Influence of preparation and analysis methods on determination of Rh, Pd and Pt content in automotive catalysts samples

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Abstract. Use of catalytic converters is of great importance in modern transportation allowing conversion of exhaust gases produced during combustion of fuel into less toxic pollutants. The catalysts itself are mostly precious metals dispersed onto catalyst carrier which should be mechanically resistant and guarantee high surface area required for effective utilization of catalytic converter. Precious metals like rhodium, palladium and platinum commonly used in automotive catalytic converters are expensive and their content remains important even in scrapped converters from which they are extracted. In this paper various approaches for determination of precious metals in used and unused automotive catalysts were described. Two analytical techniques were applied: Inductively Coupled Plasma Optical Emission Spectrometry and Wavelength Dispersive X-Ray Fluorescence and three methods of sample preparation differing in terms of time and cost: (a) microwave-assisted digestion with inorganic acids, (b) fusion with flux and (c) pressed powder method. The latter two methods were used for WD XRF measurements while the first one for the ICP OES. Statistical data analysis was applied in order to assess accuracy and precision of the results obtained and to compare different sample preparation and analytical techniques. Repeatability of sample preparation and measurement, calibration curves, selectivity and recovery were presented.

1. Introduction

Automobiles are one of the most common used mean of transport in everyday life. According to Eurostat in 2014 passengers cars accounted for 83.4% of inland passenger transport [1]. As long as cars' engines need petrol or diesel to work, exhaust gases are produced. The fact that both spark and compression ignition engines produce harmful and undesirable substances during fuel combustion is well known. For example, compression engines are significant source of environment pollution, despite carbon dioxide, due to high particulate matter (PM) and nitrogen oxides (NO_x) emission [2-4]. The other main air pollutants emitted during fuel combustion are carbon monoxide (CO) and hydrocarbons (HC). The emission level of these substances has to be compliant with law requirements, which became more and more restrictive. This accounts significantly for progress in automotive

industry as for this reason reduction method's development is necessary [5-9], as well as actions aimed to fuel consumption reduction.

Control and reduction of exhaust emissions level may be achieved in different ways like improvement of fuel combustion or the use of alternative fuels. There are examples of non-catalytic solutions like one of the most common used in diesel engines: Exhaust Gas Recirculation system (EGR), which allows to reduce NO_x emission *in-situ* (in the place where exhaust gases are emitted) [3,4]. Another way for emitted pollutants reduction is the use of catalytic converters. According to European regulations, since 1994 each produced vehicle has to be fitted with such catalyst [10,11]. Its objective is to convert harmful compounds CO, NO_x and HC into other, less harmful or neutral to atmosphere compounds, that is carbon dioxide (CO_2), nitrogen (N_2) and water (H_2O) [5,10-14]. The result obtained is reduction level of undesirable compounds from exhaust gases.

One of the main characteristics of catalysts is their large surface area which ensures a sufficiently long contact time of exhaust pollutants molecules, flowing at high speed in exhaust gases stream, and the catalyst' active phase [15,16]. Catalytic converters consist of carrier with porous structure of honeycomb, coated with washcoat layer and layer of dispersed Platinum Group Metals (PGM). The carrier is a monolith typically made of ceramic (most often magnesium cordierite, $2MgO.Al_2O_3.5SiO_2$), seldom metal [10-13,16], and washcoat is typically γ-Al_2O_3 (10-30%) with various base metals [5,11,13,15,16]. Ce, Zr or La oxides are commonly used to provide high surface area film allowing high dispersion of active sites, and therefore improving catalytic efficiency of PGM [5,11-13,16].

Active sites corresponding to catalytic performance are usually metals from platinum group, that is platinum, palladium and rhodium [10,11,14-16]. Precious metals particle size varies from 1 to 15 μm, their concentration is relatively low (0.1-0.3%), and their role is both reduction and oxidation of pollutants molecules. Yakoumis et al. [16] found that the average concentration level of Pt, Pd and Rh in used car catalyst was 601-885 ppm, 1302-1884 ppm and 248-343 ppm, respectively. The most frequently used mixture of PGM is Pt:Rh = 5:1, Pd:Rh = 7:1 [10], or Pt:Pd:Rh = 2.4:5.4:1.0 [11]. From three mentioned PGM elements, platinum is the most catalytic active metal, used both for oxidation and reduction. Palladium plays oxidation role, and rhodium has reduction properties [11,15,16]. The basic physical properties of PGM are presented in table 1 [18].

Table 1. Basic physical properties of Pt, Pd and Rh

Property	Platinum	Palladium	Rhodium
Density (g/cm^3)	21.46	11.99	12.40
Melting temperature (°C)	1768.4	1554.9	1964
Boiling temperature (°C)	4170	2940	3760
Brinell Hardness (MPa)	300	400	1 400
CAS no.	7440-06-4	7440-05-3	7440-16-6

On the other hand, used (poisoned) catalytic converters are important, secondary source of precious PGM, as their concentration is considerably higher in converters than in ores from which they are primarily extracted [13]. The amount of precious metals restored from used catalysts have reflection in catalytic converter price. For this reason a reliable and precise analytical method for determination of rhodium, palladium and platinum need to be applied. It should be mentioned that determination of rhodium and palladium can be a challenge for chemical analyst because of analytical methods limitations due to complicated matrix. Moreover, when analyzing those elements at low concentration levels large sample amount and pre-concentration step are required [14,19].

Sample of catalyst should be as homogenous as possible to represent the overall material [16], and has to be prepared properly prior to analysis. Examples of samples preparation are: leaching in aqua

regia, leaching in solution of H_2SO_4 and HNO_3 [13], fusion with SiO_2, NaOH and Cu [11], fusion with $Li_2B_4O_7$ and KNO_3 [16], enrichment with NiS_2 fire assay, Pb fire assay, high pressure digestion, liquid extraction, solvent extraction, Na_2O_2 fusion [16], and others. Among analytical methods involved in Pt, Rh and Pd determination following can be mentioned: EDS SEM [10], ICP OES, LA ICP MS, GD MS, SOES, ICP MS [16,20].

The aim of present work was elaboration, optimization and validation of preparation and analysis method of PGM in catalyst samples. The method should be applicable to both new and used catalyst, be reliable and independent from sample matrix and concentration level of determined elements.

2. Methodology
Two analytical techniques were applied: Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) and Wavelength Dispersive X-Ray Fluorescence (WD XRF) and three methods of sample preparation: microwave-assisted digestion with inorganic acids, fusion with flux and pressed powder method.

2.1. Chemicals, samples and Reference Materials
Three samples of automotive catalysts, two new catalysts and one used, were chosen for analysis. Before analysis samples were grounded to fine powder in agate mortar. Different standard reference materials (SRM) were applied to check analytical method performance: used automobile catalyst ERM®-EB504a (BAM, Germany), used auto catalyst (pellets) 2556 (NIST, USA) and used auto catalyst (monolith) 2557 (NIST, USA). The certified values for each catalyst are presented in table 4.

The catalysts tested differed in chemical composition of matrix, which was determined by means of WD XRF method after fusion with $Li_2B_4O_7$ flux. All tested samples and reference materials consisted of ceramic carrier, but the ratio of particular oxides in samples was different (for RM EB504a $SiO_2:Al_2O_3:MgO = 48:37:10$; for SRM 2556 $SiO_2:Al_2O_3:MgO = 38:39:11$; for SRM 2557 $SiO_2:Al_2O_3:MgO = 0:81:0.15$; for new catalyst 1 $SiO_2:Al_2O_3:MgO = 27:31:8$ with addition of 3% BaO; for new catalyst 2 $SiO_2:Al_2O_3:MgO = 44:36:12$; for used catalyst $SiO_2:Al_2O_3:MgO = 26:30:7$ with addition of 2% BaO).

Inorganic acids (nitric and hydrochloric) used for extraction of PGM prior to analysis by means of ICP OES were of suprapur grade (Merck, Germany). Working standard solutions prepared from single standard solutions of platinum (1000 μg/mL in 10% HCl, VWR Chemicals, USA), palladium (10000 μg/mL in 10% HCl, VWR Chemicals, USA) and rhodium (1000 μg/mL in 10% HCl, VWR Chemicals, USA) were prepared and used for spectrometer calibration.

Fluxes ($Li_2B_4O_7$; $Li_2B_4O_7+LiBO_4$) and oxidizer (KNO_3) for sample preparation prior to WD XRF analysis were of ultrapure grade (SpexCertiPrep, USA).

2.2. ICP OES method – sample preparation and analysis (method 1)
Each sample (catalysts with unknown PGM concentrations and SRMs) were weighted (0.1 g) into Teflon vessel in duplicate, and 6 mL of *aqua regia* (4.5 mL of HCl and 1.5 mL of HNO_3) was added to each vessel. Samples were digested in closed high pressure microwave-assisted oven (SpeedWave 4, Berghof, Germany), filtered before analysis and diluted to 50 mL with deionized water.

Concentration of platinum, rhodium and palladium was determined by means of ICP OES (Optima 8300, PerkinElmer, USA). Multipoint calibration curves were prepared for each element. Measuring conditions of spectrometer were as follows: RF generator power: 1300 W; plasma gas flowrate: 12 L/min; auxiliary gas flowrate: 0.2 L/min; nebulizer gas flowrate: 0.6 L/min; nebulizer: Meinhardt concentric; spray chamber: glass cyclonic.

2.3. WD XRF method – sample preparation and analysis
The X-ray fluorescence method, as many other techniques, requires proper sample preparation prior analysis. Powder samples are usually prepared in two ways: pressed in press to form of tablet or fused in high temperature with flux. Concentration of PGM was determined by means of WD XRF (ZSX

Primus II, Rigaku, Japan). Multipoint calibration curves were prepared for each element on the basis of matrix reference materials prepared in the same way as samples. Measuring conditions of X-ray fluorescence spectrometer were as follows: tube: above sample; tube voltage: 60 kV; tube current: 50 mA; target: Rh; window: Be 30 μm; sealing: out; atmosphere: vacuum; crystal: LiF(200) and LiF(220).

2.3.1. Pressed powder method (method 2). Grounded samples of catalysts of unknown PGM concentration and reference materials were pressed in duplicate in manual hydraulic press (pressure of 10T). No binder or wetting agent was added during sample preparation. Pressed samples in form of tablets of 10 mm size each were then analysed directly by means of WD XRF.

2.3.2. Fusion with flux (method 3). Grounded unknown samples and reference materials were weighted (0.7 g) into platinum-gold (95%+5%) crucibles, 5 g of $Li_2B_4O_7+LiBO_4$ (50+50) flux and 0.2 g of KNO_3 oxidizer were added. Samples were fluxed in automatic electric fluxer (SPEX X-300, Katanax, Canada) at temperature of 1050°C, after oxidation step at 900°C. Total fluxing time was 35 minutes. Obtained pearl samples of 32 mm size each were then analysed directly by means of WD XRF.

3. Results and discussion

3.1. Spectrometric analysis (method 1)
In spectrometric analysis (ICP OES) the first step was to choose proper analytical line which is not affected by spectral interferences. For nearly each element several lines are available, and for elements under study following were chosen at the beginning: Pd - lines 340.458 nm, 324.270 nm, 248.892 nm, and 363.470 nm; Rh - lines 343.489 nm, and 233.477 nm; Pt - lines 265.945 nm, 214.423 nm, 204.937 nm, and 299.797 nm. There are more lines available for each element in spectrometer library, but many of them are not sensitive enough or are affected by spectral interferences (i.e. Rh line 328.055 nm is overlapped with Ce and Nb lines). Different samples with different matrix were analyzed, and spectrum were recorded.

Spectrum for each selected line are presented in figures 1…5. As can be seen in figure 1 Pt line 299.797 nm lies close to very intensive double line of Hf, Zr, Ru, V, Cu, Zr, Th or V, which was noticed especially in new catalyst 2 spectrum. Similar situation was observed for Pt line 204.937 nm which is affected by other elements (Pb, Co, Cr, V, Mo, W, Rh, Re, Ru…) lines from both sides, and interferences differ depending on sample matrix. In the case of Pt line 265.945 the peak signal was very wide, moreover background line raising with sample matrix changes was observed. No relevant analytical signal could be observed in that case. The only proper, sensitive and narrow line for platinum, which can be applied for analysis of automotive catalyst was line 214.423 nm (figure 2). In this case two-point background correction was used.

Spectrum for palladium was observed for four analytical lines, but again only one of them was selected as appropriate for further analysis (line 248.892 nm, figure. 3). In this case two-point background correction was used. Possible spectral interferences from other elements are far enough to not affect signal from Pd. On the opposite was line 324.270 nm, which, depending on sample matrix, was significantly affected by lines of other elements: Zr, Ho, Th, Fe, Ti, V and W (figure 4). Moreover, the signal from palladium was very weak, and the interferences resulted in its intensity increase, and therefore too high analysis results. Similar situation was observed for Pd 340.458 nm, which was overlapped by lines of Zr, W and Fe. Line 363.470 nm could not be used for Pd analysis because of strong Ar signal (Ar is used in ICP-OES technique as carrier and fuel gas).

In case of rhodium situation was much more complicated. From all available lines only two were selected: 343.489 nm, and 233.477 nm. The remaining were not sensitive enough to record any significant analytical signal. Unfortunately, it turned out that line 233.477 nm could not be used also

because of not-analytical signal. For that reason only line 343.489 nm can be used for automotive catalyst analysis. In this case one-point background correction was used (figure 5).
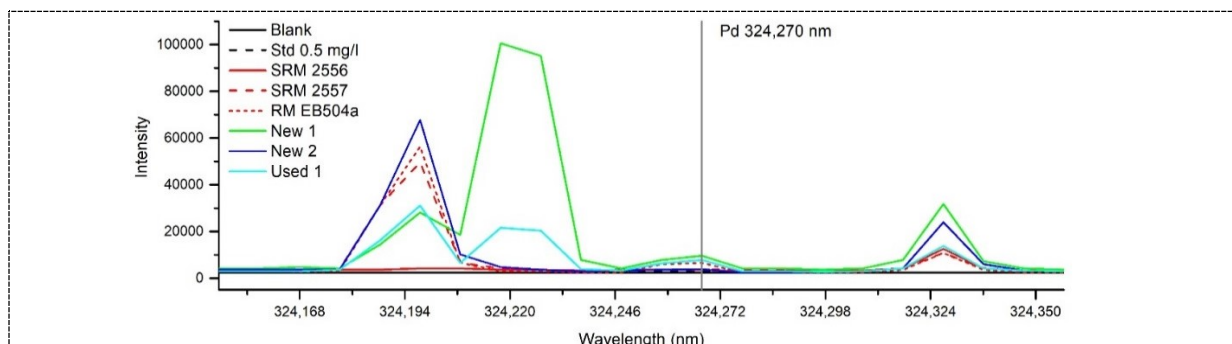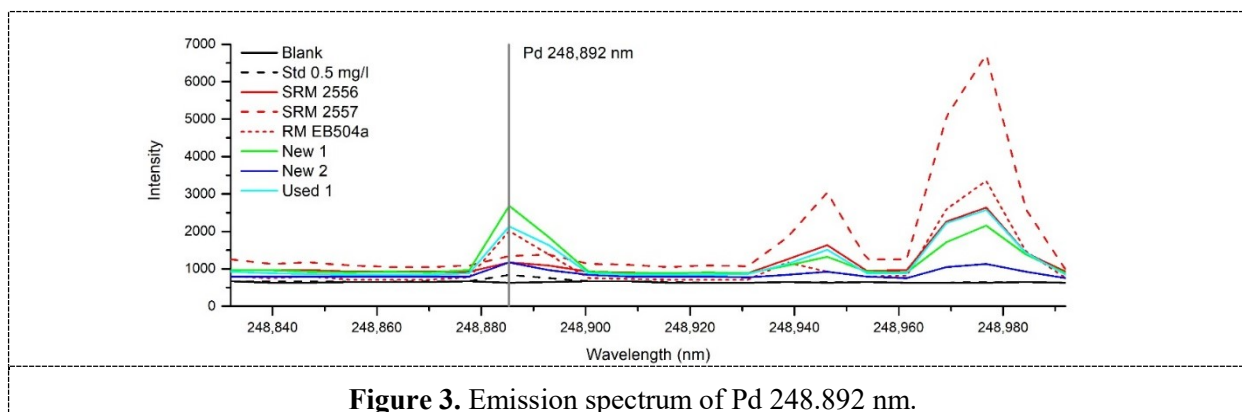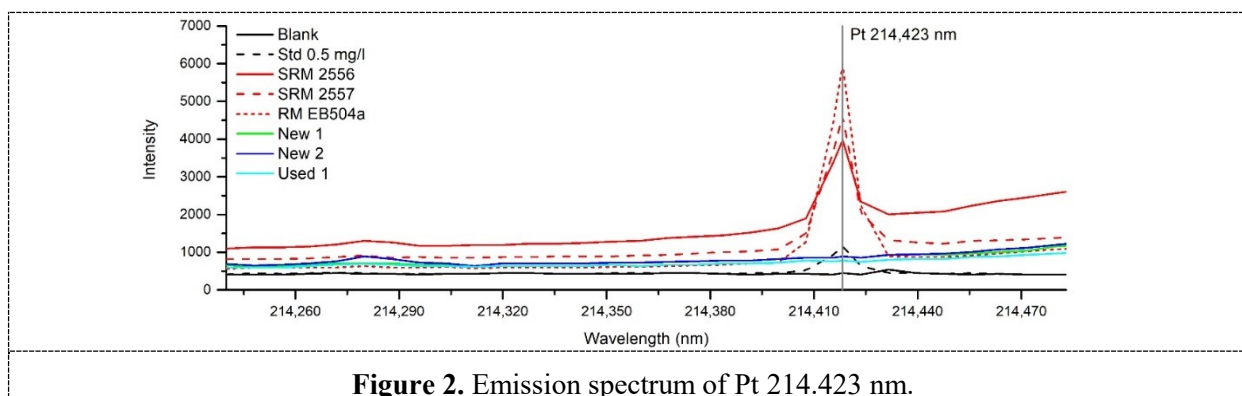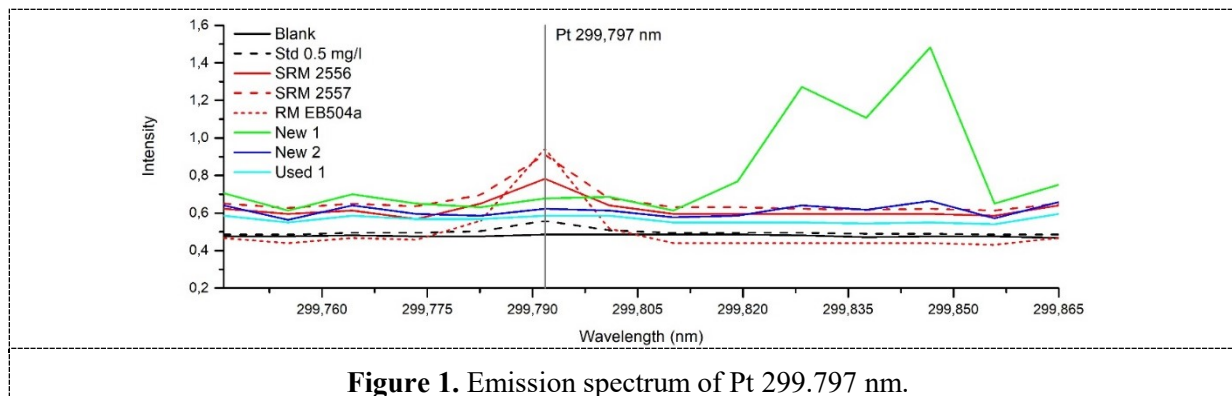

Figure 1. Emission spectrum of Pt 299.797 nm.

Figure 2. Emission spectrum of Pt 214.423 nm.

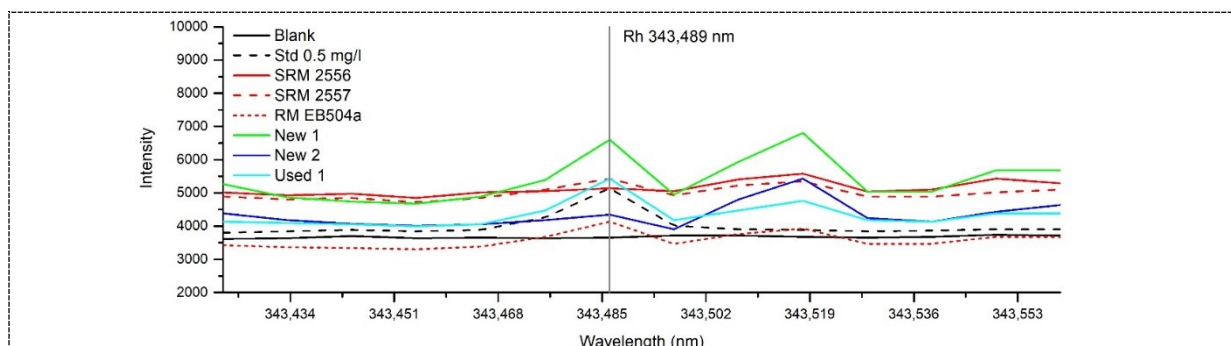**Figure 3.** Emission spectrum of Pd 248.892 nm.

Figure 4. Emission spectrum of Pd 324.270 nm.

Figure 5. Emission spectrum of Rh 343.489 nm.

One proper, selective and sensitive line for each PGM was selected for method validation. Analysis method was validated in the following range: sample preparation repeatability, measurement repeatability, recovery, recovery by the standard addition method, calibration curves statistics, and expanded uncertainty was calculated. The results obtained are presented in table 2.
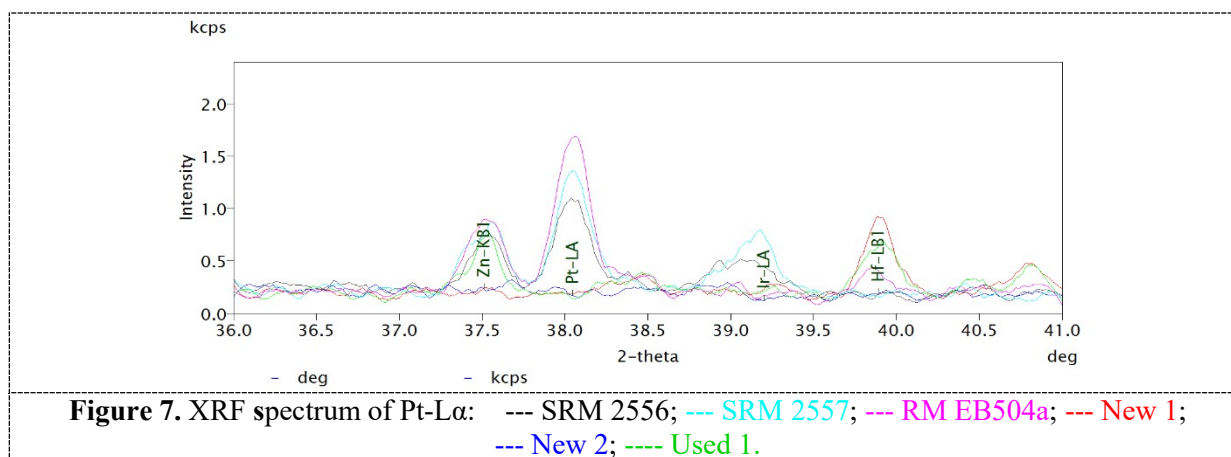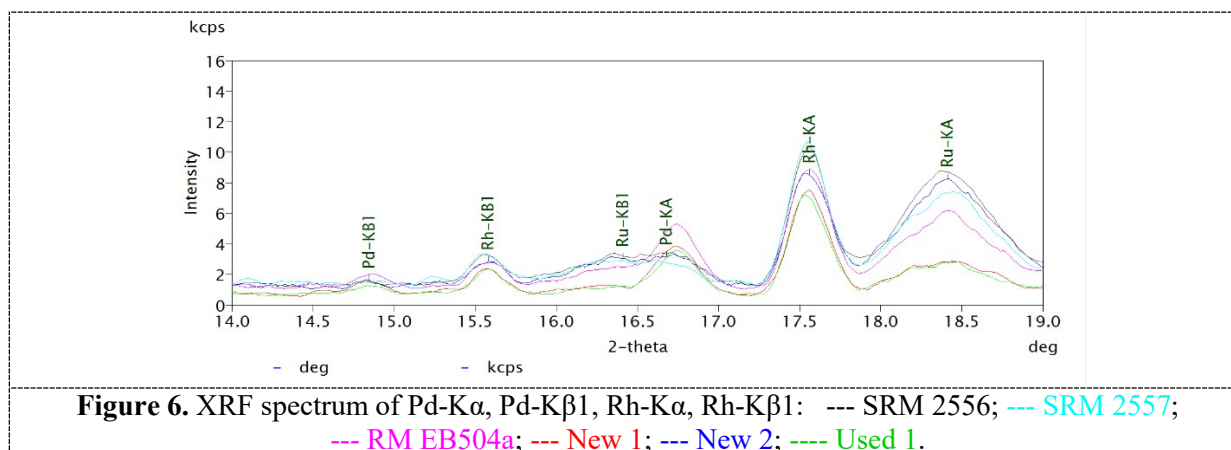
Table 2. Validation parameters of method 1

Property	Platinum	Palladium	Rhodium
Analytical line (nm)	214.423	248.892	343.489
Repeatability of sample preparation (%)	1.08	1.76	0.67
Repeatability of measurement (%)	1.05	2.15	4.65
Recovery – standard addition method (%)	98.5	97.5	91.8
Coefficient of variability, V_m (%)	1.59	1.80	0.85
Correlation coefficient, r^2	0.9999	0.9999	1.0000
Expanded uncertainty (%), p=0.95, k=2	2.00	3.90	7.65

Calibration curves were linear in whole analytical range, and the correlation was very strong ($r^2 > 0.999$). Repeatability of spectrometric measurements was high (CV < 5%), and so was repeatability of sample preparation (CV < 2%). Moreover, recovery by standard addition method was above 90% which means that extraction method applied allowed for quantitative PGM transition into solution. The verification of correctness of elaborated method was confirmed by standard reference materials analysis (results in table 4). Moreover, samples with unknown Pt, Pd and Rh concentration were analysed and results were compared with results from WD XRF method (table 5).

3.2. X-ray fluorescence analysis

In X-ray fluorescence the analysis is based on measurement of energy emitted by excited atoms. Each element has its characteristic energy, and for elements under study characteristic (the most energetic) emission lines were selected. Following lines were chosen: Rh – lines Kα and Kβ1; Pd - lines Kα and Kβ1; Pt – lines Lα and Lβ1. For each line qualitative analysis was performed, that means analytical spectrum (figure 6 and 7) was recorded for both sample preparation method in order to assess their usefulness in quantitative analysis.

Figure 6. XRF spectrum of Pd-Kα, Pd-Kβ1, Rh-Kα, Rh-Kβ1:   --- SRM 2556; --- SRM 2557; --- RM EB504a; --- New 1; --- New 2; ---- Used 1.

Figure 7. XRF spectrum of Pt-Lα: --- SRM 2556; --- SRM 2557; --- RM EB504a; --- New 1; --- New 2; ---- Used 1.

The recorded spectrum for method 3 (sample fusion) had higher intensity (approximately one order higher) in comparison to method 2 (pressed powder). Unfortunately, distinction between analysed elements and interfering elements was significantly lower. Moreover, the observed correlation between concentration changes and intensity was weaker in method 3 than in method 2.

The main problem in WD XRF analysis is scattering of Rh and Ru lines from X-ray tube (target Rh) on lines of analysed elements. As it is presented in figure 6 line Ru- Kβ1 overlap line Pd-Kα, and line Ru-Kα overlap line Rh-Kα, which has a result in signal enhancement for palladium and rhodium, respectively. Similar situation was observed for line Pt-Lβ1 which was overlapped by Rh line from tube. This problem theoretically can be solved by inserting the primary beam filter (Ni400 in this case), but significant decreasing of elements signal intensity was observed. There is also possibility to use other than Rh target tube, i.e. Pd, W, Cr or Au, but just Rh target is the most common used in universal spectrometers. To sum up, careful attention should be paid when analysing Rh and Pd with Rh target, because complete selectivity of these elements lines cannot be guaranteed.

From the other interferences, it can be seen that Pt-Lα line may be overlapped by line Zn-Kβ1, when Zn is present in analysed sample (figure 7). On the basis of qualitative analysis, for the analysis of unknown samples one line for each element was chosen: Pt-Lβ1, Pd- Kβ1, and Rh-Kα. For selected rhodium line theoretical α-correction was applied.

In next step validation was performed for each sample preparation method and measurement in the following range: sample preparation repeatability, measurement repeatability, recovery, calibration curves statistics, and expanded uncertainty was calculated. The results obtained for method 2 and 3 are presented in table 3.

Calibration curves in method 2 were linear in whole analytical range, and the correlation was very strong ($r^2 > 0.995$), while in method 3 the correlation was strong with correlation coefficients

$r^2 > 0.879$. The best linear calibration curve in method 3 was achieved for palladium, and in method 2 for platinum.

Table 3. Validation parameters of method 2 and 3

Property	Platinum	Palladium	Rhodium
Analytical line	Lβ1	Kβ1	Kα
Angle (deg)	54.912	21.074	17.558
Correction	no	no	α-correction
Method 2			
Repeatability of sample preparation (%)	1.06	1.35	1.11
Repeatability of measurement (%)	1.19	4.91	4.70
Correlation coefficient, r^2	0.9996	0.9966	0.9976
Expanded uncertainty (%),p=0.95, k=2	2.12	9.87	13.4
Method 3			
Repeatability of sample preparation (%)	1.22	2.34	3.15
Repeatability of measurement (%)	1.61	4.40	3.96
Correlation coefficient, r^2	0.8790	0.9964	0.9768
Expanded uncertainty (%), p=0.95, k=2	3.56	9.60	10.2

Repeatability of pressed samples measurements was high (CV < 5%), and so was repeatability of sample preparation (CV < 2%). Similarly, repeatability of fused sample preparation was high, and so was the measurement repeatability. The best repeatability of sample measurement in both methods was observed for Pt (CV < 2%), while for Pd and Rh repeatability was at the same level in both methods. Similarly, in ICP OES method the best sample measurement repeatability was also observed for Pt, and for Rh it was at the same level like in method 2.

The expanded uncertainty in both WD XRF methods was significantly higher than in ICP OES method for palladium, and rhodium. The highest expanded uncertainty for rhodium and palladium was observed in method 2 (13.4% and 9.87%, respectively), and the lowest in method 1 (3.90% and 7.65%, respectively). Platinum can be measured with the best accuracy when using method 1, however in other methods uncertainty of this element measurement is relatively low (3.56% in the worst case).

The verification of elaborated method correctness was confirmed by standard reference materials analysis (results presented in table 4). Moreover, samples with unknown Pt, Pd and Rh concentration was analysed and results obtained by different methods were compared (table 5).

Recovery, calculated as a ratio of measured value to certified value, was high for each element and method (76.6%…135.4%). The average recovery for Pt was 99.6%, for Pd 89.4%, and for Rh 94.3%. On the other hand, the average recovery for ICP OES method was 87.2%, for pressed sample and WD XRF method it was 101.0%, and for fluxed samples and WD XRF method the recovery was 94.8%. High recovery ratio confirmed usefulness of all methods applied.

Comparison of results for samples with unknown concentration of PGM also confirmed the high correctness of different analytical method used. The most similar results were obtained for method 1 and method 3. None of tested automotive catalyst contained platinum, the main catalytic element used in these catalyst was palladium with some rhodium addition. The ratio Pd:Rh was approximately 7:1 which is similar to the one reported by [10].

Table 4. Recovery of PGM by different analytical methods

Property	SRM 2557	SRM 2556	RM EB504a
Platinum			
Certified value (mg/kg)	1131 ± 11	697.4 ± 2.3	1414 ± 9
Measured value - method 1 (mg/kg)	1113 ± 22	701.8 ± 14	1322 ± 26
Measured value - method 2 (mg/kg)	1110 ± 23	707.0 ± 14.4	1434 ± 29.4
Measured value - method 3 (mg/kg)	964 ± 45	812 ± 38	1431 ± 66
Recovery - method 1 (%)	98.4	100.6	93.5
Recovery - method 2 (%)	98.1	101.4	101.4
Recovery - method 3 (%)	85.2	116.4	101.2
Palladium			
Certified value (mg/kg)	233.2 ± 1.9	326.0 ± 1.6	1596 ± 11
Measured value - method 1 (mg/kg)	167.7 ± 6.5	282.4 ± 11.0	1493 ± 58
Measured value - method 2 (mg/kg)	185.0 ± 18.3	343.7 ± 33.7	1635 ± 161
Measured value - method 3 (mg/kg)	206 ± 15	289 ± 20	1416 ± 100
Recovery - method 1 (%)	71.9	86.6	93.5
Recovery - method 2 (%)	79.2	105.4	102.4
Recovery - method 3 (%)	88.4	88.7	88.7
Rhodium			
Certified value (mg/kg)	135.1 ± 1.9	51.2 ± 0.5	210.0 ± 2.2
Measured value - method 1 (mg/kg)	114.6 ± 8.8	40.2 ± 3.1	160.8 ± 12.3
Measured value - method 2 (mg/kg)	141.0 ± 18.8	69.3 ± 9.3	176.0 ± 23.5
Measured value - method 3 (mg/kg)	118.0 ± 6.6	50.0 ± 2.8	210.0 ± 11.8
Recovery - method 1 (%)	84.9	78.6	76.6
Recovery - method 2 (%)	104.4	135.4	83.8
Recovery - method 3 (%)	87.3	97.7	100.0

Table 5. Results for catalysts samples of unknown composition by different methods

Sample		Method 1	Method 2	Method 3
New catalyst 1	Platinum	< 0.001	< 0.001	< 0.001
	Palladium	0.23 ± 0.01	0.15 ± 0.01	0.19 ± 0.02
	Rhodium	0.039 ± 0.003	0.025 ± 0.002	0.037 ± 0.004
New catalyst 2	Platinum	< 0.001	< 0.001	< 0.001
	Palladium	0.048 ± 0.008	0.052 ± 0.005	0.047 ± 0.003
	Rhodium	0.0067 ± 0.0005	0.0052 ± 0.0004	0.0061 ± 0.0006
Used catalyst	Platinum	< 0.001	< 0.001	< 0.001
	Palladium	0.21 ± 0.01	0.13 ± 0.01	0.17 ± 0.02
	Rhodium	0.027 ± 0.002	0.028 ± 0.002	0.036 ± 0.004

4. Summary

Three methods of catalyst preparation and analysis of Pt, Pd and Rh was described and compared. Both ICP OES measurement after sample digestion, and WD XRF measurement after sample fusion are time consuming and require expensive additional equipment (microwave-assisted oven or electric fluxer). Moreover ICP OES method require calibration each working day, which additionally increases analysis time, however is not as affected by matrix or inter-element interferences as X-ray fluorescence.

The least time consuming method of PGM determination was sample-pressed WD XRF measurement. However, this method is the most prone to sample inhomogeneity due to segregation, grain size or mineralogical effect. Theoretically, sample fluxing should led to the most repeatable and exact results, because grain size and mineralogical effect are removed and matrix is diluted during fusion. Despite higher measurement uncertainty, this method allows to obtain very similar results to results from ICP OES after sample digestion.

On the basis of results obtained it can be stated, that proposed methods allows for reliable determination of platinum group metals in both new and used automotive catalysts, disregarding their chemical composition

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