Real life experimental determination of platinum group metals content in automotive catalytic converters

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Abstract. The real life experimental protocol for the preparation of spent automobile catalyst samples for elemental analysis is thoroughly described in the following study. Collection, sorting and dismantling, homogenization and sample preparation for X-Ray fluorescence spectroscopy and Atomic Adsorption Spectroscopy combined with Inductive coupled plasma mass spectrometry are discussed in detail for both ceramic and metallic spent catalysts. The concentrations of Platinum Group Metals (PGMs) in spent catalytic converters are presented based on typical consignments of recycled converters (more than 45,000 pieces) from the Greek Market. The conclusions clearly denoted commercial metallic catalytic foil contains higher PGMs loading than ceramic honeycombs. On the other hand, the total PGMs loading in spent ceramic catalytic converters has been found higher than the corresponding value for the metallic ones.

1. Introduction
Catalytic converters are devices that control the exhaust emissions of an internal combustion engine by converting the exhaust toxic gasses into less toxic substances. Since 1994, when the European Directive 94/12/EEC (on ambient air quality) was implemented, all the motors produced or imported in EU are obliged to be fitted with catalytic converters that reduce emissions of carbon monoxide, hydrocarbons and nitrogen oxides below the legislative levels. These converters are installed on all petrol-engine vehicles since 1993 and diesel-engine vehicles since 1997 in order to fight traffic-related pollution. The main part of the autocatalyst is an internal honeycomb structure, made either of ceramic or metallic material, coated by an alumina layer (called a “wash coat”) that is enriched with PGMs. Today, the mostly used automotive catalytic converters are the “three-way converters” (TWC), which are comprised of Platinum (Pt) or Palladium (Pd) and Rhodium (Rh). Among these metals, Pt is the most active catalyst and is used both as an oxidation and as a reduction catalyist; Pd is used as an oxidation catalyst and Rh, as a reduction one. Such catalysts require careful engine design and management in order to ensure the engine operates in accordance to the stoichiometry. The reactions that take place in the converter are described in Figure 1.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Catalytic reactions of nitrogen oxides, oxidation of carbon monoxide and oxidation of unburnt hydrocarbons in automotive catalysts.$^{[1]}$}
\end{figure}
A large reactive surface area is required to convert the high speed exhaust gases. This is accomplished by the surface enlarging wash coat. The surface of a conventional substrate is approximately $3m^2$ at $1dm^3$ and is multiplied to thousands of $m^2$ using the wash coat. Commercial automotive catalysts are separated in two different categories, depending on the substrate which is implemented. The most common ones are the catalytic converters using ceramic substrate i.e. 90%, while the 10% of the used converters have metallic substrate.[3] The difference in the structure of the converters is described in Figure 2, while physical properties comparison is described in Table 1.

Metallic converters have demonstrated advantages over the physical properties of ceramic converters, such as lower wall thickness and lower thermal resistance, which enhance flow rate through the metallic network and horsepower. Moreover, metallic infrastructures are easier to pack, less fragile and more robust and tolerant in vibrations. On the other hand, wash coat adhesion issues on metallic parts arise in heating cooling cycles.

Table 1. Physical properties of ceramic and metallic converters.[3]

|                        | Ceramic converter | Metallic converter |
|------------------------|-------------------|-------------------|
| Cell density (#/cm²)   | 62.00             | 62.00             |
| Wall Thickness (mm)    | 0.16              | 0.05              |
| Solid Fraction         | 0.24              | 0.09              |
| Material density (g/cm³) | 1.70          | 7.10              |
| Bulk Density (g/cm³)   | 0.41              | 0.63              |
| Material Porosity (%)  | 35.00             | 0.00              |
| Heat Capacity (kJ/L°C) | 0.43              | 0.32              |
| Thermal expansion (Rel)| 1.00              | 17.00             |
| Thermal conductivity (Rel)| 1.00          | 20.00             |

A mixture of silica and alumina is often used wash coat on the honeycomb substrate. The wash coat forms and irregular surface which has a far better surface area than the flat substrate, providing the autocatalyst with more place for active precious metal sites. In the case of wash coat usage, the catalyst is added to the wash coat before application to the core. After years of exposure in harsh and severe conditions of a catalytic reaction process, spent catalyst have no longer homogeneous catalyst distribution. By the end of their life, either they have accumulated many different contaminants of various densities, organic compounds, oils and water or they are broken. Examples of ceramic and
metallic de-activated catalytic convertors are shown in Figure 3. Thus, once they are recycled, appropriate sampling procedure should be established in order to obtain a homogeneous representative sample for qualitative and quantitative analysis.

Although there are a broad variety of possible combinations of PGMs in the catalytic converters, bibliographic data suggest that the total content of these metals is up to 2,000 ppm in the ceramic substrate or in some cases $10^{-3}$-$10^{-5}$%. In other bibliographic references it is mentioned that an automobile catalytic converter contains typically 0.08% Pt, 0.04% Pd and 0.005-0.007% Rh supported on a base. Dong et al. also refer that the total PGMs loading fluctuates between 0.1-0.5%. Moreover, Kuczynski et al. suggest that automobile catalysts can contain up to 30 tr oz of PGMs per short ton of catalyst (1,000 ppm). Kim et al. refer that an autocatalyst essentially comprises a refractory oxide support, on which two or more precious metals are dispersed in very low concentrations (0.1-0.3 wt% of the monolith). Ravindra et al. generally mention that a vehicle exhaust catalyst contains around 1-3 g of PGMs corresponding to approximately 1.8 mg PGMs/cm³ of the catalyst. Finally, Barefoot et al. refers that platinum concentrations, which are generally larger than those of the other precious metals, have ranged from 300 to 1,000 μg/g, palladium from 200 to 800 μg/g and rhodium from 50 to 100 μg/g. On the other side, Jimenez de Aberasturi et al. and Fontas et al. suggest that the total content is always lower than 1,000 ppm.

![Figure 3. Deactivated (a) Metallic and (b) Ceramic autocatalysts.](image)

2. Recycling process steps

Recycling of the spent automotive catalysts targets the extraction of the contained precious metals, contributing significantly towards safeguarding of the natural resources and ensuring the minimization of the environmental pollution, related both to the catalysts disposal and PGMs production. Additionally, the high value of PGMs in spent catalysts justifies their recycling. Nowadays, the state of the art technology is pyrometallurgy. Spent chemical catalysts are considered non-hazardous wastes according to European Regulation EC No 2150/2002. Effective recycling requires a well-tuned recycling chain, consisting of different specialized stakeholders. The whole process is designed to enable the separation and recovery of the precious metals from automotive catalysts, with the highest possible yield and efficacy. The main parts of recycling procedure are described in Figure 4 and discussed below.
2.1 Collection and classification of the converters from the scrap yards or car service workshops. This step is performed throughout Europe from numerous small-sized companies and natural entities. Appropriate classification is the foundation for ensuring that the collection, transportation, storage and treatment of spent autcatalysts are carried out in a manner that provide protection for the environment and human health and in compliance with legal requirements (Figure 5).

2.2 Sorting and dismantling the converters. The precious-metal-bearing carrier material and the non-precious-metal-bearing steel casing are separated (De-canning of ceramic converters / Shredding of metallic converters). Inlet and outlet exhaust extension tubes are cut (Figure 6) and main bodies of the catalysts proceed to the sorting step (Figure 4).
6). This process is mainly done some form of hydraulic shear. The PGMs content in each converter is highly dependent on:
- the power of the engine of the car,
- the year of manufacturing of the car,
- the fuel that the car uses (diesel or gasoline) and
- if the converter is the genuine part or a replacement part (Original Equipment Standard or Aftermarket).

Figure 6. Inlet and outlet exhaust tubes are removed from the main body of the catalysts during the shredding procedure.

After the sorting, the converters are de-canned, i.e. the metallic canister and the wool (fibre mat) are removed from the ceramic catalyst using mechanical process which is usually called guillotine or modified alligator shear (Figure 7). Most damage occurs during the dismantling process. The steel casings are removed by an automatic cutting machine. This may also damage the catalyst inside, while further losses may occur through handling and transit.

Figure 7. (a) Automatic cutting machine for the ceramic catalyst decanning (b) empty case of ceramic catalyst and (c) crashed ceramic honeycomb.
2.3. Homogenization, sampling and assaying.
The ceramic monoliths (or the metallic converters) are driven to a pre-crusher in order to downsize their
dimensions and to a mill in order to extract a fine homogeneous powder, which contains the PGMs.
Metallic foils are mechanically separated from the wash coat, which contains the PGMs.
Different minerals behave differently during pulverization – most (brittle) minerals will easily break
down to small particles while some will just change their shape if proper sample preparation methods
are not used. Due to the fact that the recovery of PGMs requires sophisticated large-scaled metallurgical
processes, the most common approach is to extract samples from each consignment in order to determine
the PGMs content of each lot, in every stage of the procedure. The subsequent sampling process is used
to collect a small representative sample of material on the basis of which a valuation is made for several
tonnes of material.
2.4. Recovery and refining facilities
Recovery and refining is mainly carried out by large infrastructures. Umicore, at its integrated smelter-
refinery in Antwerp, Belgium, currently recovers and supplies back to the market via its main process
route seven precious metals (amongst them Platinum, Palladium and Rhodium). Johnson Matthey, at its
 refineries in Brimsdown and Royston, UK, recovers PGMs. Overseas, Multimetco Inc. (Anniston,
Alabama, USA) and Techemet LP (Pasadena, Texas, USA) are specialized in refining PGMs from
automotive catalysts. At this stage, the recovery of PGMs, their separation and purification are
accomplished. The main process technologies applied today for the PGMs recovery from the spent
automotive catalytic converters are classified in three groups: (a) hydrometallurgical, (b)
pyrometallurgical and (c) volatilization.
The industrial recovery rates of PGMs are extremely high, i.e. for Pt and Pd is 98%, while the recovery
for Rh is 87.5%. The cost of the refining process is more or less 4,000€/ton of ceramic monoliths or
2,500€/ton of metallic converters. The refining cost represents 6.5% of the actual value of the recovered
PGMs for ceramic monoliths and 13.6% of the actual value of the recovered PGMs for metallic catalytic
converters. The total value of recovered PGMs, based on economic figures of July 2017, is estimated at
73,000€ per ton of ceramic monoliths. The metals prices are based on Johnson Matthey Precious Metal
Management sales prices for 16 October 2017. More specifically the prices were: Pt: 28,436€/kg, Pd:
30,343€/kg and Rh: 39,539€/kg.

3. Experimental
To accurately determine the amount of precious metal present in the monoliths, suitable samples for
laboratory analysis were prepared. The goal of the experimental protocol is to obtain a sample that is a
precisely representative of the overall material, as homogenous as possible of the recoverable metals
within the lot. Deficient sampling and sample preparation can have high financial impact. Moreover, a
constant protocol ought to be firmly followed in order for the measurements to be reproducible and
comparable.
Measurements took place in ceramic and metallic batches of commercial spent catalysts. Twenty nine
ceramic batches consisting roughly of 1,400 pieces per batch and nine metallic batches consisting in
average of 450 pieces per batch were converted into homogeneous mass. The sampling and
homogenization processes are described in Figures 8a for ceramic honeycombs and Figure 8b for
metallic foils.
One batch, consisting of approximately 1,400 spent catalysts, was originally de-canned. The total mass
of each batch for the ceramic honeycombs was roughly 1,047kg, which in average is 0.7374kg per
honeycomb with particle size 10cm.
Each batch was introduced to the ball mill (Figure 9a) in order to obtain particle size 2mm. 90% of the
milled powder was sent for recycling/ storage and the rest 10%, (100kg) remained in the ball mill and
grounded again, in order to obtain particle size 1mm. 90% of the milled powder was removed and sent
for recycling/storage and 10% (10kg) proceeded in the analytical mill (Figure 9c) to grounded to 160μm.
Figure 8. Sampling and homogenization process for (a) ceramic and (b) metallic catalytic converters.

Finally, 90% of the powder was sent for recycling/storage and the rest 1kg was used for elemental analysis. Ceramic honeycomb final step powder was collected so as to prepare one set of 10 samples, each one of 10g. Each sample was used for elemental XRF analysis. In case where the standard deviation of the identified values of the set was greater than 5%, then samples were mixed again and proceeded with homogenization. On the other hand, if standard deviation was lower than 5%, the experimental values were reliable, revealing that the batch was homogeneous.

Similar procedure was also followed for the treatment of metallic catalysts. Nine batches, consisting in average of 450 catalysts per batch were used for analysis. The metallic catalysts were initially crushed, where ferrous and stainless steel metallic parts were removed. The average mass of the metallic foil was 0.2143kg per catalyst. The metallic foils were introduced into the crush mill (Figure 9). 90% of the metallic foil was sent for storage/recycling and the rest 10% remained in the mill to be grounded again in order to obtain particle size 1mm. 90% of the milled foil with particle size 1mm was sent for storage/recycling and the rest 10% proceeded to the analytical mill. Analytical mill downsized the particle size to 160μm. Finally, 10% of the fine catalyst powder was used to prepare one set of 10 samples in order to verify the PGM loading on ceramic catalyst. In case where the standard deviation of the identified values of the set was higher 5%, then the samples were mixed again and proceeded with homogenization. On the other hand, if standard deviation was lower 5%, the experimental values were reliable, revealing that the batch was prepared homogeneously. The size of the particles was determined between the mill crushing steps using a series of stainless steel sieves with appropriate Mesh porosity.
The content of spent catalysts in Pt, Pd and Rh was determined with X-Ray fluorescence spectroscopy (XRF) on solid samples. Since, small variations in analytical determinations impact critically on financial performance, XRF analysis was used for determination of noble metals. The XRF analyzer provides a high level of performance when measuring metals such as Pt, Pd, Rh in catalytic converters loading and in recovered metals from spent catalysts. While benefiting from the convenience of fast analysis, it is also of high confidence obtaining results that help assure high level of accuracy, repeatability and precision of almost 1%. The accuracy of the method is verified by ICP-MS technique.\textsuperscript{[15-18]} The content of the other metals existing in the ceramic monolith and the wash coat were determined with a combination of the Atomic Adsorption Spectroscopy (ASS) and the Inductive Couple Plasma Mass Spectrometry (ICP-MS), using liquid samples produced after fusion of solid samples with LiB\textsubscript{4}O\textsubscript{7} & KNO\textsubscript{3}. Before XRF analysis and fusion procedure, the solid samples were dried overnight at 110°C for the adsorbed water to be removed.

*\textbf{X-Ray Fluorescence Spectroscopy}*

The absorption of X-Ray radiation is element and concentration dependent thus the radiation is absorbed more strongly by elements with higher molar mass. Moreover, the higher the concentration of a metal the more is the radiation absorbed.\textsuperscript{[19]} As a result, X-Ray techniques are appropriate for qualitative and quantitative analysis of noble metals.\textsuperscript{[20]} Additionally, in very short time, reliable results are available. Chemical analysis of autocatalyst samples was performed using a SPECTRO Xepos spectrophotometer that is established in the Laboratory of Metallurgy of the National Technical University of Athens.

\textit{Combined technique of XRF, AAS and ICP-MS}

The laboratory elemental analysis of the spent autocatalysts samples was demonstrated with a combined technique that was based on the XRF method for the determination of PGMs and on the methods of Atomic Adsorption Spectroscopy and Inductive Couple Plasma Mass Spectrometry for the determination of the other elements existing in samples. For AAS method, a Perkin Elmer 2100 Spectrometer was used, while for ICP-MS method, a Thermo Scientific X-Series II Spectrometer was used. Both instruments are established in the Laboratory of Metallurgy of the National Technical University of Athens.

\textbf{4. Results - PGMs content in spent catalytic converters}

For the most accurate and reliable determination of the noble metal concentration on ceramic honeycombs and metallic foils, we chose to investigate a large number of auto-catalysts in order to obtain the highest possible homogenization and representative values. More than 40,000 ceramic catalytic converters and more than 4,000 metallic catalysts were collected and treated for the elemental analysis.
The precious metal loading in each batch of ceramic and metallic catalysts was determined by X-Ray Fluorescence spectroscopy and the results are described in Table 2 for the ceramic honeycombs and in Table 3 for the metallic foils. Commercial data of an actual recycled quantity of more than 40,000 catalytic converters demonstrate that the mean concentration of PGMs in spent ceramic catalytic converters is 2,596 ppm or 0.26% w/w for the case of ceramic catalysts (Table 2). The mean concentration is 200% higher for the case of metallic catalytic foils, i.e. 7,872 ppm or 0.79% (Table 3).

Table 2. PGMs concentration of twenty-nine typical consignments of spent ceramic catalytic converters recycled from the Greek market.

|          | weight of ceramic honeycomb(kg) | Number of Ceramic converters | weight of ceramic monoliths (kg) | Pt (ppm) | Pd (ppm) | Rh (ppm) | Total PGMs (ppm) |
|----------|---------------------------------|------------------------------|---------------------------------|----------|----------|----------|------------------|
| 1        | 0.758                           | 1,600                        | 1,212.27                        | 724      | 1,633    | 302      | 2,659            |
| 2        | 0.740                           | 1,597                        | 1,181.75                        | 731      | 1,521    | 255      | 2,507            |
| 3        | 0.739                           | 1,526                        | 1,127.28                        | 760      | 1,620    | 305      | 2,685            |
| 4        | 0.737                           | 1,374                        | 1,012.12                        | 673      | 1,734    | 315      | 2,722            |
| 5        | 0.734                           | 1,377                        | 1,010.76                        | 710      | 1,471    | 295      | 2,476            |
| 6        | 0.739                           | 1,516                        | 1,120.41                        | 734      | 1,522    | 285      | 2,541            |
| 7        | 0.729                           | 1,383                        | 1,008.89                        | 705      | 1,606    | 283      | 2,594            |
| 8        | 0.720                           | 1,369                        | 985.09                          | 749      | 1,573    | 308      | 2,630            |
| 9        | 0.700                           | 1,476                        | 1,032.44                        | 630      | 1,760    | 299      | 2,689            |
| 10       | 0.706                           | 1,496                        | 1,056.03                        | 661      | 1,701    | 343      | 2,705            |
| 11       | 0.736                           | 1,360                        | 1,001.32                        | 720      | 1,533    | 301      | 2,554            |
| 12       | 0.780                           | 1,270                        | 990.52                          | 811      | 1,426    | 294      | 2,531            |
| 13       | 0.756                           | 1,335                        | 1,008.90                        | 802      | 1,541    | 284      | 2,627            |
| 14       | 0.791                           | 1,280                        | 1,012.54                        | 830      | 1,505    | 312      | 2,647            |
| 15       | 0.770                           | 1,304                        | 1,005.00                        | 821      | 1,360    | 302      | 2,483            |
| 16       | 0.788                           | 1,336                        | 1,053.54                        | 885      | 1,302    | 293      | 2,480            |
| 17       | 0.775                           | 1,287                        | 997.07                          | 819      | 1,373    | 287      | 2,479            |
| 18       | 0.748                           | 1,329                        | 994.29                          | 660      | 1,702    | 295      | 2,657            |
| 19       | 0.729                           | 1,369                        | 997.33                          | 693      | 1,572    | 290      | 2,555            |
| 20       | 0.756                           | 1,368                        | 1,034.25                        | 656      | 1,611    | 286      | 2,553            |
| 21       | 0.725                           | 1,382                        | 1,001.54                        | 625      | 1,780    | 312      | 2,717            |
| 22       | 0.748                           | 1,358                        | 1,015.73                        | 705      | 1,531    | 276      | 2,512            |
| 23       | 0.745                           | 1,351                        | 1,007.44                        | 801      | 1,511    | 285      | 2,597            |
| 24       | 0.696                           | 1,611                        | 1,120.87                        | 711      | 1,818    | 298      | 2,827            |
| 25       | 0.714                           | 1,405                        | 1,003.94                        | 743      | 1,884    | 308      | 2,935            |
| 26       | 0.687                           | 1,459                        | 1,001.85                        | 673      | 1,784    | 306      | 2,763            |
| 27       | 0.727                           | 1,386                        | 1,007.01                        | 625      | 1,532    | 264      | 2,421            |
| 28       | 0.696                           | 1,959                        | 1,362.74                        | 634      | 1,553    | 289      | 2,476            |
| 29       | 0.718                           | 1,401                        | 1,005.94                        | 601      | 1,423    | 248      | 2,272            |
| average  | 0.737                           |                              |                                | 720.414  | 1,582.138| 293.793  | 2,596            |
As it is already mentioned, a typical consignment of spent ceramic automotive catalytic converters contains 2,596 ppm of Platinum Group Metals (Platinum, Palladium and Rhodium) in the ceramic substrate (or 1.913g PGMs per catalytic converter, average weight of ceramic converter = 0.737 kg). The mass ratio of the three precious metals is: 2.7/ 6.2/ 1.1 Pt/ Pd/ Rh. This rate is highly dependent on the commercial price of each metal.

**Table 3.** PGMs concentration of nine typical consignments of spent metallic catalytic foils recycled from the Greek market.

| Weight of metallic foil (kg) | Metallic converters | Weight of metallic foils (kg) | Pt (ppm) | Pd (ppm) | Rh (ppm) | Total PGMs (ppm) |
|-----------------------------|---------------------|-------------------------------|----------|----------|----------|------------------|
| 1                           | 0.206               | 484                           | 0.214    | 99.61    | 1,619    | 5,877            | 757              | 8,253            |
| 2                           | 0.233               | 482                           | 112.234  | 1,130    | 6,442    | 692              | 8,264            |
| 3                           | 0.214               | 445                           | 95.344   | 1,766    | 5,411    | 619              | 7,796            |
| 4                           | 0.210               | 423                           | 88.621   | 1,503    | 6,334    | 748              | 8,585            |
| 5                           | 0.208               | 412                           | 85.685   | 1,608    | 4,935    | 625              | 7,168            |
| 6                           | 0.242               | 447                           | 107.966  | 1,851    | 4,718    | 480              | 7,049            |
| 7                           | 0.209               | 438                           | 91.338   | 1,555    | 6,306    | 654              | 8,515            |
| 8                           | 0.223               | 439                           | 98.098   | 1,242    | 5,112    | 577              | 6,931            |
| 9                           | 0.184               | 529                           | 97.59    | 1,069    | 6,587    | 626              | 8,282            |
| average                     | 0.214               |                               | 1,482.55 | 5,747    | 642      | 7,872            |

Quantitative analysis of nine batches of metallic foils showed that the average PGM loading was 7,872ppm on the foil (or 1.68gr PGM per catalysts, with average foil weight 0.214kg). The mass ratio of the noble metals is 1.02/ 3.9/ 0.5 Pt/ Pd/ Rh and the average PGM loading is 1,482ppm for Pt, 5,747ppm for Pd and 642ppm for Rh.

Analytical measurements of PGMs and the other elements of spent catalytic converters were performed on one single batch and the results are presented in Table 4. The total amount of noble metals is 0.2375% w/w or 2,375 ppm (Table 4). Therefore, the laboratory analysis confirms the aforementioned commercial catalysts measurements. Furthermore, the poisoning of the wash coat of the ceramic honeycomb is clearly listed in Table 4.

The studied ceramic-based catalyst contains up to 40% SiO₂, up to 10% MgO and up to 5% Ce, Zr and Ti and other mixtures introduced from gasoline and oil additives during operation. The identified values are in accordance with spent catalysts studied in the literature. Several oxides such as Na₂O and P₂O₅ and Fe₂O₃ were also determined on the structure of the spent catalyst as poisoning substances in particular high concentration.

**Table 4.** Laboratory chemical analysis of typical spent catalytic converters ceramic honeycomb.

| Oxide/Metal | w/w | (ppm) |
|-------------|-----|-------|
| **Ceramic Monolith - Cordierite** |     |       |
| MgO         | 8.51% | 85,100 |
| Al₂O₃        | 37.15% | 371,500 |
| SiO₂        | 35.33% | 353,300 |
| **Poisoning (Lubricants - Fuels)** | | |
| Na₂O       | 3.07% | 30,700 |
| P₂O₅       | 1.81% | 18,100 |
| CaO        | 1.16% | 11,600 |
| Cr₂O₃     | 0.80% | 8,000 |
Fe₂O₃  2.44%  24,400
ZnO   0.33%  3,300
BaO   0.77%  7,700
S     0.44%  4,400
C     0.43%  4,300

**Catalyst Support (Wash coat)**

|          |       |
|----------|-------|
| TiO₂     | 0.29% |
| ZrO₂     | 4.55% |
| La₂O₃    | 0.29% |
| CeO₂     | 3.51% |

**Catalyst (Noble Metals)**

|        |       |
|--------|-------|
| Pd     | 0.1364% |
| Pt     | 0.0754% |
| Rh     | 0.0257% |

**PGMs sum**  0.2375%

In both cases, the PGMs concentration in spent automotive catalytic converters is significantly higher than the PGMs content in primary ores (on average 10-20 ppm). The high intrinsic metal values make recycling attractive from an economic point of view and, due to the much higher concentration compared to mined ores, it also helps to reduce the environmental burden of metal supply significantly, especially with the respect to the impact of climate.

5. **Conclusions**

The recycling of platinum group metals from spent automotive catalysts is becoming increasingly important. Thus, the procedures related to the evaluation of the spent catalyst and the recycled metals loading ought to be designed in detail. This study has determined that particular steps should be constantly followed in sampling procedure in order to obtain representative, reproducible and high quality analytical data for spent catalysts loading.

In this work more than 40,000 spent ceramic catalytic converters have been collected and pre-processed in order to extract homogeneous samples of ceramic honeycomb. The average content of ceramic honeycomb has been found to 2,596ppm or 1.913 gr of PGMs per catalyst. In the same time more than 4,000 spent metallic catalysts have been collected and pre-processed in order to extract honeycomb metallic foil. The average PGM content of metallic honeycomb has been found to be 7,874ppm (or 1.68gr of PGM per spent metallic converter). The PGM loading in ceramic honeycomb was also verified with laboratory analysis based on a combination of XRF, AAS and ICP-MS methods, where less than 1% deviation was noticed for the combined technique than XRF. In conclusion, XRF analysis provides an accurate and quick tool to determine PGM loading reducing cost, since the use of expensive lab wet chemistry reagents is avoided. Further, the analyses are quick and straightforward without the need of being contacted by highly educated and experienced analytical professionals.

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