

Disassembly of Small Engine Catalytic Converters and Analysis of Washcoat Material for Platinum Group Metals by X-Ray Fluorescence Spectrometry

Jennifer Suggs, Benjamin Burns, Richard Martinez, Don Smith, and Amelie Isin
U.S. Environmental Protection Agency

ABSTRACT

The United States Environmental Protection Agency (U.S. EPA) National Enforcement Investigations Center (NEIC) has developed a test method for the analysis of washcoat material in small engine catalytic converters. Each small engine catalytic converter contains a metallic monolith. Each metallic monolith is removed from its outer casing, manually disassembled, and then separated into washcoat and substrate. The washcoat material is analyzed for platinum group metals (PGMs) using X-ray fluorescence (XRF) spectrometry. Results from the XRF analysis are used to calculate PGM ratios in the washcoat. During monolith disassembly, care is taken to minimize loss of washcoat or substrate, but some material is inevitably lost. The recovered washcoat mass does not necessarily equal the quantity of washcoat that was present in the intact catalytic converter. A maximum washcoat mass can be estimated by combining the masses of the recovered washcoat and the material loss during monolith disassembly. PGM concentrations, the recovered washcoat mass, the estimated maximum washcoat mass, and the monolith volume are used to calculate the PGM loading value range for the catalytic converter.

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INTRODUCTION

Catalytic Converters and Platinum Group Metals

Catalytic converters are designed to reduce harmful air emissions such as carbon monoxide, hydrocarbons, and nitrogen oxides. Carbon monoxide is a poisonous gas that displaces oxygen in blood. Hydrocarbons and nitrogen oxides contribute to the generation of lower atmospheric ozone [1, 2, 3, 4, 5, 6]. Ozone is a strong oxidant that damages tissues in humans and animals and hinders photosynthesis in plants [7].

Catalytic converters vary in structural features and active materials. The general structure includes an outer metal casing and an inner ceramic or metal monolith which consists of coating material applied to the substrate form. Ceramic monoliths are used in automobile catalytic converters. Metal monoliths are used in small engine catalytic converters, which are the focus of this work.

Monolith design varies to meet requirements for performance and durability. One metal monolith design is the honeycomb structure, and this structure provides tensile strength and

resistance to thermal shock (Figure 1). The honeycomb is designed using layers of smooth and structured (or angled) metal foils with solder joints between the layers [8].

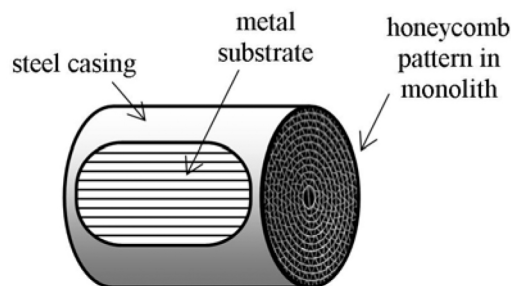


Figure 1. Diagram of a Metal Monolith in Casing

The coating material on the substrate is a carrier, an inorganic material that is highly porous, and it is most commonly aluminum oxide (Al_2O_3), also known as alumina. The carrier provides the surface for catalytic reactions to take place [9]. The carrier can be called washcoat, which is a reference to the process used to apply the carrier to the substrate [10]. Washcoat contains active elements or compounds that catalyze reactions to convert and reduce the amount of harmful chemicals exhausted from the engine [9,11].

PGMs are the primary components used to catalyze engine exhaust reactions. Platinum (Pt) and palladium (Pd) catalyze the reactions for carbon monoxide and hydrocarbon oxidation to carbon dioxide and hydrogen gas. Rhodium (Rh) catalyzes the nitrous oxide reduction reactions to selectively form nitrogen gas; platinum reduces nitrous oxides to ammonia. Compounds such as cerium oxide, lanthanum oxide, titanium oxide, and zirconium oxide can be added to washcoat to enable oxygen storage and promote the catalytic reactions [1,12,13].

Regulatory Interest in Catalytic Converters

The U.S. EPA has the authority to set air quality standards under the federal Clean Air Act (CAA). The CAA establishes the regulation of both stationary and mobile sources of air emissions [14,15]. Mobile sources include motor vehicles, recreational vehicles, motorcycles, construction equipment, farming equipment, aircraft, marine engines, locomotives, and other sources of air emissions that move or can be moved [16,17]. These mobile sources (engines and vehicles) are regulated regardless of origin (domestic or international).

All engines and vehicles must be covered by a certificate of conformity stating compliance with air emission standards prior to importation or introduction into U.S. commerce [18]. This certificate covers only those engines or vehicles that are materially the same as those tested for certification and described in the documentation submitted to the U.S. EPA for a certificate. The required documentation includes the full technical specifications of the catalytic converter used for the engine or vehicle, if applicable. When a catalytic converter is found to be materially different from the design specified in the vehicle or engine certificate documentation, the vehicle or engine is out of compliance with the CAA. Catalytic converter specifications for these vehicle types include the dimensions, the pore count, and the amount of catalytic material present as PGM ratios and loading values.

To compare a catalytic converter to the specifications listed in its certified design, physical measurements of the converter and a chemical analysis of the catalytic material are required. Therefore, a method was needed to analyze converter washcoat for PGM concentrations, calculate PGM ratios from the concentrations, and then apply the physical measurements to determine the loading values for PGMs in the converter.

In order to design the method, it was necessary to determine a way to remove the washcoat from the surface of the metal substrate, determine the method of PGM analysis, evaluate the performance of the method, and use the data to calculate specifications for comparison to the technical specifications sheets. To develop a method, NEIC searched published work for information regarding PGM and washcoat removal from catalytic converter monoliths and methods of analysis of PGMs in washcoat material; minimal results were found involving

work with metallic monoliths. Separation and analysis of washcoat on ceramic monoliths, used in automobile applications, is very prominent in the literature.

EVALUATION AND APPLICATION OF PUBLISHED METHODS

Sample Preparation

PGMs are expensive, and demand for their use in catalytic converters is high. PGM recovery from the washcoat is an important process in the economics of catalytic converter recycling [19]. Several methods have been proposed for removal of PGMs from automotive catalytic converters, which have a ceramic monolith. Crushing the ceramic monolith to achieve a homogenous sample with the washcoat is the first step [20]. The crushed ceramic and washcoat materials are ground and exposed to a leaching solution for the extraction and isolation of the PGMs. The crushing, grinding, and leaching steps can be performed on an individual catalytic converter or scaled up to bulk quantities.

Washcoat also can be removed from metal monoliths through a crushing process. The process is designed for PGM recycling of large quantities of catalytic converter monoliths [21,22]. This method utilizes comminution and segregation steps to separate the washcoat material from the metal substrate, with some retention of washcoat on the pulverized metal. Some PGM loss can occur during crushing. Washcoat material can be retained on pieces of metal substrate and within the crushing apparatus. When compared to the quantity of PGMs in a bulk batch, this loss would be negligible.

Metal monoliths with washcoat containing varying PGM concentrations can be combined through this crushing process into a bulk batch. Analysis of the bulk washcoat can provide the PGM concentrations in the batch for recovery purposes, but cannot provide the PGM concentrations for the washcoat in a single metal monolith. Comminution of a single metal monolith could incur significant loss of washcoat as the material could be retained on the grinding and crushing mechanism, in addition to the amount retained on the pulverized metal.

When the NEIC test method development began, a combination of nitric acid and hydrogen peroxide was employed to free the washcoat from the metal substrate [23]. This chemical method of removal was replaced by a physical process, which proved more effective at freeing the washcoat from the honeycomb substrate.

Whether retained on the substrate surface or completely recovered from the substrate, preparation of washcoat material for PGM analysis can be complex and time-consuming. Fire assay, acid digestion, and fusion procedures can be used to extract PGMs from washcoat samples into a solution ready for

analysis by common elemental analysis techniques [24, 25, 26]. Analysis of the solid washcoat sample is also possible [27, 28, 29, 30, 31, 32].

Sample Analysis

Researchers have compared the techniques used for the analysis of PGMs in automotive catalysts. Van Meel, et al., treated washcoat samples with a five-day fire assay and acid digestion process, and then analyzed the resulting solutions using inductively coupled plasma-optical emission spectroscopy (ICP-OES). Washcoat samples also were ground and prepared as pressed pellets and analyzed using an energy dispersive X-ray fluorescence spectrometer (EDXRF). Results from 29 samples demonstrated that the techniques were comparable and that accuracy requirements could be reached using EDXRF, but with less time required for the overall preparation and analysis [29].

Brown, Jr., et al., prepared samples using microwave digestion and analyzed for PGMs using inductively coupled plasma-mass spectrometry (ICP-MS). Those results were compared to samples prepared as pressed pellets and analyzed using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF). The results from both techniques compared favorably for the PGMs [30]. Yoon, et al., also used microwave digestion to prepare pre-concentrated automotive catalyst samples and standards for analysis by atomic absorption spectroscopy (AAS), ICP-OES, and ICP-MS [31]. Samples and standards were also prepared as pressed pellets for WDXRF analysis. XRF was recognized among the techniques for the ease of sample preparation and a better balance between detection limit and dilution factors when compared to the other techniques.

Both WDXRF and EDXRF are established instrumental techniques for the analysis of PGMs in various forms (solid alloy, pellet, and solution) [27]. Samples of automotive catalyst have been prepared as thin wafers and analyzed by XRF [28].

Total reflection X-ray fluorescence (TXRF) has also been used for the analysis of catalytic components and contaminant elements in automotive catalysts. One method of sample preparation used by Fernández-Ruiz, et al., was the suspension of finely ground and homogenized particles in high-purity water on a flat plastic carrier, followed by water evaporation under vacuum [33]. Fernández-Ruiz, et al., also performed a microwave digestion procedure on samples and a Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST) [34]. The SRM analyzed was NIST 2557 - Used Auto Catalyst (Monolith). The TXRF used for both of these studies was the same, and the recoveries for the PGM analysis of the NIST SRM were excellent.

XRF was used exclusively by Yoon, et al., for the analysis of PGMs in pre-concentrated spent automotive catalyst [32]. Two NIST SRMs were also analyzed by XRF: NIST 2556 - Used Auto Catalyst (Pellets) and NIST 2557. Different matrix modifiers were studied (aluminum oxide and aluminum oxide

with various metals) to determine the best matrix modifier for the analysis of PGMs in spent auto catalyst. Aluminum oxide (Al_2O_3 , alumina) was found to cause the least deviation from the true value of the NIST standards of the matrix modifiers studied.

Matrix effects are a consideration in the analysis of solid samples by XRF. If a calibration is used for sample analysis, the calibration standards should be prepared from a matrix similar to that of the samples. Quality control standards used for the analysis should also have a matrix similar to the samples. Automotive catalysts are known to have an unlimited variety of mixtures of PGMs and added materials (stabilizers, promoters, etc.) [27,35,36]. Yoon, et al., determined that Al_2O_3 was the most abundant material present in the spent automotive catalyst and selected it as a matrix-modifying material [32]. Aluminum oxide can be used to prepare synthetic calibration standards for PGM analysis by XRF. Samples and standards can also be diluted with Al_2O_3 so that PGM concentrations remain within the limits of the calibration.

These papers demonstrate that XRF is an appropriate technique for the analysis of PGMs in washcoat and that Al_2O_3 is a useful matrix modifier. XRF was chosen as the instrumental analysis technique for the work at NEIC because of the advantages of rapid sample preparation and analysis and reduced chemical waste when compared to the digestion methods needed for other analytical techniques, such as AAS, ICP-OES, or ICP-MS [24, 25, 26,29,30].

U.S. EPA NEIC METHOD

Background

NEIC analyzes the catalytic converters removed from new vehicles or engines. Each converter becomes a sample and is labeled with a unique identifier. The work performed by NEIC was described in a paper prepared for the 9th International Conference of the International Network for Environmental Compliance and Enforcement (INECE) [23]. Catalytic converters arrive at NEIC intact, with a cylindrical steel casing surrounding a metal honeycomb monolith. Within the pores of the honeycomb is the washcoat, which is removed and analyzed by XRF spectrometry to determine the concentrations of the PGMs. Additional data collected from each sample include dimensional measurements, weights, and pore counts. The results are provided to the U.S. EPA Air Enforcement Division (AED) for comparison to the technical specifications provided by the manufacturer of the vehicle containing the catalytic converter.

The technical specifications sheets are not provided to NEIC before or during sample analysis. All physical measurements and chemical analysis are performed on each sample without knowledge of which PGMs are present in the catalytic converter and without knowledge of the PGM ratio or loading value for that catalytic converter. After all data have been reviewed for quality and reported to the U.S. EPA AED, the details of the technical specifications sheets are made available to NEIC.

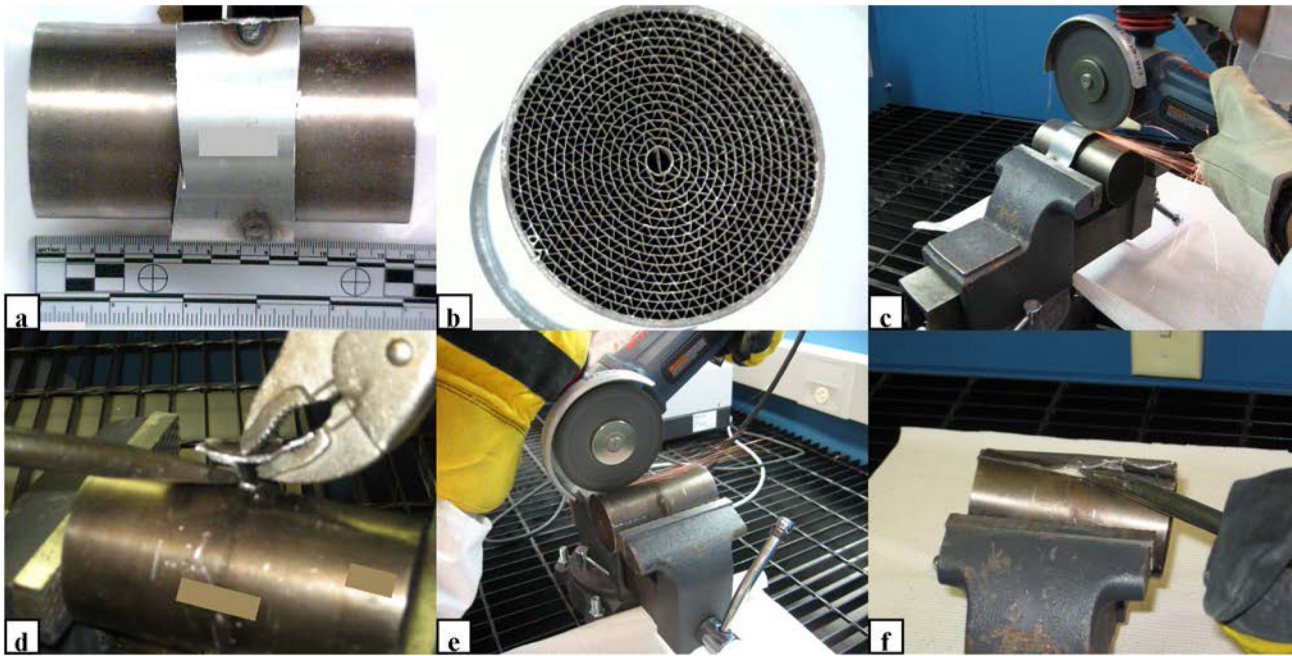


Figure 2. Photos: a) catalytic converter with exterior bracket, b) end photo of catalytic converter showing monolith and pores of the substrate, c) cutting the bracket on the catalytic converter using the angle grinder, d) prying the bracket from the casing of the catalytic converter, e) cutting the casing using the angle grinder, and f) prying the casing to determine if the casing is cut completely.

The test method described in the INECE paper and described herein has not been subject to an inter-laboratory validation study. However, quality control data have been compiled to support individual data sets and for assessment of the test method performance characteristics. The samples listed in this paper come from vehicles and engines built by 13 different manufacturers.

Measurements and Photographs

Catalytic converters, cut free from the exhaust system, are received at the NEIC. The weight of each intact catalytic converter is measured using a standard laboratory balance. Dimensions are measured with digital calipers and a metal metric ruler. The digital calipers are used to obtain the diameter of the monolith while it is in the casing. The length of the monolith is estimated using the metric ruler while the monolith is still in the casing (Figure 2a), and a second, more accurate, measurement is made after the outer casing is removed.

Catalytic converters are photographed using a digital microscope to record markings, brackets, and welds on the exterior of the casing. Photographs are also taken of the ends of the monolith to show the pores in the honeycomb substrate (Figure 2b). Pores of the monolith are counted for comparison to the technical specifications of the catalytic converter.

Disassembly of Catalytic Converters

The physical process of washcoat removal requires the full disassembly of the catalytic converter. Disassembly includes cutting and removing the casing (Figures 2c-f, 3a-b), separating the pores of the substrate (Figure 3c), and scraping

the washcoat from the casing and substrate pieces (Figures 3d-f) [23]. Although this process is time-intensive, full disassembly provides the best means of recovering the maximum amount of washcoat from the catalytic converter.

Casings on catalytic converter samples are cut using a 4½" angle grinder (7.5 A; 11,000 RPM) and cut-off wheel (4½" diameter, 1/16" thick). Catalytic converter samples are cut lengthwise on opposite sides, creating two halves of the casing. Close attention is paid to the cutting depth; it is important to minimize damage to the monolith inside. After the casing is cut, the sample is weighed again.

Casings are removed from the monolith using a combination of tools: large, flat screwdrivers; crescent wrenches; and needle-nose pliers (Figure 3). Puncture-proof gloves are necessary personal protective equipment. After casings are removed, the monolith lengths are measured using digital calipers or a metric ruler.

The pores in the metal substrate are broken apart using the assortment of tools plus small awls and rubber mallets. If the monolith has been constructed with minimal welds, it is sometimes possible to peel away sections of the substrate layers that form the honeycomb pattern.

Washcoat is scraped from the pieces of substrate and the casing halves with metal brushes. Substrate pieces and casings are visually inspected to ensure that no washcoat remains on the metal. Washcoat is collected throughout disassembly; magnets and needle-nose pliers are used to