Sample preparation for PGM analysis of automotive catalyst

Abstract

The recycling of spent catalysts in order to refine valuable metals is a major venture. Reliable sample preparation for analysis by means of XRF is done with pressed pellets. This application note provides a short introduction to sample preparation techniques and equipment used to prepare sample of new and spent automotive catalyst.

Keywords

- Automotive catalyst • recycling • PGM (Platinum Group Metals) • sample preparation • laboratory automation • pressed pellet • XRF

Introduction

Automotive catalysts were introduced in the 1970's to reduce harmful atmospheric emissions. Today, three-way-catalysts are able to decrease the emission of carbon monoxide, hydrocarbons and nitrogen oxides. Those compounds are captured through the catalytic properties of precious metals like platinum, rhodium and palladium. Due to this application and their monetary value, PGM have become an important part of industrial processes. Automotive catalysts are generally composed of ceramics. These ceramics are loaded with precious metals which are located on the wash coat (Mohalleem et al., 2011). About 50-60% of the precious metals contained in catalysts are recycled worldwide (Hagelüken, 2012). To achieve recycling rates of up to 98%, milling, sampling and refining has to be done with modern technologies. In 2002 about 260t of PGM were refined from spent catalytic converters (Hagelüken et al., 2003).

It is well known that deficient sampling and sample preparation can have high financial impact. Therefore, during sub-sampling of the primary lot the integrity of the sample has to be preserved (Minnitt, 2007). Additionally, the high prices for precious metals require an analytical accuracy of at least 0.02% (Hahn-Weinheimer et al., 1995).

Representative sampling and sample preparation are also crucial because the PGM credit is an important part of the contract between the refinery and the raw material supplier (Hagelüken et al., 2003).

Linear and fully automatic laboratories are available to manage the high sample loads of large scale recycling facilities. Depending on the complexity of the preparation method and sample load, automations significantly decrease turnaround times and laboratory costs.
Typical Analytical Methods

Samples from automotive catalysts are commonly analysed by AAS, ICP-OES and XRF. Wet chemical sample preparation is time consuming and, due to its complexity, not suitable for industrial applications. The same is true for Fire Assay analysis, especially when the slag is re-assayed to ensure full recovery of precious metals. On the other hand borate fusion in a Pt-crucible is complicated, as Pt, Pd and Rh, which are contained in the sample, will alloy with the crucible wall (Lupton et al., 1998). Nevertheless, the application of the more difficult fused bead method can improve the accuracy of analysis by the factor 5 (patent WO 2005/064323 A1).

For these reasons, samples of catalytic materials are usually prepared as pressed pellets. The analysis of pressed powders requires a particle size, which is at least smaller than 70 μm. A comparison between the pressed pellet method and classical analytical methods (ICP-OES & Fire Assay) is presented by Drews (2002). Crucial for analytical accuracy is the reproducibility of sample preparation to match the matrix of the calibration samples. Additionally, sample loss and cross contamination has to be minimized. Recovering the whole sample is important by the fact that ceramic dust is enriched with PGMs by the factor 2-3 (Hagelüken et al., 2003). The fine powdered catalysts are sensitive for re-agglomeration. Therefore, the parameterization for grinding has to be versatile and steplessly adjustable.

Automation

Linear automations

Before analysis, the catalyst needs to be dismantled and the steel shell must be removed. Afterwards, the whole carrier is prepared for analysis. The monolith has to be crushed and pulverized down to a suitable size (Hensel et al., 2000; Saternus & Fornalczyk, 2013). This can be done with a special mortar crusher (HP-C/M AUT) and the automatic mill HP-MA. Sometimes drill cores are additionally taken from catalysts. The size of a catalytic monolith can be quite variable so that the automatic mill must provide a batch processing function to allow a convenient and reproducible sample preparation. The sample preparation equipment is either directly connected to the spectrometer or provides a magazine for finished pressed pellets.

Fully automated laboratories

Also bigger lots of pretreated catalytic monoliths are analyzed. A stock of dismantled catalysts is comminuted to a fine powder. This powder needs to be blended before it is transferred to the refining processes. Sampling is done after blending to ensure a homogeneous composition. The samples are transferred to the laboratory for PGM and base metal analysis. With the HP-M1500 the samples are ground down to a suitable particle size which allows sub-sampling. For sub-sampling the dosing machine HP-SCD can be used to extract a representative volume. This volume is used for final sample preparation with the automatic mill (HP-MA) and press (HP-PA). Cup handling between each machine can be realized with industrial robots.

Laboratory equipment

Catalyst crusher HP-CM/AUT

The HP-CM/AUT is a crusher especially designed for automotive catalyst. Entire monoliths can be crushed down to a particle size suitable for fine grinding. The crushed material is captured in a special container (3 l), which can be easily removed by the operator. The material loss is reduced to a minimum and cleaning of the crusher is achieved by compressed air.

Fig. 02:
The automatic mill HP-MA and the automatic press HP-PA with a sample storage magazine in the front. Automatic batch processing allows minimizing laboratory work load and decreases the turnaround times.
Conclusion
The well-proved laboratory equipment is capable to meet the analytical requirements of PGM refinery from spent automotive catalysts. Turnaround times are decreased and laboratory work load is minimized by the introduction of laboratory automation. A diversity of optional sample preparation features is available to customize the equipment and optimize preparation techniques.

Contact us for further information.

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Automatic mill HP-MA
The automatic mill HP-MA is especially suitable for preparing precious metal bearing materials because the machine offers various cleaning options to avoid cross contamination. Three cleaning features namely compressed air, sand cleaning and wet cleaning allow a sufficient material removal. Using the different cleaning functions, cross contamination can be reduced to a low ppm-level. Furthermore, spoon sampling during the material input provides the possibility to pre-contaminate the grinding with the following sample. The final particle size after ± 30 seconds of milling is commonly 90 % below 50µm. Grinding vessel, ring and puck have to be made from chrome steel in order to avoid line overlapping by elements introduced by the grinding stones.

Automatic press HP-PA
Almost no additional binding agents are necessary to achieve a high quality pressed pellet with a smooth surface. Cleaning of the automatic press is commonly done by means of compressed air. If cleaning by air is not sufficient, a Mylar foil can be used to cover the pressing tool. The pressed pellets can be prepared by using the automatic HP-PA, which can be connected with the HP-MA in a linear automation. This allows batch processing of up to 100 samples with a minimum work load.