EDXRF Analysis of Precious Metals in Catalytic Converters

Precious metal content is a key component to the functionality of a catalytic converter. The X-5000 provides a fast, easy-to-operate, and reliable method for determining the Platinum (Pt), Palladium (Pd) and Rhodium (Rh) content of catalyst materials recovered from converters. Non-destructive energy dispersive X-ray fluorescence (EDXRF) testing helps preserve the quantity and quality of the collected sample materials.

Introduction

Catalytic converters play an essential role in air-quality improvement and are a mandatory component for nearly all new-production engine exhaust systems. They typically consist of a ceramic or metal honeycombed monolith substrate bearing a washcoat material that contains a combination of one or more of the following precious metals; Platinum (Pt), Palladium (Pd), and Rhodium (Rh).

Global economy factors have caused large numbers of regulated recreational and small spark ignition engines to be imported to the United States. Many of these engines have been found to be in violation of Environmental Protection Agency (EPA) standards. A common issue is inferior catalytic converter quality.[1] Poor quality control, design changes or efforts to cut costs have resulted in substandard converters that do not conform to the original certificate of conformance specifications and result in illegal levels of engine exhaust emissions. Engine manufacturers, importers and regulators need a fast, easy-to-operate and reliable method for determining catalytic converter Pt, Pd and Rh content.

Sample Preparation

The most difficult and essential step in sample preparation is the mechanical removal of the precious metal containing washcoat from the catalytic converter substrate/support. An innovative procedure is described by Smith, Suggs and Isin in the EPA National Enforcement Investigations Center (NEIC) publication, *Laboratory Analysis of Catalytic Converters Leads to Better Enforcement Results.*[1] (Also, see HORIBA SLFA AN207.)

Test Specimen Preparation

Once sample collection is accomplished, the ability to evaluate a test specimen for precious metal content is simplified with the use of the HORIBA X-5000 EDXRF Analyzer. The collected and cleaned catalyst containing powder may be analyzed without the need for additional sample treatment. The test is non-destructive, which preserves the quantity and quality of the sample material, eases sample retain, and chain of custody procedures.

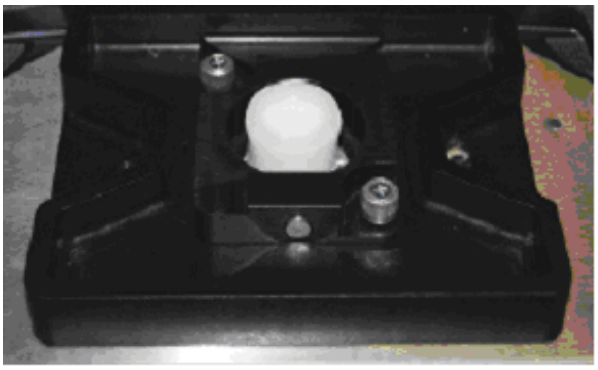

Figure 1: Sample Tray ensures proper placement of sample every time.

Testing

Analysis is accomplished by placing a test specimen into a standard 31 mm diameter X-ray sample cell to a depth of 2-3 mm. This small test specimen volume requirement is important since the amounts of recovered washcoat are often small (less than 5 g). Mylar film (2-6 µm) is used to provide the sample cup seal. Once the cup is sealed, it is placed in an analysis window (Figure 1) that allows exposure to an X-ray pathway after the sample compartment is sealed and the analysis begins.

Factory Calibration for Multiple Elements

The X-5000 is calibrated in-factory for a wide variety of elements and equipped with a tantalum anode and large silicon drift detector, providing superior detection limits and sensitivity. Figure 2 provides an example of the large and easy-to-navigate user interface.

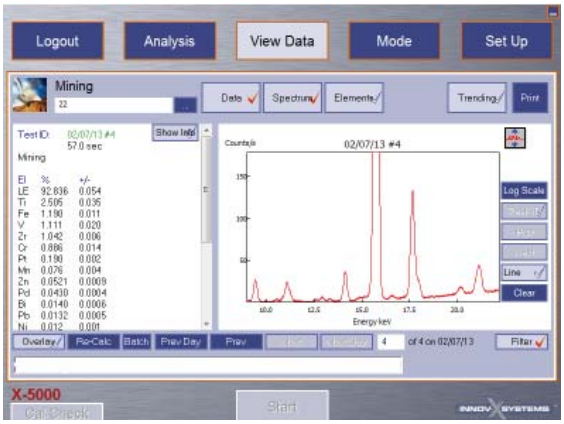

Figure 2: X-5000 User Interface

Easy In-Field Calibration

The user can easily enhance factory calibration accuracy with the analysis of several known or reference materials that closely match the matrix of the samples to be analyzed.

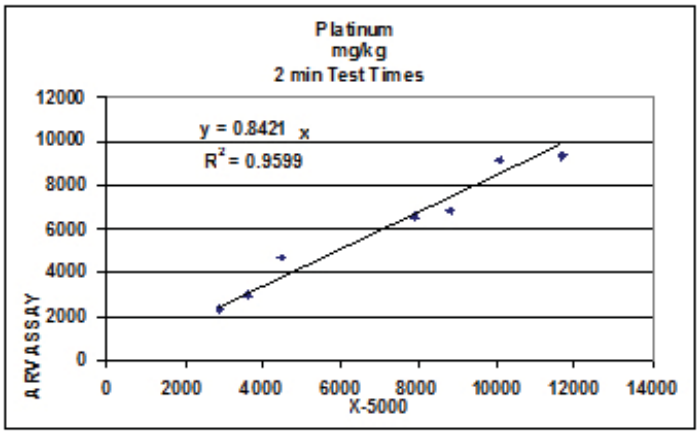

Figure 3: X-5000 Platinum Field Calibration

Figure 3 illustrates how this is done using a group of homogenous catalyst samples. Each sample had an assigned reference value (ARV) for Platinum. The assayed samples are analyzed on the X-5000 and the results derived from the factory calibration are then plotted against the ARV for each sample. Trend line analysis yields a correction factor that can be applied to analytical results of similar samples with unknown concentrations. Once the correction factors are established they may be verified by an analysis of a certified control sample or a standard reference material.

Transportable Simultaneous Quantitative Data

Once field calibration is accomplished, X-5000 portability allows analysis of similar materials at various locations. For example, the field calibrated X-5000 described above was transported to another site where washcoat materials from four catalytic converters were analyzed. The previously described specimen preparation procedures and established calibration curve were utilized. However, since sample preparation (collection) procedures were unknown, sample homogeneity was examined by gently agitating and rotating the test specimen approximately 90 degrees after each analysis. Each test was done in triplicate using a two minute analysis time. Results are listed in Table 1.

Sample ID-1	AVG	1st	2nd	3rd	%RSD
Pt- mg/kg	268	263	269	272	1.8%
Pd- mg/kg	1777	1765	1779	1786	0.6%
Rh- mg/kg	216	215	218	217	0.7%
Sample ID-2	**AVG**	**1st**	**2nd**	**3rd**	**%RSD**
Pt - mg/kg	916	901	996	850	8.1%
Pd - mg/kg	717	796	685	670	9.6%
Rh - mg/kg	122	127	109	128	8.7%
Sample ID-3	**AVG**	**1st**	**2nd**	**3rd**	**%RSD**
Pt- mg/kg	30	39	21	31	29.7%
Pd-mg/kg	1481	1482	1488	1472	0.5%
Rh- mg/kg	99	97	102	99	2.5%
Sample ID-4	**AVG**	**1st**	**2nd**	**3rd**	**%RSD**
Pt- mg/kg	84	89	79	84	6.0%
Pd- mg/kg	43	47	43	39	9.3%
Rh- mg/kg	ND	ND	ND	ND	N/A

Table 1: Simultaneous Pt, Pd, & Rh
Sample Analysis Catalyst Washcoat Materials

The results in Table 1 for the four catalysts indicate that sample 2 was less homogeneous than samples 1, 3 and 4. The relatively high percent RSD for Sample 3, Pt and Sample 4, Pd reflect concentrations of <50mg/kg.

Note: Known sample preparation (collection) procedures, as previously described, often reduce the need for mandatory homogeneity testing.

Qualitative Data

As the elements of interest are analyzed, valuable information regarding other elements present in the test specimen can be monitored or discovered. Figure 4 depicts an overlay of an analysis of three different samples that contained varying levels of Pt, Pd and Rh. The spectral data also provides evidence for the presence of varying levels of strontium (Sr) and zirconium (Zr) in all three samples.

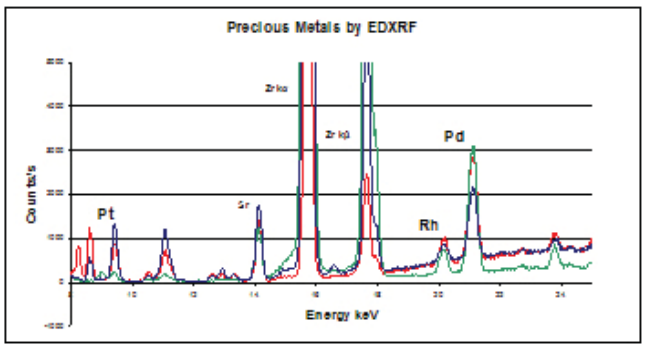

Figure 4: Overlay of spectra demonstrates ability to simultaneously evaluate primary (Pt, Pd & Rh) and as example, secondary elements of interest (Sr & Zr).

Key Features and Benefits

- No daily calibrations
- Simultaneous multi-element measurement capability
- Closed beam operation for user safety
- Data is stored automatically in tamper proof format
- Compact form factor that is portable and lightweight
- Fast start-up and flexible sample cup options
- Level of detection for Pt, Pd and Rh – (20-30) mg/kg

Conclusion

The HORIBA X-5000 provides a compact, yet powerful, easy to use analytical solution for the determination of the precious metal types and concentrations contained in catalytic converters. Information is simultaneously collected for multiple other metals that may be of interest. Small test specimen volume requirements and non-destructive testing ease sample size collection requirements, as well as simplify sample retain and chain of custody procedures. Evaluation of sample homogeneity is enabled while information is promptly and readily obtained from an on-board integrated computer and user-friendly interface.

Bibliography

[1]Smith, D., Suggs, J., and Isin, A., *Laboratory Analysis of Catalytic Converters Leads to Better Enforcement Results*, presented at the 9th International Conference on Environmental Compliance and Enforcement, Canada, June 20-24, 2011, http://inece.org/conference/9/papers/SmithSuggs_USEPA_Final.pdf.

This application note was produced by HORIBA Instruments, Inc., A published EPA document is referenced. EPA does not endorse any particular product or service.

labinfo@horiba.com
www.horiba.com/scientific
USA: +1 (800) 446-7422 • France: +33 (0)1 64 54 13 00 • Japan: +81 (0)3 38618231