APPLICATION NOTE

Analysis of automotive catalytic converter to determine precious metal content with ARL QUANT'X EDXRF Spectrometer

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Keywords

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Introduction

Automotive catalytic converters (ACCs) play an essential role in the exhaust system to reduce the emission of harmful pollutants, such as carbon monoxide (CO), hydrocarbons (HC) and nitrogen oxides (NOx). A converter typically consists of a so-called honeycomb substrate. Such structures contain many fine channels similar in appearance to honeycombs as produced by honey bees in nature. The majority of ACCs are ceramic based and consist of a like substrate made of cordierite ($2MgO.2Al_2O_3.5SiO_2$). This material is wash-coated with alumina (Al_2O_3) to which a combination of platinum group metals (Pt, Pd, Rh) and rare earth oxides such as CeO_2, ZrO_2, etc. are added. Recovery of precious metals by recycling spent ACCs represents a substantial economical value. Energy-Dispersive X-ray Fluorescence (EDXRF) offers a quick and accurate determination of Pt, Pd and Rh content in spent ACCs.

Sample preparation

Down to the microscopic level, ACCs are inhomogeneous and require a thorough sample preparation before reproducible analysis is possible. A first step consists of grinding the material using a vibratory disk or ring and puck mill. It is worthwhile to check element characteristic line intensities as a function of grinding time and to assure that these have reached a constant value. This should not only be checked for the precious metals but also for the other elements present (i.e. Al, Zr, Ce, etc). Grinding sets made of tungsten carbide (WC) should be avoided because contamination of the sample by tungsten will result in characteristic lines of tungsten interfering with the lines of platinum.
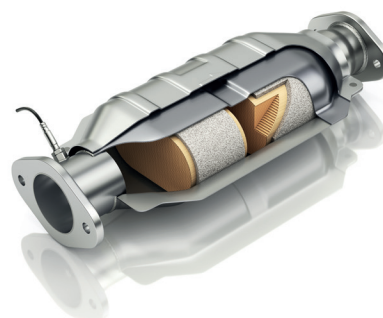
Once ground, the powders can be pressed into a pellet with aid of a binder. Similar to geological samples, the inhomogeneous nature of ACC will still lead to mineralogical effects. To avoid these, some laboratories prefer to fuse the sample but this leads to other difficulties related to the instability of precious metal oxides and their tendency to agglomerate or alloy with Pt/Au crucibles. For this note we opted to prepare pressed samples of 32 mm diameter using an automatic press applying 20 tons of pressure for 15 s.

Instrument sensitivity

The Thermo Scientific™ ARL™ QUANT'X Spectrometer is equipped with a large area (30 mm²) Silicon Drift Detector (SDD) offering excellent sensitivity for precious metals. Table 1 shows the detection limits obtained for Rh, Pd and Pt in a typical ACC matrix.

Table 1. Typical ARL QUANT'X Spectrometer minimum detection limits for Rh, Pd and Pt in an ACC matrix.

	Rh	Pd	Pt
MDL (100s), ppm	2	3	5

Quantitative analysis using UniQuant program

As explained, ACCs are quite complex samples and require a large suite of calibration standards to cover the variation in composition for this material. Although preferred, such a set of standards is not always available or the standards are not fully characterized which makes correct estimation of inter-element effects impossible. This application note presents an alternative based on standardless fundamental parameters.

Sample composition has been determined using Thermo Scientific UniQuant, a standardless fundamental parameters program well-known for WDXRF and now also available for EDXRF. The UniQuant program comes pre-calibrated using a set of pure elements and compounds and will correct not only for matrix effects but also for spectral interferences. It utilizes eight primary beam filters available with the ARL QUANT'X Spectrometer and pre-set voltage settings to produce the best possible profile of any unknown sample without user intervention or optimization. A complete analysis takes about 10 minutes per sample and returns the entire sample composition.

Results

A set of 10 ACC samples have been analyzed to determine Rh, Pd and Pt concentrations independently using ICP-OES and EDXRF combined with UniQuant. Figures 1 to 3 show the results of this study. A good agreement is obtained between both techniques with average relative differences of less than 3%. Given the intrinsic heterogeneity of the samples and uncertainty in results, this is very acceptable.
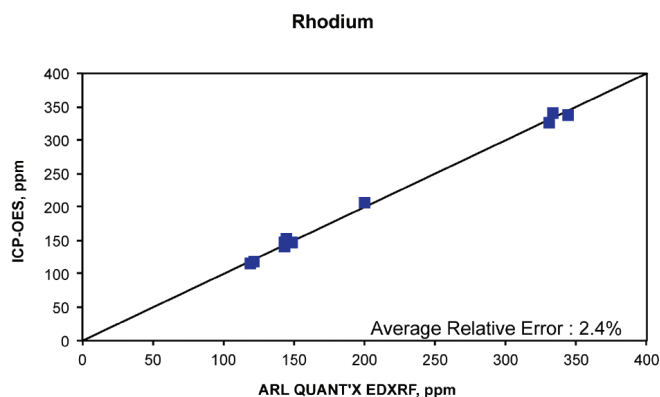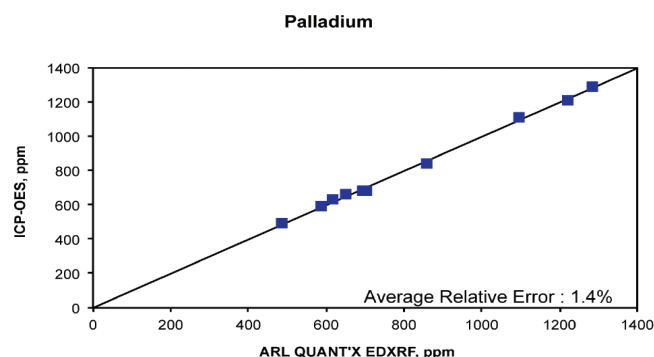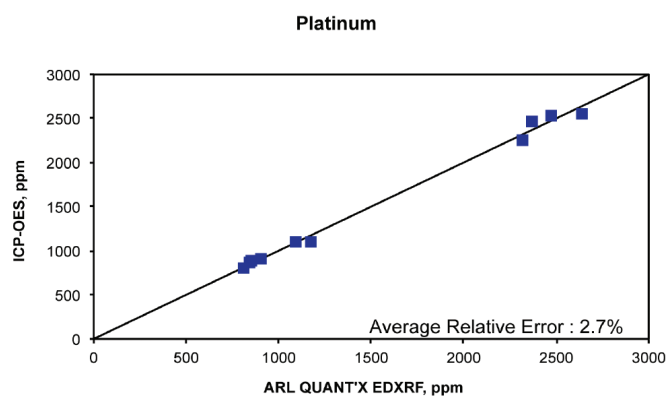

Figure 1.

Figure 2.

Platinum

Figure 3.

Figures 1, 2 and 3 show comparisons of ACC analysis results obtained using ICP-OES and the ARL QUANT'X EDXRF Spectrometer combined with UniQuant standardless FP software.

Repeatability

To ascertain the instrument repeatability of this method we have repeatedly analyzed a catalyst sample eleven times in a row. In between measurements the sample was removed from the sample holder and placed back again. The measurement time was set to 30s for the conditions involving the elements of interest. Table 2 below shows the test results. The average relative standard deviation at 1 sigma turns out to be 2% or less.

Table 2. Repeatability results obtained upon analyzing NIST 2557.

	Rh	Pd	Pt
Counting time	30s	30s	30s
Run nr	ppm	ppm	ppm
01	133	224	1040
02	136	227	1060
03	137	225	1060
04	135	226	1040
05	136	228	1080
06	136	230	1040
07	136	230	1070
08	140	228	1090
09	137	230	1080
10	133	226	1020
11	134	225	1070
Average [ppm]	136	227	1059
St. Dev [ppm]	2	2	22
Relative St.Dev. [%]	1.5	1.0	2.0

Conclusions

The ARL QUANT'X Spectrometer in combination with the UniQuant software is used to analyze automotive catalytic converters (ACCs) to determine Rh, Pd and Pt content. Combination of EDXRF with UniQuant standardless fundamental parameters yields results which show good agreement with those obtained via ICP-OES.

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