

The Effect of Complexity of a Matrix on Variation of Platinum Group Metal Determination Using ICP OES and Correction Method: A Spent Catalyst as a Case Study

Ha Bich Trinh, Seunghyun Kim, Taehun Son, and Jaeryeong Lee*



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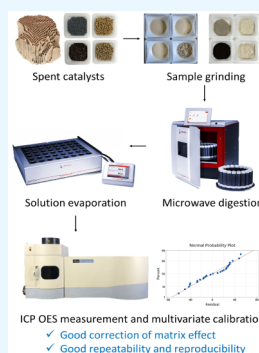
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ABSTRACT: Recycling of platinum group metals (PGMs) from spent catalysts is a promising alternative to the sustainable metallurgy of critical metals, which requires an accurate and reliable analytical approach for their determination. A potential microwave-assisted digestion and multivariate calibration procedure was investigated to determine the PGM contents in various spent catalyst samples. The effect of several interelements (Al, Mg, Ce, and Na) was evaluated by the single factor at once and multilinear regression models, which demonstrated a significant variation in PGM determination using inductively coupled plasma optical emission spectrometry. The magnitude of effect due to these interferences can be -30% for Pt and Pd, and 20% for Rh. The application of multivariate calibration was effective for Pt and Pd determination from spent catalysts by reducing standard error of prediction from $>10\%$ to $<3.5\%$ for Pt and 8.0% to 2.6% for Pd; however, the effectiveness was more moderate for Rh. The crossed gage repeatability and reproducibility (GR&R) study showed a high value of contribution by part-to-part variation to the total variation ($>98\%$) for all PGMs. Although the total GR&R contribution for Rh determination 19.77% was higher than those of Pt and Pd (11.03% and 8.31%), the analytical procedure was acceptable as a reliable approach. Microwave-assisted digestion and multivariate calibration showed efficient dissolution of the samples and less effects by interelements, which was suitable for investigating PGM-containing samples with a complicated matrix.



1. INTRODUCTION

Spent catalysts are potential resources for platinum group metal (PGM) recovery to maintain the long term availability and sustainable metallurgy of such critical metals.^{1–4} The effective recycling of spent catalysts can alleviate the imbalance between the rapid increase in PGM demand for important applications and gradual reduction in their high-grade ores. PGM metallurgy from spent catalysts involves simpler processes, lower energy consumption, and less emission gases than those from the mining of natural resources; therefore, it moderates the harmful impacts to the environment and provides potential economic benefits.⁴ The recycling of spent catalysts certainly increases with the higher demand to determine PGMs at trace levels for content analysis, efficiency evaluation, product purity, or environmental impact, which requires more accurate and reliable analytical approaches.

Generally, the analysis procedure involves two major stages: sample decomposition using an effective dissolution method (wet digestion, fire assay, or oxidizing fusion) and instrumental determination of PGMs.^{5,6} A mixture of mineral acids and oxidants is commonly used to extract PGMs; however, it cannot obtain the completed dissolution due to the significant refractory nature of substrate materials (Al_2O_3 or cordierite). Fire assay selectively converts PGMs from a complex matrix of samples at high temperatures to metal alloys with suitable collector metals.⁵ Oxidizing fusion is exclusively used to

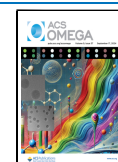
decompose Rh with high resistance to acid media or a refractory Al_2O_3 -based or cordierite substrate.⁵ Although fire assay or oxidizing fusion is more effective for sample preparation than wet digestion, the procedures are complicated and require numerous chemicals or unique equipment and conditions. Moreover, fire assay is energy-consuming and more suitable for a large variety of samples,⁷ while oxidizing fusion can introduce high concentrations of interfering metals into solutions due to the high amount of fusion fluxes.⁵ Therefore, microwave-assisted digestion is preferred for sample preparation, because it offers a simpler procedure and less chemical consumption. Microwave-assisted digestion is widely applied for PGM extraction from a variety of sample types such as dust and plants,⁸ soil and dust,⁹ biological samples,¹⁰ and spent autocatalysts.⁷ The significant advantages of this method are rapid and efficient heat supply, reduction of reagent usage and time consumption, less volatilization of analytes, and minimization of contaminants.^{11,12} However, the efficient dissolution of PGMs and other materials from samples leads

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to the concern of interferences by matrix complexity during analysis by a corresponding instrumental technique.

Among available instrumental techniques, inductively coupled plasma optical emission spectrometry (ICP OES) has been widely used for PGM determination with excellent accuracy, sensitivity, and detection limit.^{5,6} Although ICP OES can provide better results for samples with high dissolution of matrix elements and low concentrations of PGMs (Yoon et al., 2005),¹³ interferences on the quality and accuracy of PGM determination were still significant.^{14–16} The presence of several interelements (Al, Mg, Ca, Fe, and Cu) could generate the under/overestimation of PGM concentration related to the major factors: emission wavelength, analyte concentration, interferent concentration, and the number of matrix elements.^{14,17} Another investigation demonstrated the effects of Al, Ca, K, and Na on the variation of PGM determination at different emission lines, which could induce an intensive bias up to ~30%.¹⁵ Conventional methods were applied to reduce the effect of matrix complexity, such as matrix matching, standard addition, or interelement corrections. However, these techniques were not efficient for a large number of samples with complex composition.^{18–22} An alternative approach based on multivariate calibration has been proposed to effectively moderate the variation in PGM determination induced by interference of matrix elements. For example, the range of standard errors of prediction for a set of simulated samples with a single interelement reduced from 4.9–45.8% to 1.2–17.1%, and the relative standard error for Pt and Rh determination in a reference sample reduced from –12.5% and 8.0% to –2.5% and –5.4%, respectively.¹⁵ Therefore, there is potential to investigate the combination of an effective digestion process and a correction method to enhance the accuracy of PGM determination from spent catalysts.

In the present work, PGMs (Pt, Pd, and Rh) in spent catalysts were determined using microwave digestion followed by ICP OES using multivariate calibration to minimize the effects by the complexity of a sample matrix. The variation in PGM determination using ICP OES due to the presence of several interelements was investigated by two approaches: single factor at once and multiple liner regression (MLR) models. Different types of PGM-bearing spent catalysts were collected, and microwave-assisted digestion was employed to achieve efficient dissolution. Subsequently, ICP OES with the multivariate calibration technique was used for PGM determination to reduce the influences by the complex matrix of samples. The crossed gage repeatability and reproducibility (GR&R) study was used to evaluate the analysis process for all the PGMs.

2. MATERIALS AND METHODS

2.1. Reagents and Materials. Simulated PGM-bearing leach liquors were prepared using standard solutions of 1000 mg/L monoelements (Merck KGaA, Darmstadt, Germany) and analytical grade nitric salts: Al(NO₃)₃·9H₂O (98%, Junsei Chemical Co., Ltd.), Mg(NO₃)₂·6H₂O (98%, Junsei Chemical Co., Ltd.), Ce(NO₃)₃ (97%, Daejung Chemicals and Metals Co., Ltd.), and NaNO₃ (99%, Daejung Chemicals and Metals Co., Ltd.). All solutions were diluted using HNO₃ at 2.0% to reach the desired concentration for the corresponding investigations (PGMs including Pt, Pd, and Rh at 0.1 to 1.0 mg/L and other interelements at 100 to 500 mg/L).

2.2. Sample Collecting and Digestion. The spent catalyst samples were collected and provided by the Korea

Institute of Geoscience and Mineral Resources (KIGAM), and the PGM contents were determined by the fire assay method. The collected spent catalysts were classified as Al₂O₃-based catalysts and cordierite-based catalysts (autocatalysts). The phase of the major components and the morphology of the samples were analyzed by X-ray diffraction (XRD; D2 Phaser, Bruker, Germany) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS; Hitachi S-4800, Japan).

A microwave digestion system (Multiwave 5000) and Teflon vessels were used for the acid dissolution of the spent catalysts. A 0.1 g of powder sample was placed in the vessel, and 7 mL of aqua regia (HCl:HNO₃ = 3:1), 2 mL of hydrofluoric acid, and 1 mL of perchloric acid were added to assist the dissolution of the refractory spent catalysts. The digestion was performed under the following conditions: power of 2000 W, temperature of 220 °C, and a holding time of 20 min. The obtained solutions were transferred to PTFE vials and evaporated at 90 °C using a heating block (Multicube 48). After evaporation, 5 mL of aqua regia was added, and the solutions were heated again to achieve near dryness. This procedure was repeated three times with the addition of concentrated HCl. The final samples were dissolved in 10 mL of HCl 2.0% and stored at 4 °C until further analysis.

2.3. Instrumentation. The PGM-containing standard and sample solutions were introduced and analyzed using an ICP OES (OPTIMA 7300DV, PerkinElmer, USA), with a MEINHARD concentric nebulizer, a 50 mL standard Baffle cyclonic spray chamber, an alumina 2.0 mm injector tip, and a quartz torch, under the optimal instrumental conditions as listed in Table 1. The PGM wavelengths were selected based

Table 1. Optimal ICP OES Instrumental Parameters

instrumental parameters	optimal conditions
forward power (W)	1300
plasma gas flow rate (L/min)	20
auxiliary gas flow rate (L/min)	1.0
nebulizer gas flow rate (L/min)	0.65
sample flow rate (L/min)	1.5
wash flow rate (L/min)	1.5
elements and wavelengths (nm)	Pt, 265.945; Pd, 363.470; Rh, 343.489

on previous investigations.¹⁵ The results were obtained from the average of three replicate measurements for each solution. The limits of detection (LODs) were calculated using the three times the standard deviation of background from measurements of the blank solution (3σ criterion), and the limits of detection quantification (LOQ) were evaluated as three times the LOD value.⁷ The LODs and LOQs were less than 0.1 mg/L for all PGMs, which enables the quantification of concentration in the calibration range of 0.1 to 1.0 mg/L (Table S1).

2.4. Matrix Correction Based on Multivariate Calibration. A multivariate calibration technique using the MLR model was used to establish the linear mathematical relationship between the dependent variable (response: the intensity of PGM emission line) and the independent variables (predictors: concentrations of PGMs and matrix elements) (eq 1).¹⁵

$$Y = \beta + \alpha_1 \times X_1 + \alpha_2 \times X_2 + \dots + \alpha_p \times X_p + \varepsilon \quad (1)$$

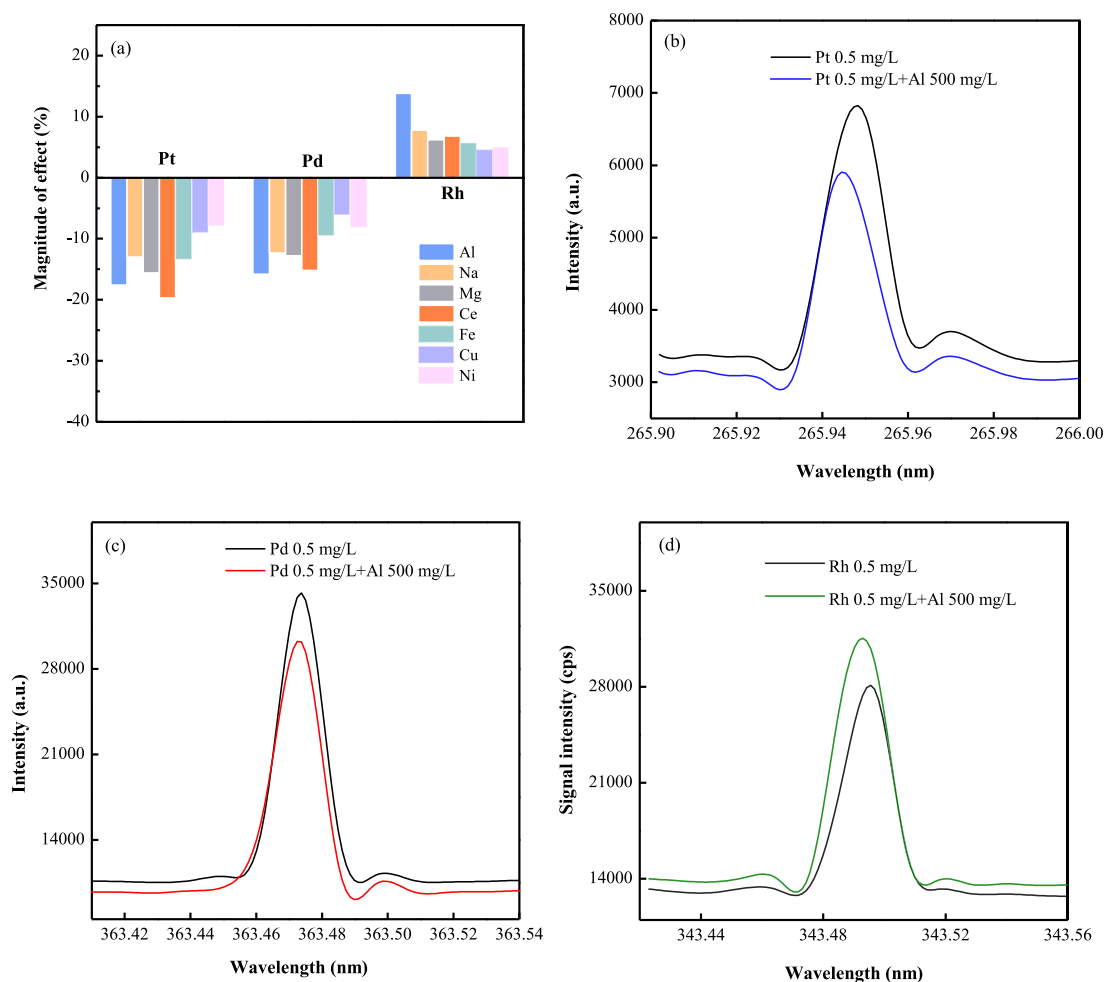


Figure 1. Effect of different interelements on PGM determination (PGM concentration 0.5 mg/L; interelement concentration 500 mg/L). a) Effect of different interelements (Al, Na, Mg, Ce, Fe, Cu and Ni). (b–d) ICP OES spectra of the analysis of solution containing PGM at 0.5 mg/L and Al at 500 mg/L.

where Y is the dependent variable (response); X_1, X_2, \dots, X_p are the independent variables (predictors); β is the intercept (constant); $\alpha_1, \alpha_2, \dots, \alpha_p$ are the coefficients of the predictors; and ε is the residue term.

An array of calibration solutions with variations of matrix elements and PGM concentrations was prepared, and the measured data were used to build the regression model the using Minitab 19.0 software. The deviation between the actual and predicted concentrations based on the model for the individual sample was estimated with the relative standard error (RSE) value (eq 2).¹⁸ The performance of the correction method was evaluated by the standard error of prediction (SEP) (eq 3).¹⁸

$$\text{RSE}(\%) = 100 \times \frac{(C_{\text{predicted}} - C)}{C} \quad (2)$$

$$\text{SEP} = \sqrt{\sum_{\text{predicted}} (C - C)^2 / n} \quad (3)$$

where $C_{\text{predicted}}$ is the predicted concentration of PGMs from the model, C is the actual concentration of PGMs in the solutions, and n is the number of samples.

3. RESULTS AND DISCUSSION

3.1. Effect of a Single Interferent on PGM Determination.

The effect of matrix complexity was investigated by estimating of the RSE values when determining PGM concentrations of 0.5 mg/L in the presence of interelements at 500 mg/L. Several interelements were investigated based on the major components of the spent catalysts (Al, Mg, Ce), the metallic collector using in the fire assay (Fe, Cu, Ni), and the additive using in oxidizing fusion (Na). The magnitude of the effect was present in terms of the RSE value by following eq 1, using the subtraction between the values from ICP OES analysis and the actual PGM concentrations. The positive or negative sign of the magnitude value indicated the overestimation or underestimation in PGM determination, respectively. The results in Figure 1a show a significant variation in PGM determination due to the presence of the investigated interelements. The influences induced by the selected elements had the same tendency for Pt and Pd, which was attributed to the similarity of their first ionization potential energies and chemical properties.^{14,15} There were underestimations in Pt and Pd concentrations and overestimations in the Rh concentration. The effects of Al and Ce (above -15%) were more dominant than those of other elements for Pt and Pd. Al was the most significant interelement (14%), and the others showed the relatively equal effects on Rh determination

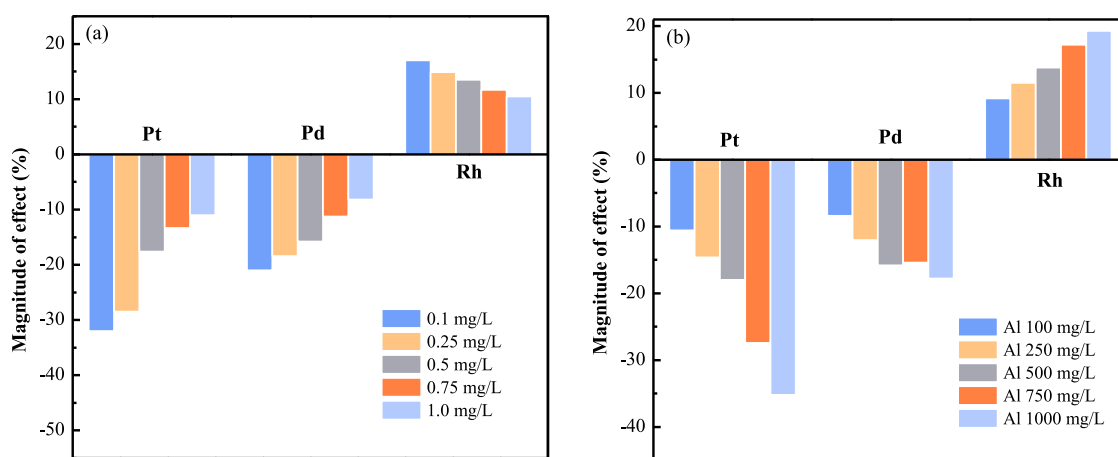


Figure 2. Effect of PGM and interelement concentrations. a) Effect of PGM concentrations (Pt, Pd, and Rh: 0.1–1.0 mg/L). b) Effect of Al concentrations (100–1000 mg/L).

Table 2. Summary of the Regression Model Statistics between the RSE Values and the Investigated Parameters

source	Pt		Pd		Rh	
	AdjSS	P-value	AdjSS	P-value	AdjSS	P-value
PGM concentration	3040.0	0.000	994.7	0.000	1671.3	0.000
interelement concentration	239.0	0.012	164.5	0.021	253.6	0.101
number of interelements	394.3	0.002	2539.2	0.000	4529.0	0.000
regression	3673.3	0.000	3698.5	0.000	6543.9	0.000
model summary	$R^2 = 77.46\%$		$R^2 = 80.63\%$		$R^2 = 69.42\%$	

(Figure 1a). The corresponding spectra of the solution containing PGM at 0.5 mg/L and Al 500 at mg/L showed a suppression in the analytical signals for Pt and Pd and an enhancement in the intensity of the Rh peak (Figure 1c,d), which clearly demonstrated the variation on PGM determination due to the interelements.

A reduction in the PGM concentration (from 1.0 to 0.1 mg/L) and an increase in the Al concentration (100 to 1000 mg/L) could enhance the variation in PGM determination up to -30% for Pt, -20% for Pd, and $\sim 20\%$ for Rh (Figure 2). The complex compositions of the spent catalysts and the reagents used to extract PGMs can generate a leach liquor with low contents of the target analyte PGMs and high contents of interelements, and the investigations of single elements did not sufficiently describe the impacts of such complex systems on PGM determination. Therefore, it should consider the interactions of related parameters under different conditions such as the PGM concentration, the concentration of each interelement, and the total number of elements.

3.2. Effect of Matrix Complexity Based on the Multilinear Regression Model. The RSE value was assumed to be a function of the PGM concentration, the interelement concentration, and the total number of interelements, and the MLR between the RSE value and the investigated parameters was established based on the model shown in eq 1 (the experimental matrix of solutions is listed in Table S2). Four interelements (Al, Mg, Ce, and Na) were selected to investigate by MLR. Al, Mg, and Ce were the major components of the spent catalyst analyzed in the study, and Na_2O_2 or NaOH flux was mainly used in oxidizing fusion to dissolve the refractory catalyst (Na). The effect of each parameter was estimated based on the significance at the 95% confidence interval with the student's *t*-distribution. The model was refitted to the data after removing the insignificant

parameters, and the results present only the significant parameters in the final model (Table 2).

The small *P*-value of the model (<0.05) and the high value of R^2 ($\geq 69\%$) for all the PGMs indicated that the regression model was adequate to explain the variation in the determination, and the investigated parameters had strong effects on the RSE values. Pt and Pd appeared to have negative biases, and all three parameters distributed significant influences on the determination error. The PGM concentration was the highest major influence for Pt, and two other parameters had relatively equal contributions to the RSE values. Although the significance of the three factors was similarly observed for Pd, the contribution of each factor was different, regarding the descending order from the impact of the number of interelements, PGM concentration, and interelement concentration. Conversely, the error for Rh quantification had a positive bias and was primarily affected by the number of interelements and analyte concentration. The impact of interferent concentrations was not a significant factor to Rh determination due to the large *P*-value (>0.05), which was different from the case of Pt and Pd.

Although the model cannot predict all the effects of the related parameters on the measurement error, except for three selected factors at specific levels, it presented the importance of the influence of matrix complexity on PGM determination under the investigated conditions. Generally, the analyte concentration has an important impact on the measurement; however; the presence of other interelements with variation of concentration in the solution could reduce the accuracy and precision of the measurement. It is an intensive challenge for quantitative analysis and requires an appropriate solution to decrease the related variation, because these effects cannot be avoided due to the matrix complexity of the sample or digestion method.

3.3. Determination of PGMs from the Spent Catalyst.

PGM-bearing catalysts have been used in a variety of industrial fields such as chemical production (synthesis of mineral acids and organic compounds), petrochemical processing (reforming, isomerization, and hydrocracking), and automotive markets (converting toxic emissions to less harmful gases).² The compositions of these catalysts are simpler than those of the geological or biological samples, including three major parts: supportive materials (aluminum, cordierite, or active carbon), coating layer (aluminum), and catalytic metals (individual metal or mixture of PGMs). The presence of interelements from the matrix of samples or chemicals used in the extraction process can reduce the accuracy of PGM determination. Multivariate calibration based on the MLR model is a more efficient and convenient method to correct the influences by the multielement matrix for a large number of samples than other conventional methods. Herein, microwave-assisted digestion and multivariate calibration were used to estimate PGM contents in spent catalysts, and the results were compared with the PGM concentration determined by the fire assay.

3.3.1. PGM Determination from the Spent Al_2O_3 -based Catalyst. The spent Al_2O_3 -based catalysts in this study were commercial petroleum catalysts used for the refinery and petrochemical industries in Korea, which were collected by the KIGAM with different shapes (sphere or cylinder) and sizes (Figure 3a). The major component of carriers was $\gamma\text{-Al}_2\text{O}_3$ or a mixture of $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ (Figure 3c). The SEM image showed that a thin layer was coated on the Al_2O_3 substrate to enhance the porosity, and active metals were implemented in this coating layer (Figure 3b). The catalytic metals were Pt or

Pd with the concentration varied from 0.25 wt % to 0.45 wt %. The catalysts were ground using a ball miller and treated at 600 °C for 30 min to remove contaminated organic compounds before being subjected to microwave digestion. The PGM determination after digestion without the correction method demonstrated the influence of major interelement Al on the quality of the analysis, which generated an underestimation of Pt or Pd concentrations (from -12.5% to -6.3% , Table 3).

Table 3. RSE Values in Pt/Pd Determination from Spent Al_2O_3 -Based Catalysts before and after Correction

sample number	PGM content by fire assay (wt %)		RSE (%)			
	Pt	Pd	Pt		Pd	
			before	after	before	after
1	0.45	-	-10.5	-1.2		
2	0.40	-	-10.1	-1.5		
3	0.20	-	-12.3	-3.4		
4	0.45	-	-11.2	-2.3		
5	0.25	-	-12.5	-2.9		
6	0.40	-	-10.7	-1.6		
7	-	0.30 ^a			-6.3	-2.1
8	-	0.30 ^a			-8.5	-3.0
9	-	0.30 ^a			-7.6	-1.8
10	-	0.35			-8.7	-2.5
SEP (%)			11.3	2.3		

^aSamples 7, 8, and 9 were collected from different companies in Korea: Gumho Petrochemical, Daelim, and SK Energy.

The difference in the error values between the samples was not significant since the concentrations of Al and PGM were relatively similar ($\text{Al}_2\text{O}_3 > 90$ wt %, Pt at 0.20–0.45 wt %, and Pd ~ 0.3 wt %). The application of multivariate calibration reduced the RSE value from $>-10\%$ to $<-3.5\%$ and the SEP from 11.3% to 2.3% for Pt determination (Table 3). The variation in Pd determination reduced 4–6% before and after applying the correction (Table 3). The reduction in the RSE value to the acceptable range of quantification (less than 5.0%) demonstrated the effectiveness of the correction method.

3.3.2. PGM Determination from the Spent Autocatalyst.

There are different types of autocatalysts based on the structure, the material of substrate, or the number of active metals. The spent autocatalysts in the study were three-way autocatalysts with a honeycomb structure of cordierite substrate ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) (Figure 4a). The substrate surface was coated with a thin layer of $\gamma\text{-Al}_2\text{O}_3$ with a high surface area and good thermal stability (Figure 4b). The SEM-EDS images describe the morphology and the major compositions of the cordierite substrate and washcoat layer (Figure 4b–f). The cordierite substrate contained mostly Al, Mg, and Si, whereas the washcoat had different thicknesses on the wall and at the corner of the honeycomb cell with the main chemical compositions Al and Ce. The major components including the cordierite substrate, $\text{CeO}_2\text{-ZrO}_2$ as an additive, and $\gamma\text{-Al}_2\text{O}_3$ as a washcoat layer were identified by XRD analysis (Figure 4g). The investigation of 200 spent autocatalyst samples by the KIGAM presented the average chemical compositions for the substrate and washcoat layer ~ 40.0 wt % Al_2O_3 , ~ 34.0 wt % SiO_2 , ~ 9.0 wt % MgO , ~ 7.0 wt % CeO_2 , 0.2–4.0 wt % ZrO_2 , and ~ 0.5 wt % BaO ; and the active metals ~ 900 mg/kg Pt, ~ 1600 mg/kg Pd, and ~ 120 mg/kg Rh.⁴

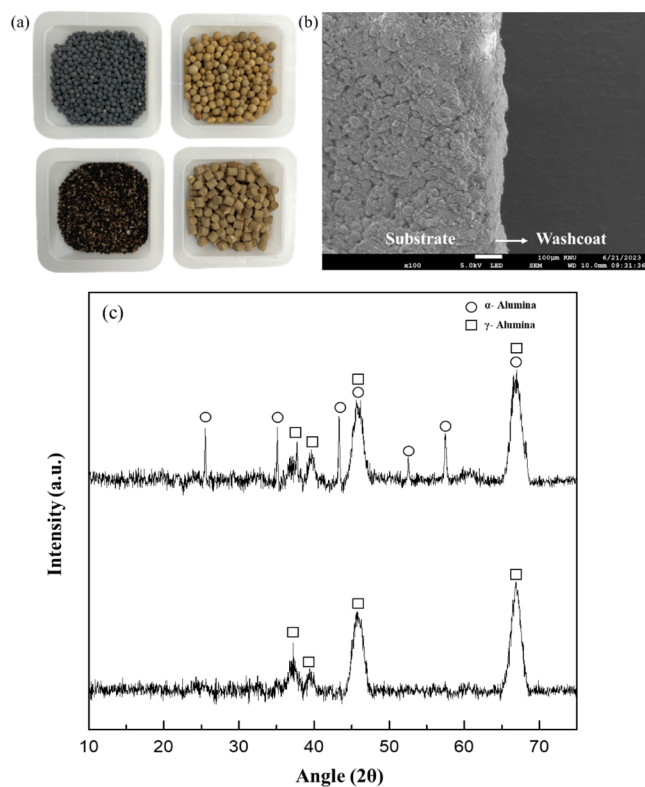


Figure 3. Spent Al_2O_3 -based catalysts. (a) Shape of the spent Al_2O_3 -based catalysts. (b) SEM image of the washcoat layer on the Al_2O_3 substrate. (c) XRD analysis of the spent Al_2O_3 -based catalyst samples.

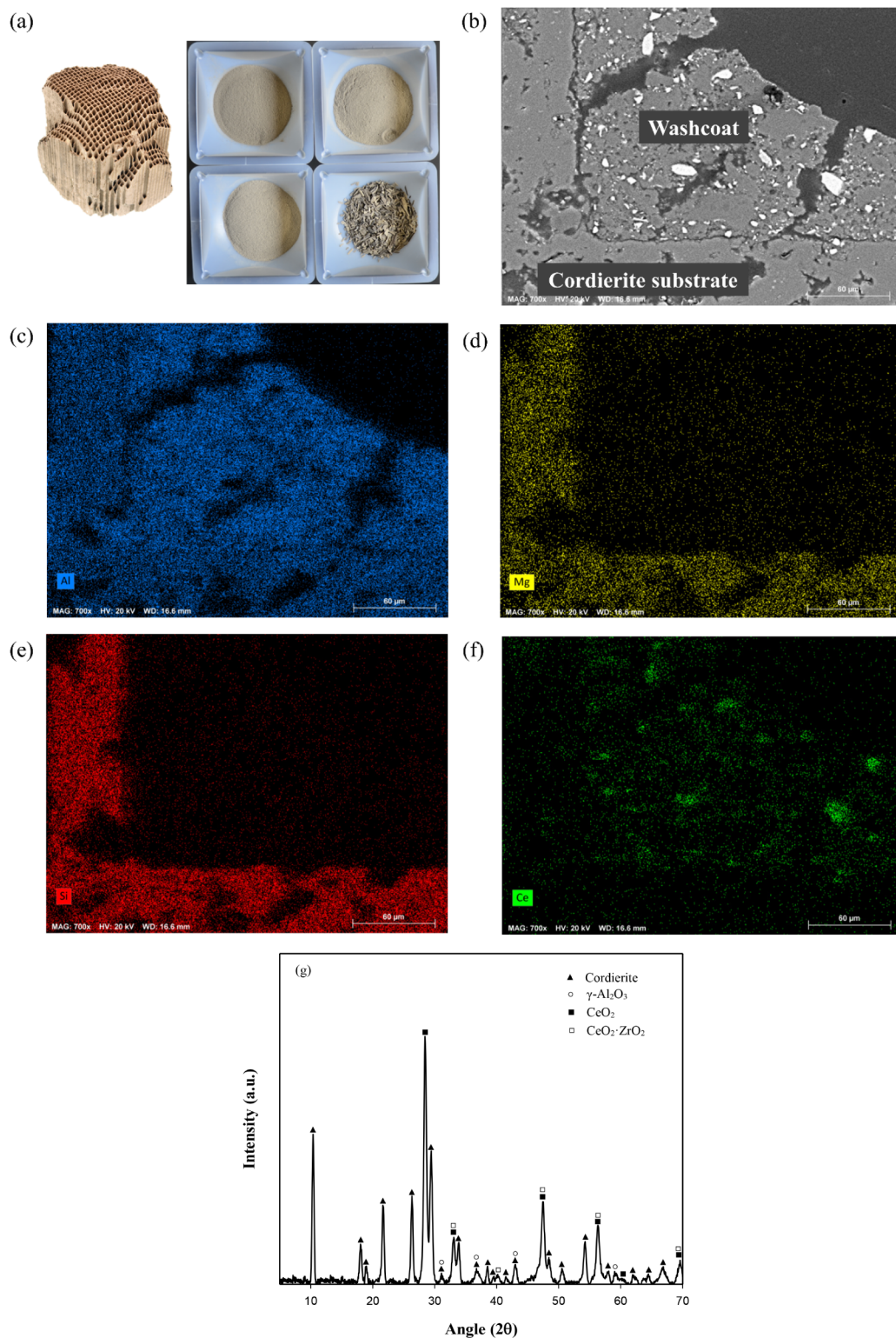


Figure 4. Shape and compositions of spent autocatalysts. Reprinted with permission from ref⁴. Copyright 2020, Elsevier Inc. (a) Honeycomb structure of spent autocatalysts and ground samples. (b) SEM image of the washcoat layer on the cordierite substrate (c–f) EDS images of substrate elements Al, Mg, Si, and Ce. (g) XRD analysis of spent autocatalyst sample.

In the study, 25 samples of spent autocatalysts were selected for PGM determination by using microwave-assisted digestion and multivariate calibration. Similar effectiveness was observed for Pt and Pd; the RSE value for each sample was significantly reduced by application of a correction method (Figure 5 and Table S3). The SEP decreased from 10.7% to 3.2% for Pt and

8.0% to 2.6% for Pd, and the RSE distribution changed from -10% to $\pm 5\%$ (Figure 5a,b). However, the correction was not sufficiently efficient for Rh. The RSE distribution of Rh determination was mainly between 5% and 10%, and the SEP value was slightly reduced from 9.5% to 6.6% after correction (Figure 5c). It can be attributed to the results of the

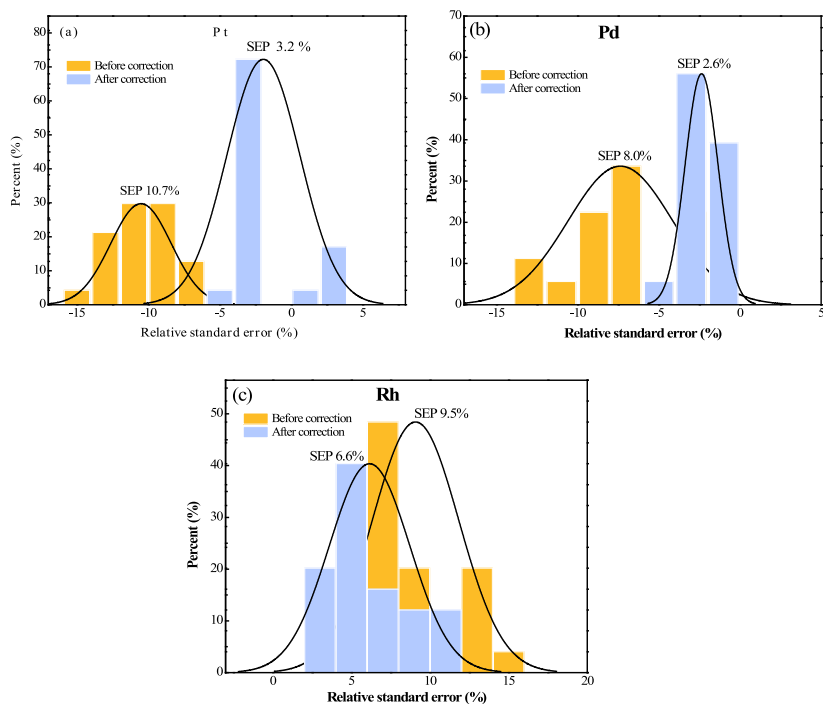


Figure 5. Comparison of RSE distribution before and after correction in PGM determination from the spent autocatalysts: a) Pt, b) Pd, and c) Rh.

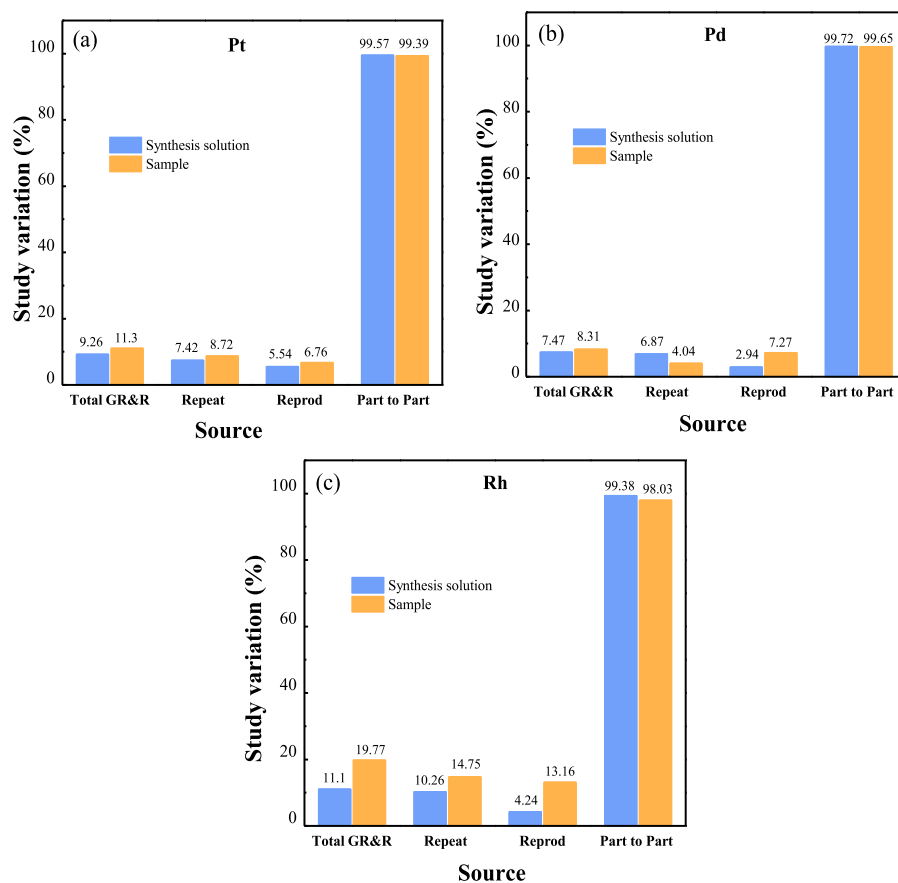


Figure 6. Gage evaluation (% study variation) for PGM determination in synthesis solutions and spent autocatalysts: a) Pt, b) Pd, and c) Rh.

investigation on the regression between RSE and the related parameters shown in section 3.2. The regression model indicated that the RSE value was a function of the PGM concentration, the concentration interelement, and the total

number of elements for Pt and Pd. Therefore, the variation can be corrected using multivariate calibration to recalculate Pt and Pd concentrations based on the relationship between the intensity of the emission line and the PGM and matrix element

concentrations. Meanwhile, the RSE value in the case of Rh determination did not depend on the interelement concentrations, which could reduce the effectiveness of the correction method using the MLR model.

3.4. Evaluation of the Analysis Procedure Using Gage Repeatability and Reproducibility Study. Errors in a measurement system can be generated from various sources, such as sample variation, sample preparation procedure, measurement method, instruments, environmental conditions, operators, and other influences.²³ It is important to identify and quantify the sources of variation as well as the associated contribution of each source.^{23,24} Gage repeatability and reproducibility (GR&R) is an effective study to assess the precision of a measurement system and decide its capability and performance. The possible sources of variation are classified as three major types: (i) error due to measurement devices (repeatability), (ii) error due to differences between operators (reproducibility), and (iii) the error due to variation within samples (part-to-part variation). The GR&R study requires the data collection from at least 3 operators and 10 samples, and operators should measure each sample at least twice for an adequate study. Therefore, 10 samples were selected for ICP OES analysis by 3 different operators, and each sample was repeated 3 times ($10 \times 3 \times 3$ GR&R study). The samples were divided into two groups: synthesis solutions (Pt, Pd, and Rh at 0.1–1.0 mg/L) and 10 random samples of spent autocatalysts. The collected data were inserted and analyzed with the Minitab by the crossed GR&R study (Figure S1–3).

Overall, the gage evaluation presented a high value of the contribution by part-to-part variation to the total variation (>98%) for all PGMs (Figure 6). The measurement is reliable, and the variation is mainly due to the different contents of analytes in samples. The total GR&R contributions of measuring the synthesis solutions were close to 10% (9.26%, 7.47%, and 11.1% for Pt, Pd, and Rh respectively), meaning that the PGM determination is acceptable with good accuracy and precision. These values slightly increased for the spent autocatalyst samples in the case of Pt (from 9.26% to 11.03%) and Pd (from 7.47% to 8.31%) (Figure 6a,b); however, it showed a relatively significant difference for Rh, from 11.1% to 19.77% (Figure 6c).

The analysis procedure shows high reliability for Pt and Pd determination because the total GR&R contribution for the measurement of spent catalyst samples was in the range of acceptable values $\sim 10\%$. However, the process was less effective for Rh due to the high total GR&R contribution of 19.77%. A possible reason for poor repeatability in Rh determination is the inconsistent content of Rh in the autocatalyst samples. The formation of Rh_2O_3 as a protective layer on the surface of the washcoat layer can occur during the operating time of the autocatalyst at high temperatures, and the oxide layer restricts the PGM digestion in an acid solution.^{25–27} The sample has a large surface due to the honeycomb structure and porosity of the washcoat; hence, the oxidation of Rh is not certain to have a similar yield. Consequently, the oxide and metallic forms of Rh could exist in an ununiformed ratio at different positions in the autocatalyst samples, which induces the variation in Rh content of each spent catalyst sample and reduces the repeatability.

In summary, the process using microwave digestion and multivariate calibration was as an effective and reliable method

for PGM determination from spent catalysts. The repeatability and reproducibility are highly acceptable for Pt and Pd determination. Although the evaluation of the method for Rh determination showed the largest value of the total GR&R contribution among the three PGM, it is still acceptable considering the advantages of the method. Microwave-assisted digestion is more rapid and less time-consuming and shows less interference than fire assay and oxidizing fusion. Microwave digestion and multivariate calibration are more convenient to apply for a large number of samples than conventional methods. Therefore, it is a suitable analysis procedure for PGM determination from spent catalysts and should be further investigated for other sample types.

4. CONCLUSIONS

The effect of selected interelements on variation in PGM determination using ICP OES was investigated by two approaches: single factor at once (different elements, interferent concentrations, and PGM concentrations) and MLR between the RSE value and three main factors (PGM concentrations, interelement concentrations, and number of interelements). The results showed the similarity between behaviors of Pt and Pd, which presented an underestimation of concentration determination, and all three parameters had a strong effect on the RSE value. The effect of interferent elements induced a positive bias on Rh determination, and the Rh concentration and number of interelements mainly accounted for the influences on the deviation during analysis. Two approaches demonstrated significant variation due to the complexity of matrix on PGM determination; therefore, a reliable analysis procedure was developed using the combination of an effective extraction method (microwave-assisted digestion) and a correction technique (multivariate calibration). The PGM-bearing samples were collected and divided into spent Al_2O_3 -based catalysts and spent cordierite-based catalysts. The analytical results without correction showed large deviations of all PGM contents in the spent catalyst samples in comparison to the fire assay. The application of correction method could effectively reduce variation in Pt and Rh determination: (i) spent Al_2O_3 -based catalysts: SEP decreased from 11.3% to 2.3% for Pt and (ii) spent autocatalysts: SEP decreased from 10.7% to 3.2% for Pt and 8.0% to 2.6% for Pd. The less effectiveness for Rh determination could be attributed to the independence of the RSE on the interelement concentration. The evaluation of the analysis procedure was investigated using the crossed GR&R model, which presented a high value of contribution by part-to-part variation to the total variation (>98%) and a low total GR&R contribution of $\leq 11\%$ for Pt and Rh. Although the value of the total GR&R contribution was high for Rh (19.77%), it was in the range of acceptable values. The combination of microwave-assisted digestion and multivariate calibration shows acceptable accuracy and precision for PGM determination from spent catalysts with considering the compensation of the effect by matrix complexity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.4c05641>.

Crossed gage repeatability and reproducibility studies for Pt, Pd, and Rh determination (Figure S1–S3); fitting

graphs for multivariate calibration of Pt, Pd, and Rh from Minitab (Figure S4); LOD and LOQ quantification (Table S1); experimental matrix of PGM interelement solutions (Table S2); comparison of RSE and SEP before and after correction (Table S3) (PDF)

AUTHOR INFORMATION

Corresponding Author

Jaeryeong Lee – Department of Integrated Energy and Infra System, Kangwon National University, Chuncheon-si, Kangwon-do 24341, Republic of Korea; orcid.org/0000-0001-9559-2763; Phone: (082)-33250-6252; Email: jr-lee@kangwon.ac.kr

Authors

Ha Bich Trinh – Department of Integrated Energy and Infra System, Kangwon National University, Chuncheon-si, Kangwon-do 24341, Republic of Korea

Seunghyun Kim – Department of Integrated Energy and Infra System, Kangwon National University, Chuncheon-si, Kangwon-do 24341, Republic of Korea

Taehun Son – Department of Integrated Energy and Infra System, Kangwon National University, Chuncheon-si, Kangwon-do 24341, Republic of Korea

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acsomega.4c05641>

Notes

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