DETERMINATION OF SELECTED ELEMENTS IN CATALYTIC CONVERTERS USING ICP-MS AND MICROWAVE DIGESTION

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Abstract
Fuels combustion, polluting the atmosphere is a side effect of an engines' work. Increasing ecological awareness has led to constant pursuit of disposing harmful substances properly. Catalytic converters (car catalysts), containing precious metals from the platinum group, including palladium, platinum and rhodium, have been commonly adopted for this purpose. These critical elements can be found in many raw materials used frequently throughout the economy. Therefore, it is economically viable to retrieve these elements from, among the others, spent catalysts, so they can be reused to manufacture new converters. In order to determine a possible cost of spent car catalyst, it is essential to use the analytical techniques to determine elemental content in any given sample. X-ray fluorescence spectroscopy (XRF) is an example of such a technique. It is nevertheless advisable to use a complementary procedure to confirm any results obtained. A cross-verification technique was developed using inductively coupled plasma mass spectrometry (ICP-MS). This procedure was verified using comparative studies, which confirmed its usefulness and correctness.

Keywords
ICP-MS; car catalyst; catalytic converter; microwave digestion; circular economy.

Introduction

Combustion engines are the main source of propulsion of not only cars, but also trucks, buses, and other types of machines. During their duty cycle, fuel is burnt and, as a side effect, harmful substances are emitted into the atmosphere. Due to the increase in ecological awareness and progress as a society, attempts to neutralise the polluting compounds have been initiated, leading to the introduction of catalytic converters, known as catalysts [1,2]

One of the components forming ceramic catalysts is a ceramic monolith, a ceramic core block usually with a honeycomb structure. This structure contains tubules covered with precious metals – palladium, platinum and rhodium that are responsible for the catalytic function, which reduces harmful emissions.

Unimetal Recycling Sp. z o. o. is an enterprise whose objective is retrieving precious metals from used catalysts, fitting into pro-ecological activities and participating in creating the circular economy. Precious metals from the platinum group (PGM) are critical raw materials for the economy [3]. Implemented in many branches, they are however difficult to obtain from nature. That is why their retrieval and recycling is essential both from the economic and environmental point of view.

During normal operation, in cleaning vehicle emissions, the initial content of precious metals in catalysts reduces over time. The final amount depends on many factors such as for example, the type of combusted fuel, the vehicle's age, and even driving style. This creates a vital demand to determine the amount of the targeted elements remains. The prospective income and ability to further process the catalyst batch all depend on precise

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and accurate measurement of the palladium, platinum, and rhodium levels. Since there are no norms for elemental content in spent catalysts, the most popular technique is XRF (X-ray fluorescence spectroscopy) which is simple and easy to operate [4–6] . In performing routine tests, there is no need for specialised personnel. Only the device calibration needs the appropriate equipment and service. According to literature data, handheld XRF offers the user several essential advantages – analysis can be done in the field in a matter of seconds, instead of in a lab with wet chemistry and a highly skilled analytical professional, significantly cutting the cost of accurate analysis of precious metals concentration in catalytic converter scrap [7,8]. XRF has many advantages yet it is often necessary to confirm any results with an alternate method established on different physical and chemical principles. In our laboratory a new measurement method has been developed, allowing for cross-validation of measurement of precious metals concentration obtained using XRF technique. The developed measurement method uses inductively coupled plasma mass spectrometry (ICP-MS) technique, with samples being prepared by microwave digestion.

Methods

In this study, the chosen material, monolith from spent car catalysts, was obtained from individual and mass providers (e.g., vehicle disassembly stations, service stations, collection points) in compliance with all rules of conduct provided by the relevant laws. *Unimetal Recycling Sp. z. o. o.* performed the processes of separating the monolith from other catalyst parts and averaging and homogenising it. Homogeneous material testing was carried out with the ICP-MS spectrometer NexION2000P (*Perkin Elmer*) and the microwave mineraliser Titan MPS Microwave Sample Preparation System (*Perkin Elmer*). Digestion was carried out using a variety of acids (hydrochloric acid for trace analysis, *Honeywell Fluka* and nitric acid, *VWR AnalaR Normapur*). Calibration solutions, for standard curve determination and validation of the tested method, were prepared using commercially available standard solutions (palladium, platinum and rhodium concentration 1000mg/L, *Chem-Lab*). Suitability of the equipment was tested with NexION Setup Solution (*Perkin Elmer*). Additionally, verifying the developed sample preparation method and final analyses were performed using certified reference materials – Used Auto Catalyst FLX-CRM 132 and FLX-CRM 133 (*Fluxana GmbH & Co. KG*). To confirm the advantage of the developed methodology, parallel tests were performed. Results of which were compared with the results obtained using the XRF spectrometer (*GoldXpert, Olympus*) and ICP technique (analysis by the monolith recipient). The flow chart in Fig. 1 illustrates the procedure.

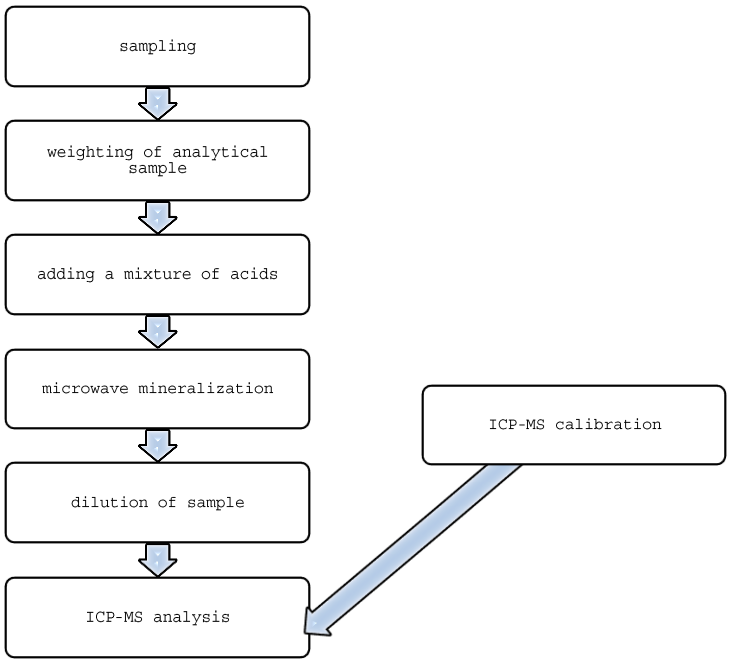

Fig. 1. Measurement procedure steps. *Source: Author's.*

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Results and discussion

The suitability of ICP-MS was tested against a corresponding solution used for optimisation of the system. The manufacturer specifies the conditions, which ensure the device having been properly adjusted and ready to work, enabling recording of reliable measurements. In this case, they are respectively:

- Be 9.0122 > 2000 [cps],
- In 114.904 > 40000 [cps],
- CeO/Ce ≤ 2.5%,
- Ce^{++}/Ce ≤ 3%.

The evaluation of the calibration curves' linearity was done based on injections of the standard solutions prepared in inorganic solvent (diluted acid) at concentrations presented in Table 1. These solutions were each analysed three times. A range of element concentrations was determined in the samples of 200-3000 ppm for palladium, 20-2000 ppm for platinum, and 10-500 ppm for rhodium, respectively. The scope of determination was selected based on own experience and literature data and indicates that the total content of these metals is up to 2000 ppm in the ceramic base. In some works, it is mentioned that car catalytic converter contains typically around 800 - 1000 ppm of platinum, 400 - 1000 ppm of palladium and 60 - 150 ppm of rhodium [9–13].

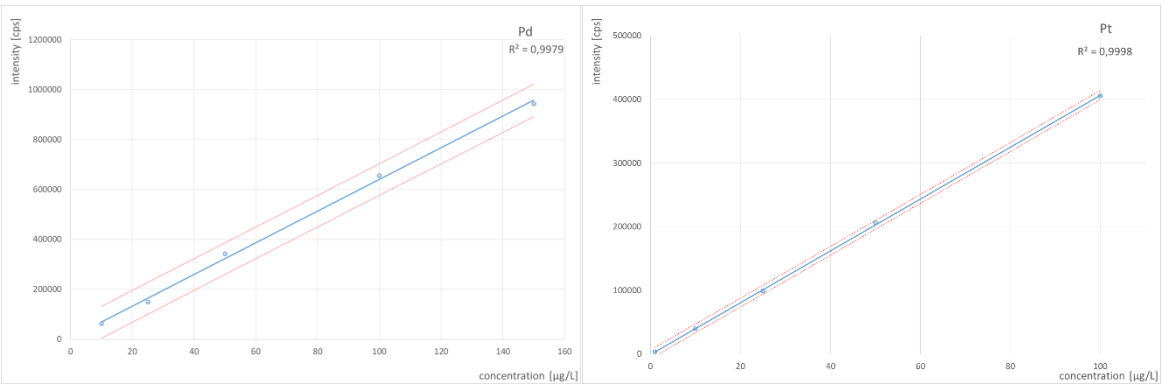
Table 1. Concentrations of calibration solutions. *Source: Author's.*

Calibration level	Palladium, c [µg/L]	Platinum, c [µg/L]	Rhodium, c [µg/L]
1	10	1,0	0,5
2	25	10	1,0
3	50	25	5,0
4	100	50	10
5	150	100	25

Calculations were performed to ascertain the average peak areas, relative standard deviations (RSD) and calibration curve equations. Coefficients of determination (r^2) and linear ranges were determined for each element analysed. Achieved linear coefficients of correlation and determination for each element are presented in Table 2 whereas calibration curves are found in Fig. 2.

Table 2. Correlation parameters for calibration curves of each element. *Source: Author's.*

	Palladium	Platinum	Rhodium
R	0,9990	0,9999	0,9999
r^2	0,9979	0,9998	0,9998



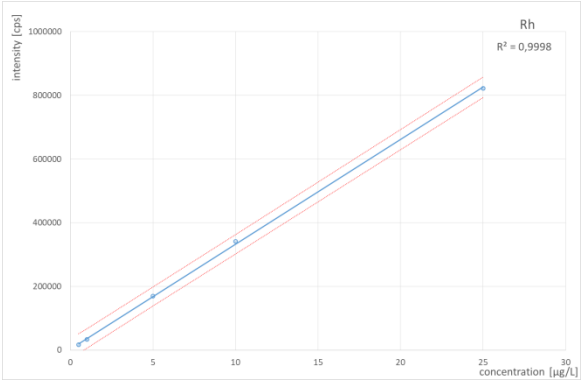


Fig. 2. Calibration curves with confidence intervals. *Source: Author's.*

Repeatability of the findings was investigated by testing the calibration solutions (n=3). Relative standard deviation (RSD) did not exceed 2% for palladium and platinum and 3% for rhodium. Accuracy was verified on a sample without any precious metals, spiked with calibration solutions. Recovery resulted in 94% for palladium and platinum, 91% for rhodium. In addition, the procedure was verified with certified reference materials (FLX-CRM 132 and FLX-CRM 133). The recovery results did not exceed 80 - 120%. Furthermore, standard uncertainty was estimated at less than 10% for palladium and platinum and less than 12% for rhodium. The validation confirmed the adequacy of the newly developed procedure in analysing platinum group elements in ceramic monolith, derived from used catalysts, with accuracy and precision.

The study was followed by determining if the procedure is complementary to standard XRF analysis and ICP method used by homogenised monolith recipients. For this purpose, 20 powder samples were examined with XRF and ICP-MS. The obtained results were compared against the recipients' results during the material verifying process. A strong correlation was found between both ICP-MS results in reference to XRF and recipients' results (Fig.3.).

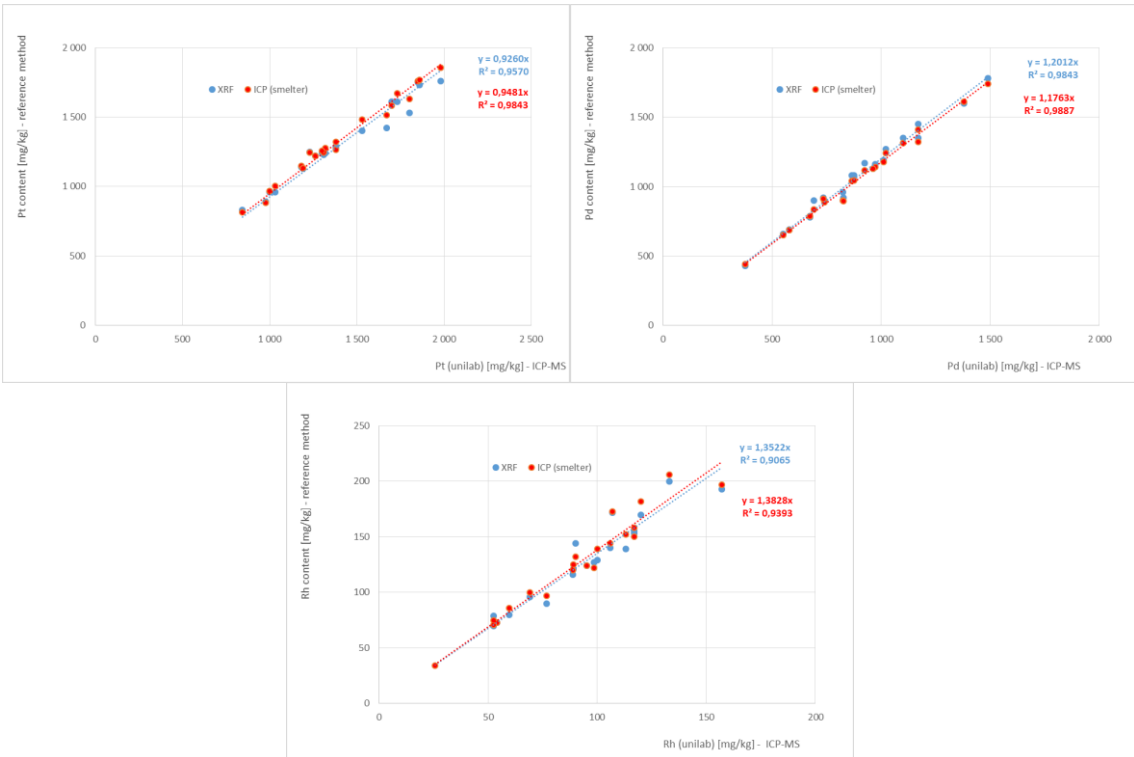


Fig. 3. Correlation between results obtained from the newly developed method, standard XRF procedure and acquired by the material recipient. *Source: Author's.*

For palladium and platinum, the coefficient of determination value was over 0.95, which implies a strong correlation. Slightly weaker results were received for rhodium. However, the r^2 value was over 0.90 for all comparisons. The obtained results confirm also the mentioned above literature data, regarding the content of precious elements in spent car catalysts [9-13] – platinum content was between 800 - 1800 ppm (average 1300 ppm), palladium – 400 - 1700 ppm (average 1000 ppm), and rhodium 30 - 200 ppm (average 130 ppm).

Impact

This study demonstrates the effectiveness of an innovative application of a modern analytical technique, complementary to XRF. The developed procedure produced adequate precision and accuracy with relatively small uncertainty, making it a good complimentary method to XRF. The research results expand current scientific knowledge, thereby raising awareness of possible analytical techniques to determine precious elements (Pd, Pt and Rh) from catalytic converters. The PGM loading in ceramic honeycomb can be determined by ICP-MS technique as confirmatory technique, according to customer's demand. It could be a big benefit for the customer - having a result from another analytical method. Important is, that – based on literature data - the ICP-MS showed the lowest detection limit and less spectral interference than the XRF technique [14].

This study also promotes the circular economy, demonstrating the impact of *Unimetal Recycling Sp. z o.o.* operations in this space. It is a good link between the industry and R&D processes. High demand requires high quality of quantification of the retrieved elements. As previously mentioned, PGM are crucial for the economy. Spent automotive catalysts are a valuable source of important metals such as platinum, palladium and rhodium. They have a high recyclability, therefore it is more convenient to reuse them than get the ores from all around the world. In South African and Russian mining concentration of Pt, Pd, Rh deposits make less than 0,001% per ore [15] (it can be lower depending on the dilution with rocks in the mining process) in car catalyst it could be more. It is the reason why is so critical to the precious metals market to recover the elements and the obtained method makes the determination of concentration in materials easier and allows to have a parallel to XRF (confirmatory) technique.

Another benefit for market and environment would be the application of PGM. Not only automotive industry is eager to use them. Due to its high temperature stability, melting point and corrosion resistance rhodium's properties are key to glass fibre production. Palladium is exploited in electronic components plating, making it more durable and effective than gold. It is also safe and efficient medium for storing hydrogen and a purifier. Platinum's 40% of the overall use is jewellery. It also plays an important role in medical applications, being biologically compatible. In compounds, it can inhibit the cancerous cells from growing [16]. Variety of industries are using the platinum group metals and the demand is growing. Considering the bigger picture, developed method shows potential and is a contribution to the industry and economy.

Conclusions

XRF technique is a fast, economical, and easy to operate analytical technique, which marks the elemental content in ceramic monolith derived from spent car catalytic converters. There is a major drawback to it, appearing in a high RSD value in results. That is why it is often necessary to implement a complimentary technique allowing achieving results with higher accuracy. One possible solution is ICP-MS, verified by the monolith recipient. The method developed produces outcomes with high precision and accuracy. The obtained results allow evaluating the used catalyst converter, for pricing in trade settlements and classification in terms of the possibility to retrieve precious metals.

Conflict of interest

There are no conflicts to declare.

References

[1] M. V. Twigg, Controlling automotive exhaust emissions: Successes and underlying science, Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. 363 (2005) 1013–1033. https://doi.org/10.1098/rsta.2005.1547.

[2] J.G. Cohn, Catalytic converters for exhaust emission control of commercial equipment powered by internal combustion engines, Environ. Health Perspect. 10 (1975) 159–164. https://doi.org/10.1289/ehp.7510159.

[3] M. Keersemaker, Critical Raw Materials, in: Suriname Revisited: Economic Potential of its Mineral Resources, SpringerBriefs in Earth Sciences, Springer, Cham., 2020: pp. 69–82. https://doi.org/10.1007/978-3-030-40268-6_9.

[4] H. Yoon, C.S. Park, C. Yoon, J. Hong, N.S. Kim, K.N. Han, Quantitative analysis of platinum group metals using X-ray fluorescence spectrometry, Miner. Metall. Process. 22 (2005) 101–106. https://doi.org/10.1007/bf03403122.

[5] K. Van Meel, A. Smekens, M. Behets, P. Kazandjian, R. Van Grieken, Determination of platinum, palladium, and rhodium in automotive catalysts using high-energy secondary target X-ray fluorescence spectrometry, Anal. Chem. 79 (2007) 6383–6389. https://doi.org/10.1021/ac070815r.

[6] H.D. Fiedler, E.E. Drinkel, B. Orzechovicz, E.C. Leopoldino, F.D. Souza, G.I. Almerindo, C. Perdona, F. Nome, Simultaneous nondestructive analysis of palladium, rhodium, platinum, and gold nanoparticles using energy dispersive X-ray fluorescence, Anal. Chem. 85 (2013) 10142–10148. https://doi.org/10.1021/ac402419r.

[7] Analytical Science Application, (2021). https://hha.hitachi-hightech.com/.

[8] Analysis of Platinum (Pt), Palladium (Pd), and Rhodium (Rh), in Recycled Catalytic Converters from Automobiles, (2020).

[9] M. Saternus, A. Fornalczyk, Possible ways of refining precious group metals (PGM) obtained from recycling of the used auto catalytic converters, Metalurgija. 52 (2013) 267–270.

[10] C. Hagelüken, Recycling the platinum group metals: A European perspective, Platin. Met. Rev. 56 (2012) 29–35. https://doi.org/10.1595/147106712X611733.

[11] C.R.M. Rao, G.S. Reddi, Platinum group metals (PGM); occurrence, use and recent trends in their determination, TrAC- Trends Anal. Chem. 19 (2000) 565–586. https://doi.org/10.1016/S0165-9936(00)00031-5.

[12] I. Iwasaki, H. Nakazawa, A.S. Malicsi, L. Xiaowei, Recovery of Platinum-Group Metals from Gabbroic Rocks, JOM. 40 (1988) 36–39. https://doi.org/10.1007/BF03258172.

[13] H. Dong, J. Zhao, J. Chen, Y. Wu, B. Li, Recovery of platinum group metals from spent catalysts: A review, Int. J. Miner. Process. 145 (2015) 108–113. https://doi.org/10.1016/j.minpro.2015.06.009.

[14] H. Yoon, C. Yoon, C.S. Park, T. Ko, N.S. Kim, K.N. Han, Quantitative determination of PGM using ICP-MS, ICP-AES, AAS and XRF, Miner. Metall. Process. 22 (2005) 59–64. https://doi.org/10.1007/bf03403197.

[15] F.K. Crundwell, M.S. Moats, V. Ramachandran, T.G. Robinson, W.G. Davenport, Platinum-Group Metals, Production, Use and Extraction Costs, in: Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals, Elsevier, 2011: pp. 395–409. https://doi.org/10.1016/b978-0-08-096809-4.10031-0.

[16] International Platinum Group Metals Association - Standards by Regions, (2020). http://www.ipa-news.com/en/123-0-Standards-by-Region.htm.