AN APPLICATION REPORT FROM
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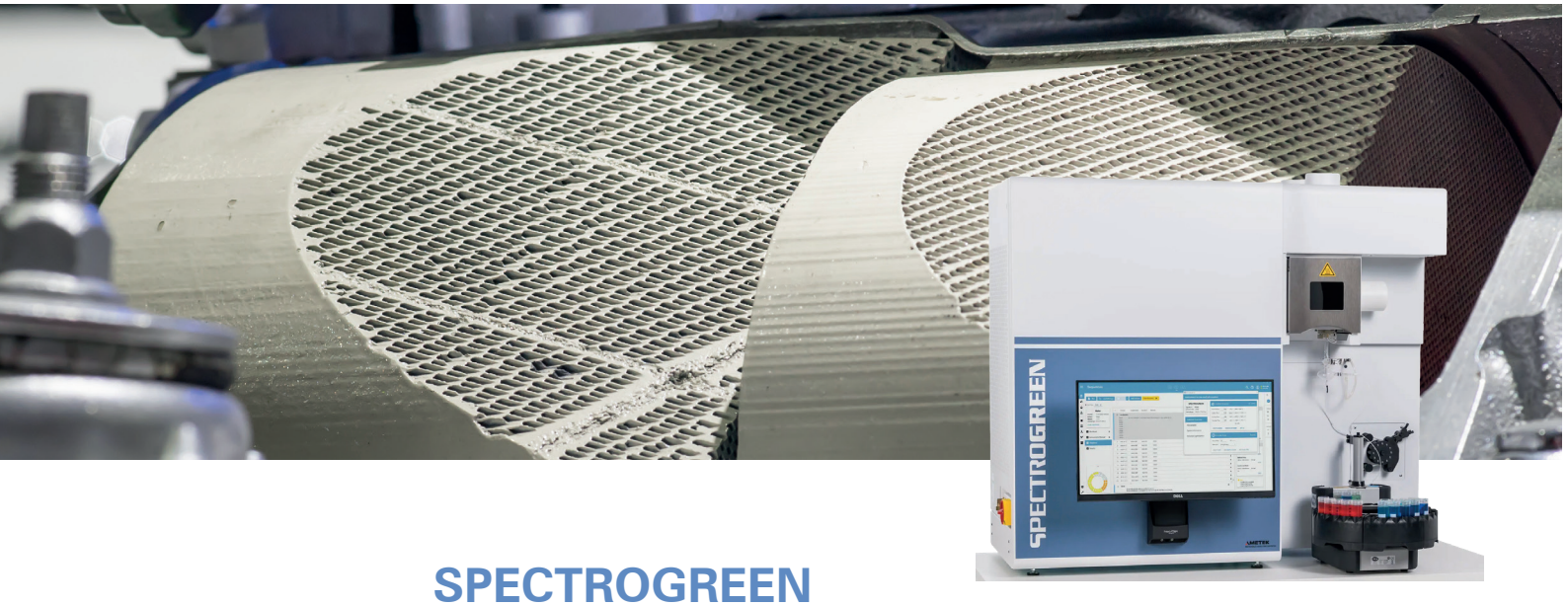
ICP-OES 159



SPECTROGREEN

Analysis of Pd, Pt, and Rh Content in Used Automobile Catalysts by ICP-OES With Dual Side-On Plasma Observation

Introduction

Platinum-group metals (PGMs), and among these especially the palladium-group platinum-group elements (PPGEs) Pd, Pt and Rh, are known for their catalytic properties which are utilized in many chemical production processes [1]. The main use for PGMs, however, comes from the production of catalytic converters for the automotive industry. In 2017, 61% of all PGMs were used in this industry sector. By 2021, this value increased to 71% [2].

The primary source of PGMs is mining, with an annual yield of around 450 tons of these rare metals. As a result of this low amount and the high cost of production, PGMs are very expensive. When used as a catalyst, however, these metals are not consumed. Thus, recycling of catalysts – especially used automobile catalysts – has become an important secondary source of PGMs while additionally helping to reduce the environmental impact of PGM production [3].

The SPECTROGREEN with dual side-on plasma observation offers a simple, fast, accurate, precise and cost-efficient method for the analysis of analyis of Pd, Pt, and Rh content in used automobile catalysts. This report describes the principal methodology and presents typical detection limits and accuracy for these elements.

Recycling of PGMs from automotive catalysts is usually performed either by pyrometallurgical or hydrometallurgical treatment. Many studies have been conducted to find procedures which provide the highest possible recovery of precious metals and their subsequent isolation for refinement. Extraction based processes provide good results, as e.g., they allow for leaching of other metals with weaker acids prior to extraction of PGMs with Aqua Regia [4,5].

As the recycling procedure is still costly and time intensive, materials need to be analyzed before they are entered into the process. ICP-OES is an excellent analytical method for this, even though it does require some sample preparation. Common ways to obtain the liquid sample for analysis are either a fire assay with subsequent dissolution in Aqua Regia, or microwave assisted digestion with a mixture of Aqua Regia and hydrofluoric acid. For this paper, however, a simplified process of microwave assisted extraction was used which avoids the matrix effects incurred from a complete digestion and at the same time can be considered to better represent the actual extraction process.

Experimental

Instrumentation

All measurements were performed with the SPECTROGREEN ICP-OES with dual side-on plasma observation. It enables an average factor 2 enhanced sensitivity compared to single radial plasma observation and a comparable sensitivity to vertical torch dual view systems, while eliminating typical axial view interferences. In addition, it offers a high matrix compatibility, linear dynamic range and precision without the need to change the plasma observation mode during analysis. The SPECTROGREEN features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. Consisting of two hollow section cast shells, optimized small volume and 15 linear CMOS detectors, the wavelength range between 165 and 770 nm can be analyzed, allowing complete spectrum capture within 3 s. Due to the unique reprocessing capabilities of the system, a new measurement is not required even if additional elements or lines are to be determined at a later point in time. The optic is hermetically sealed and filled with argon, continuously circulated through a filter, which absorbs oxygen, water vapor and other species. High optical transmission in the UV is achieved, allowing the determination of non-metals as well as the use of prominent and interference free lines in this region. An air-cooled, 27.12 MHz, free running type LDMOS ICP-generator is installed which ensures excellent stability of the forward power even in the case of rapidly changing sample loads. All relevant ICP operating parameters are software controlled, allowing easy selection of the optimum operating conditions. For sample introduction, a Crossflow nebulizer and a Scott type spray chamber were used. The ICP operating conditions, which were optimized for stability rather than sensitivity, are given in Table 1.

Plasma Power	1300 W
Observation Mode	Dual Side-On
Coolant flow	13 L/min
Auxiliary flow	0.8 L/min
Nebulizer flow	0.85 L/min
Plasma Torch	Quartz, 1.8 mm Injector tube
Spray Chamber	Scott type
Nebulizer	Crossflow
Sample aspiration rate	2 mL/min
Replicate read time	55 s

Table 1 : Typical ICP-OES operating conditions

Sample Preparation

0.5 g of dried, fine powdered solid sample material were extracted with 12 mL Aqua Regia [6] using the Milestone Ethos UP™ (Milestone, Italy) microwave system with SK-15 eT high-pressure and high-temperature rotor. After digestion, the samples were filtered and diluted with deionized water to a final volume of 50 mL. Sc [7] was added as an internal standard.

Calibration

For calibration, commercially available single element solutions [7] were used, acidified with 20% (V/V) Aqua Regia [6] and diluted by weight with deionized water to the concentrations given in Table 2. The limits of detection (LOD) refer to the original solid sample when prepared as described above. They were calculated according to the equation [8]

$$\mathbf{LOD = 3\ RSD_b\ c/100*SBR}$$

Where:

RSD_b – relative standard deviation of 10 replicates of the blank [%]

c– concentration of the standard

SBR – signal to background ratio

Element	Wavelength [nm]	Calibration Range [mg/L]	LOD (solid) [mg/kg]
Pt	177.708	0 - 15	0.26
Pd	324.270	0 - 15	0.98
Rh	343.489	0 - 6	0.82

Table 2: Wavelengths and calibration range

Results and Discussion

To validate the accuracy and repeatability of this method, the international reference sample NIST 2557 was prepared four times as described above, and then analyzed. The results obtained from these measurements can be found in Table 3.

Element	Sample	Measured [mg/kg]	Certified [mg/kg]	Recovery [%]
Pt	1	1104	1131 ± 11	97.6
	2	1102		97.4
	3	1100		97.3
	4	1093		96.6
Pd	1	232.0	233.2 ± 1.9	99.5
	2	232.9		99.9
	3	230.0		98.6
	4	231.1		99.1
Rh	1	127.5	135.1 ± 1.9	94.4
	2	128.1		94.8
	3	127.8		94.6
	4	127.1		94.1

Table 3: Analytical results for the NIST 2557 sample

The results show the excellent suitability of the trace-matrix separation sample preparation by microwave-assisted PGM extraction. No recoveries in excess of 100%, indicative of preparation errors or contamination, were found. The analysis results are in excellent agreement with the certified values, with palladium showing the best recoveries. Comparison of the four extractions also shows a good reproducibility of the preparation process.

Conclusion

The SPECTROGREEN with dual side-on interface plasma observation offers a simple, fast, accurate, precise, and cost-efficient method for the analysis of precious metals in used automotive catalysts. Analysis of the NIST 2557 standard reference material showed that excellent results can be obtained when using a microwave assisted extraction instead of the more complex procedures of fire assays or complete digestion.

Identical results can be achieved on a SPECTRO ARCOS DSOI which would be better suited overall if also high-precision analysis of the finished products using the bracketing technique need to be conducted on the same instrument [9].

In conjunction with an autosampler, the SPECTROGREEN can be fully automated. Independent from the number of lines and elements, an analysis (including three replicates and pre-flush) can be performed in less than four minutes.

References

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