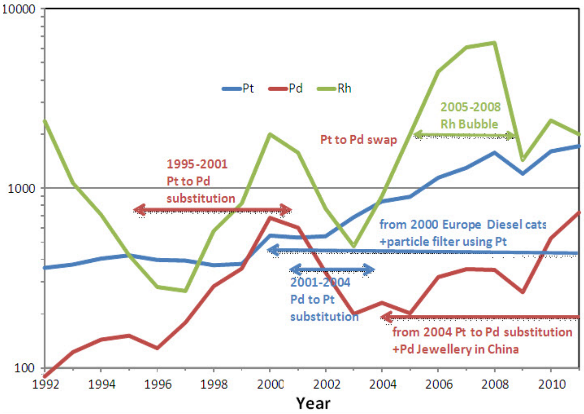


Figure 1: Pt, Pd, and Rh prices from 1992-2011 (data collected from references [3] and [5])

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

high-performance x-ray tube (50 kV/100µA max.), enabling them to quantify rare earth elements (REEs) such as cerium, lanthanum, praseodymium, and neodymium based on their interference-free K-lines. Fundamental Parameter (FP) analysis, an algorithm that corrects using theoretical constants for the influence of all elements contained in the sample, is used to measure catalyst composition. FP is suitable in the analysis of the spent catalytic materials, which show unprecedented variability in their composition. The correct knowledge of the rare earth element, as well as zirconium, lead, and other elements that are potentially present at high levels in spent catalysts is a key factor in using FP to obtain accurate results for Pt, Pd, and Rh.

Additionally, the Niton XL3t GOLDD+ analyzer with Thermo Scientific Geometrically Optimized Large Area Drift Detector (GOLDD™) technology and higher performing x-ray tube (50 kV/200µA max.) has light element capabilities (Mg, Al, Si, P) and better sensitivity.

Methodology

Automotive catalyst material is made either of a ceramic substrate, mostly cordierite coated with a precious metal containing a wash coat, or of a metallic substrate with an aluminum oxide wash coat also containing precious metals. There is no technique for analyzing non-homogeneous materials like catalytic converters directly without sample preparation. Therefore, the collected catalysts with ceramic substrate undergo a “de-canning” operation, which is the extraction of the ceramic with a honeycomb structure from the steel case. All of the ceramic is then sorted crushed, milled, and mostly blended with other catalysts [2]. In contrast, converters with a metallic substrate are first shredded or milled, and then the metallic parts are separated using magnets and winnowing from the wash coat powder containing precious metals [2]. Because of this enrichment, the precious metal content of these wash coat samples is usually much higher than that for milled ceramics. In both cases, the materials are pulverized to a maximum 250µm and loaded in XRF sample cups or sample bags for analysis.

The total measurement time for the Niton XL3t analyzer and Niton XL3t GOLDD+ analyzer was 120s respectively. Pt was measured with the main filter for one half of the total measurement time, whereas Pd and Rh were measured with the high filter for the second half.

Results

The results for the analysis of three commercially available certified reference materials (CRMs) are shown in Table 1. The values of Pt, Pd, and Rh measured with the Niton XL3t and Niton XL3t GOLDD+ analyzers show excellent agreement with the certified values. Figures 2 through 4 show the correlation curves for certified results (fire assay+ICP) vs. measured concentrations for Pt, Pd, and Rh. The coefficient of determination (R^2) for each element is provided in the figures. The R^2 value is a measure of how closely the data sets correlate with each other, where a perfect correlation would have an R^2 of 1. For all the elements determined in 130 samples, there is an excellent linear correlation over a wide range of concentration between certified and measured values: both the slopes and the coefficients of determination R^2 are close to 1. The average of the relative difference between certified and measured value was 4.1% for Pt, 2.8 % for Pd, and 3.7% for Rh. These results demonstrate the robustness of the analysis against considerable matrix changes and sometimes very high concentrations of relevant concomitant elements such as cerium, lanthanum, zirconium, lead, iron, or chromium that were found in the 130 samples (see Figure 5).

Materials/ Elements	XRF Analyzer 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

Table 1. Results of analysis for commercially available automotive catalyst CRMs

Limits of detection (LODs) for Pt, Pd, and Rh in pure cordierite are given in Table 2 for both the Niton XL3t analyzer and the Niton XL3t GOLDD+ analyzer. The superior sensitivity of Niton XL3t GOLDD+ enabled us to achieve a higher sample throughput while halving the measurement time.

Element	Niton XL3t GOLDD+ (30s/filter)	Niton XL3t (60s/filter)
The limits of detection depend on the testing time, the interferences/matrix, the level of statistical confidence		
Pt	10 ppm	16 ppm
Pd	5 ppm	7 ppm
Rh	5 ppm	6 ppm

Table 2. LODs (3σ) of precious metals in pure cordierite (common ceramic substrate of catalysts)

Conclusions

Exploration catalysts from gasoline engines with various ratios of Pt-Pd-Rh, Pt-Rh, or Pd-Rh, as well as catalysts from diesel engines containing higher amounts of Pt only or wash coats from catalysts with metallic substrates were all analyzed with good accuracy. The analysis results were comparable to lab assays, showing that Niton XL3t Series XRF analyzers can be used successfully in the field to provide a good estimation of the value of spent catalytic converters.

Important benefits derived from using Niton XL3t Series analyzers include:

- Analyses take only one or two minutes vs. time-consuming lab assays
- Ease of use with little training vs. lab analysis requiring specialized knowledge
- Robust FP-calibration is insensitive to matrix changes
- Cost efficient with reduced price per analysis

To discuss your particular applications and performance requirements, or to schedule an on-site demonstration, please contact your local Thermo Scientific portable XRF analyzer representative or contact us directly by email at niton@thermofisher.com, or visit our website at www.thermoscientific.com/niton.

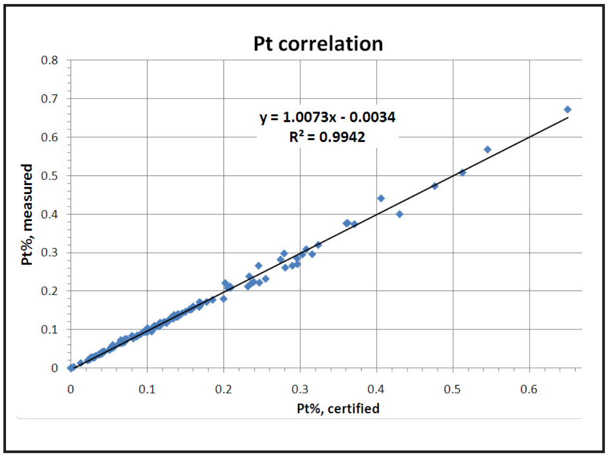


Figure 2. Correlation curve for Pt – CRM vs. Niton XL3t Series analyzers

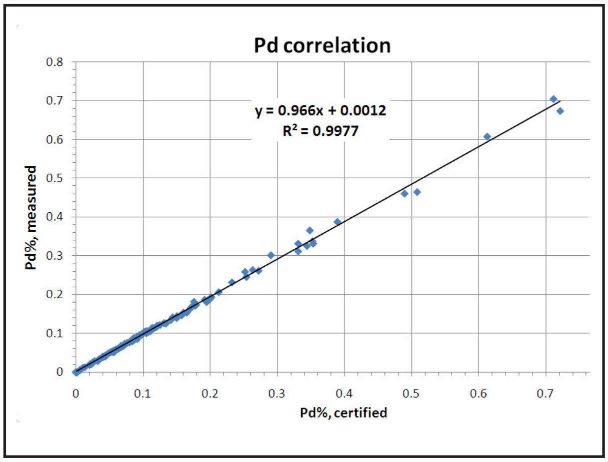


Figure 3. Correlation curve for Pd – CRM vs. Niton XL3t Series analyzers

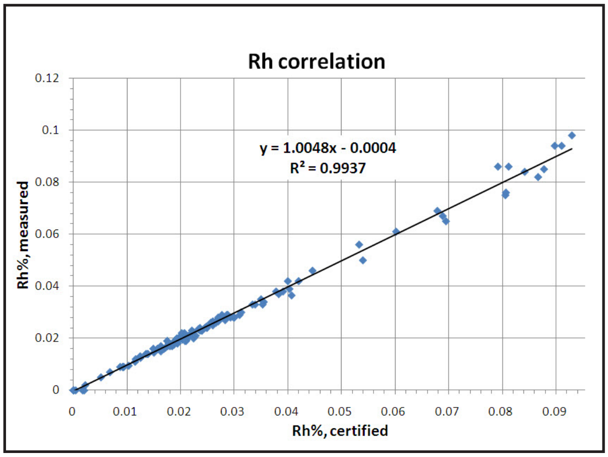


Figure 4. Correlation curve for Rh – CRM vs. Niton XL3t Series analyzers

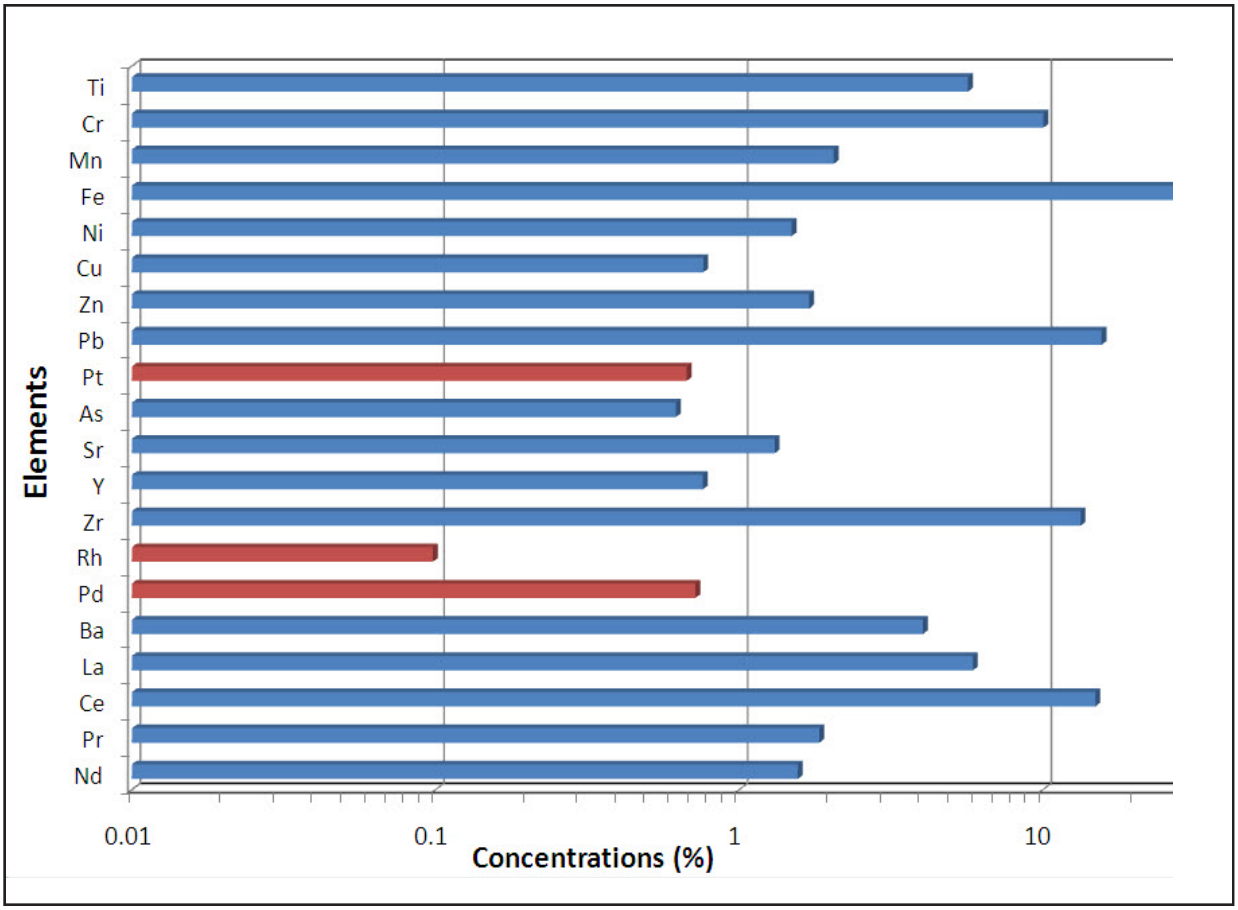


Figure 5. Range of concentration for Pt, Pd, Rh and relevant matrix elements found in the investigated samples

References

[1] Loferski, P., "Platinum-Group Metals," in 2010 Mineral Yearbook, US Geological Survey, 2011.

[2] Hagelüken, C., "Der Kreislauf der Platinmetalle – Recycling von Katalysatoren," Autoabgaskatalysatoren, Expert Verlag, 2005.

[3] Hagelüken, C., The PGM-markets and their interdependencies with the autocatalyst. Presented at the CTI Forum Material in Exhaust Gas Technology, Stuttgart, Germany. May 2008. Available at http://www.autocatalyst-recycling.umicore.com/

[4] Tollefson, J. , Worth its weight in platinum, Nature 450, 2007, 334-335.

[5] http://www.kitco.com

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