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# DETERMINATION OF PLATINUM, PALLADIUM AND RHODIUM BY NICKEL SULPHIDE FIRE ASSAY (PRE-CONCENTRATION) METHOD AND ITS OPTIMIZATION

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## ABSTRACT

The growing use of platinum, palladium and rhodium (PGM) in metallurgy, jewelry and chemical industrial applications results in the necessity of fast and accurate a method for the determination of PGM, not only in natural sources, but also in recyclable materials, such as concentrates, anode slime, polish waste and catalytic converters. In this study, the performance of the nickel sulphide (NiS) fire assay of PGM from mixtures of catalytic converters (e.g., gasoline and diesel engine catalytic converters) is investigated by assessing the effects of various flux ratios and reaction parameters on metals recovery. We found that optimum recovery was achieved with 57.5 g of flux (0.40 w/w ratio, $B_2O3$:$Na_2O$), 6.36 g (as 5 g Ni) nickel oxide and 5 g sulfur (1.0 w/w ratio, Ni:S) for five gram of sample, reacted for 90 min at 975°C. To identify the optimum condition, reference standards such as NIST SRM 2557 (honeycomb type) were used to compare efficiencies; the results were consistent with certified values. It is proposed that a method to isolate at least 99% of the Pd, Pt, and Rh present in catalytic converters.

**Keywords:** Nickel sulfide, fire assay, platinum, palladium, rhodium.

## NİKEL SÜLFÜR ATEŞ ANALİZİ (ÖN ZENGİNLEŞTİRME) YÖNTEMİYLE PLATİN, PALADYUM VE RODYUM METALLERİNİN TAYİNİ VE YÖNTEMİN OPTİMİZASYONU

## ÖZET

Metalurji, kuyumculuk ve kimya sektörlerinde platin, paladyum ve rodyum (PGM) metallerinin kullanımının artması sonucu, doğal kaynakların yanı sıra ikincil kaynaklardan (konsantreler, anot çamurları, ramat atıkları ve katalitik dönüştürücüler) da PGM'lerin belirlenmesinde hızlı ve güvenilir bir metoda ihtiyaç duyulmaktadır. Bu çalışmada; çeşitli fluks miktarları ve çeşitli reaksiyon parametrelerinin metal geri kazanımı üzerine etkilerini değerlendirmek üzere katalitik konvertör karışımında bulunan (benzinli ve dizel motorlu araçların katalitik konvertörleri) PGM'lerin Nikel sülfür (NiS) metodu ateş analizi ile geri kazanım performansını araştırılmaktadır. Yapılan deneyler sonucunda en iyi geri kazanım verimi, 5 gr katalitik konvertör tozuna 57,5 gr curuflaştırıcı ($B_2O_3$:$Na_2O$; 0,40 g/g), 6,36 gr nikel oksit (5 gr Ni) ve 5 gr kükürdün (Ni:S; 1 g/g) 975°C de 90 dakika reaksiyona girmesiyle elde edilmiştir.. En iyi geri kazanım verimini test etmek amacıyla NIST SRM 2557 (petek türü) referans standart malzemesi kullanılmış ve elde edilen sonuçlar sertifika değerleriyle uyumlu olduğu tespit edilmiştir. Bu yöntem ile katalitik konvertörlerde bulunan Pt, Pd ve Rh metalleri 99% verimle analiz edilebileceği ön görülmüştür.

**Anahtar Sözcükler:** Nikel sülfür, ateş analizi, platin, paladyum, rodyum.

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## 1. INTRODUCTION

During the past three decades, platinum (Pt), palladium (Pd), rhodium (Rh) have been used widely in all kinds of applications because of their catalytic and chemical properties. They are used in many industrial applications including dental alloys, electronics, glass-making instrumentation, electrode coatings, temperature sensors, medical implants, jewelry, medicinal drugs, thermocouples, laboratory equipment, and catalytic converters [1-3].

Since 1979, the automotive industry has become the largest consumer of the Pt, Pd, Rh with the advent of the catalytic converters in car exhaust systems. It is used as oxidation catalysts to reduce the potentially noxious emissions from exhausts [3]. As a result, the need for accurate determination of the Pt, Pd, Rh have led to the development of some analytical methods to determine Pt, Pd, Rh in a large variety of samples. The literature contains numerous studies focused on the analysis of Pt, Pd, Rh contents; the need for accurate determination of Pt, Pd, Rh have led to the development of several analytical methods [4-6]. But classic dissolution methods (i.e. acidic and alkaline leaching and fusion) are more difficult than NiS fire assay for samples to analyses quantitatively and results obtained unreliable. Since Pt, Pd, Rh are only present in small quantities in most of the materials to be analyzed and to avoid the influence of matrix components and sample heterogeneous, separation of the target elements from the matrix is required [7,8]. An efficient way to perform this isolation is the use of the NiS pre-enrichment method.

Until present time, only a few studies focused on the analysis of Pt, Pd, Rh with NiS fire assay because of its commercial issue. Studies have generally focused on the standard reference ores and compared with spectroscopic methods or, research has been done to overcome spectroscopic problems [9-11]. However, effects of the different efficiency parameters, type of flux material, flux/sample ratio, reaction temperature etc. are not explained in these studies.

This study will test untried parameters with NiS fire assay analysis on Pt, Pd, Rh reliably and accurately. We here outline an effective NiS fire assay method using catalytic converters to achieve a high recovery percentage of Pt, Pd and Rh and describe the optimum conditions and parameters for this method.

## 2. MATERIALS AND METHODS

Mixtures of automotive exhaust catalytic converters supplied by EMAK (Turkey) were employed in this work. First, outer shell surrounding the converters was removed and the honeycomb structure inside the shell was taken out. It was crushed, ground, and sieved to 100% minus 100 µm by passing through laboratory scale ring milling and homogenized using a three-dimensional shaker (Turbula T2C, USA). After these treatments, a homogeneous Pt, Pd and Rh containing catalytic converters powder were obtained each sample was independently analyzed at least twice. The concentrations of elements present in the solution were measured with a Perkin Elmer Analyst 800 atomic absorption spectrometer (Perkin Elmer Inc., USA) and Thermo Scientific X-Series 2 inductively coupled mass spectrometer (Thermo Scientific Inc., England) and used for the NiS fire assay experiments. All NiS fire assay experiments were performed on samples taken from this homogenized powder. The chemical composition, particle size and X-ray diffraction patterns of the catalytic converter powder is presented in Table 1, Figure 1 and Figure 2 respectively. All chemicals were of analytical grade unless otherwise specified.

**Table 1.** Composition of catalytic converter powder.

| **Elements** | **$SiO_2$ %** | **SiC %** | **MgO %** | **$Al_2O_3$ %** | **$ZrO_2$ %** | **$CeO_2$ %** | **Others %** | **Pt (ppm)** | **Pd (ppm)** | **Rh (ppm)** |
|---|---|---|---|---|---|---|---|---|---|---|
|  | **28.34** | **24.77** | **5.20** | **33.44** | **3.70** | **2.71** | **1.55** | **700** | **1835** | **118** |

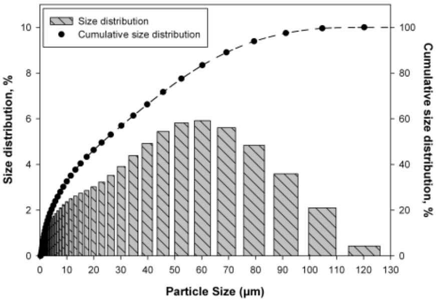

**Figure 1.** Particle and cumulative size distribution of catalytic converter powder

Cordierite, silicon carbide, cerium oxide and zirconium oxide were the major mineral phases in the catalytic converter powder (Figure 2). Cordierite, cerium and zirconium oxide correspond to the ceramic catalytic converters of gasoline and diesel engines.

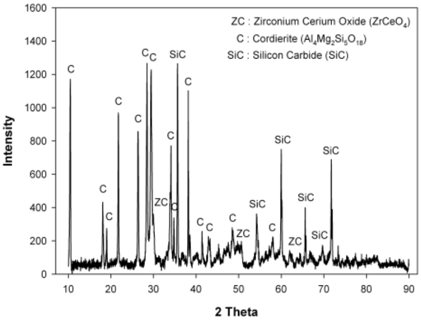

**Figure 2.** XRD patterns of catalytic converter powder

Silicon carbide is commonly used in diesel particle filter (DPF) [12]. It is one of the most technically feasible solutions to reduce particulate matters from exhaust gas of a diesel engine. The main purpose of diesel particle filter was designed to remove diesel particulate matter emissions from diesel engine and protect to the environment from diesel particulate matter emissions.

The flowchart for the preparation treatments of catalytic converters and NiS fire assay analysis are shown in Figure 3.

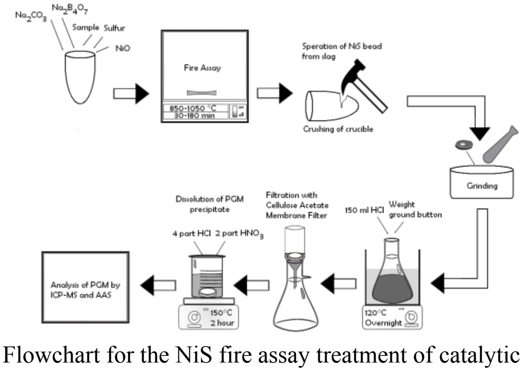

**Figure 3.** Flowchart for the NiS fire assay treatment of catalytic converters

### 2.1. NiS Fire Assay Procedure

Fire assay fluxes (sodium tetraborate, sodium carbonate, nickel oxide, elemental sulfur and flour) together with 5 g of sample powder were weighed into disposal wax paper, homogenized with an agate-piston and transferred into fire clay crucibles. The crucibles were covered with saw dust to avoid possible oxidization of elemental sulfur during fusion and inserted into a furnace pre-heated to 300°C. The temperature was raised and fusion carried out at 850 to 1050°C. During fusion the nickel oxide was reduced to metallic nickel. After it combines with sulfur to form nickel sulfide which collects the platinum, palladium and rhodium sulfide formed at the same time. This temperature was held constant at least a half hour before the oven was turned off. Crucibles were left in the oven until they had cooled to room temperature. Cold crucibles were broken by a hammer to separate the NiS-bead from the slag. The beads were weighed, crushed and ground to powder, transferred to a 400 ml Pyrex beaker and dissolved in 150 ml HCl (37% v/v, analytical grade). The ground NiS powder was weighed and transferred to a new beaker to correct for loss of material during grounding. The beaker was covered with a watch glass transferred onto a hot plate at about 120°C and the powder dissolved. All experimental steps were carried out under a fume cupboard. Hydrogen sulfur ($H_2S$) gases, formed during the dissolution reaction were successfully neutralized with the help of the fume cupboard washing unit and subsequently released to the atmosphere. Dissolution was continued overnight and the solution allowed cooling to room temperature. $TeCl_4$ (5 ml, 1000 ppm) and $SnCl_2$ (10 ml, 10% (w/w), freshly prepared) solution were added to precipitate (TePt, TePd, TeRh). The solution was again brought slowly to boiling over a period of 60 min to coagulate the black precipitate formed. Once precipitate had formed, the solution was cooled and vacuum-filtered through cellulose acetate membrane filter discs (Sartorius, Germany) fitted within screw filter devices. The Pt, Pd and Rh containing residues were washed carefully with HCl (10% v/v). After placing the filter discs in 100 ml beakers, the solids and filter paper were dissolved with a mixture of three parts HCl (12 ml) and one part $HNO_3$ (6 ml). Once the evolution of gases had ceased, 4 ml HCl and 2 ml $HNO_3$ were added. Finally, the solution was passed through a filter paper, transferred to 50 ml volumetric flasks and diluted with distilled-deionized water (TKA Smart2Pure, Germany). Each sample was independently decomposed at least twice and all decomposition analyzed twice. The concentrations of elements present in the solution were measured with atomic absorption spectrometer and inductively coupled mass spectrometer, respectively. Distilled-deionized water was used for all analyses.

## 3. RESULTS AND DISCUSSION

Since elemental sulfur is always oxidized by air at high temperature, which may result in evaporation and losses during fusion, the NiS fire assay should be carried out at low temperature. To achieve lower melting points and maximize the amount of elemental sulphur in the bead, it is necessary to calculate the mass fraction of flux mixture. Therefore, before performing the NiS fire assay experiments, a thermochemical simulation of the effect of $B_2O_3$ ($Na_2B_4O_7$) and $Na_2O$ ($Na_2CO_3$) content on the melting point of slag in the NiS fire assay was performed using the advanced "Equilib" module of FactSage 6.3 to predict possible lower melting points. As evident from the figure, approximately 0.40 (w/w), $B_2O_3$:$Na_2O$ was melted around at 550-650°C which was selected as optimum conditions for this study.

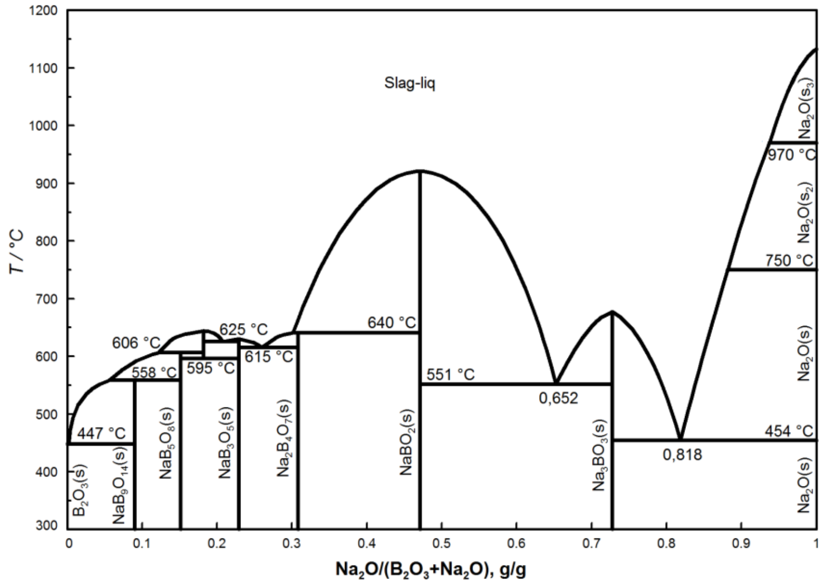

**Figure 4.** Simulation result of effect of $Na_2O/(B_2O_3+Na_2O)$ mole ratio on melting point of slag

### 3.1. Effect of Flux Quantity on NiS Fire Assay

The extent of recovery of Pt, Pd and Rh (%) as a function of flux quantity is shown in Figure 5.

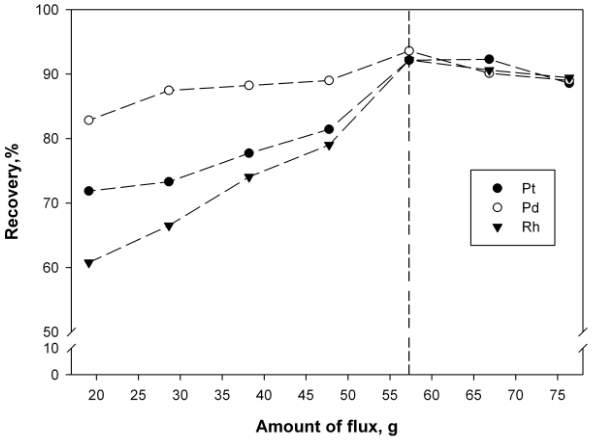

**Figure 5.** Effect of flux quantity on NiS fire assay for Pt, Pd and Rh recovery (0.40 (w/w) $B_2O_3$:$Na_2O$, 6.36 g NiO, 5 g S, 5 g catalytic converter powder, at 950°C for 60 min)

In this experimental series, the amount of sample (5 g catalytic converters) and other parameters (0.40 (w/w) $B_2O_3$:$Na_2O$; 6.36 g NiO, 5 g S) was kept constant whereas amount of flux ($Na_2B_4O_7$+$Na_2CO_3$) amount was changed so as to observe its effect on recovery percentage. The percent recovery increased with increasing flux amount of (borax+soda) until 57.5 g per five gram sample. Therefore, it is important to use 57.5 g flux in fire assays if a higher recovery percentage is desired. As can be seen from the figure that similar trend can be observed the recovery percentage of Pt, Pd and Rh increased with increasing flux quantity up to 57.5 g (Figure 5). However, increasing the flux quantity decreasing the recovery percentages [13]. Maximum recoveries were obtained at 57.5 g flux, which was selected for all subsequent experiments.

### 3.2. Effect of $B_2O_3$ to $Na_2O$ (w/w) Ratio on NiS Fire Assay

The level of recovery of Pt, Pd and Rh (%) as a function of $B_2O_3$ to $Na_2O$ (w/w) ratio is shown in Figure 6.

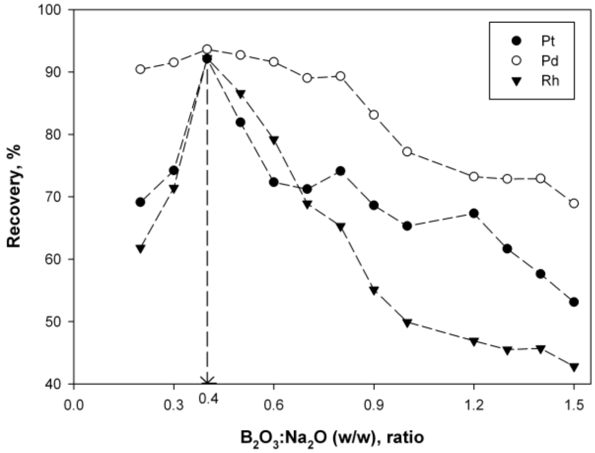

**Figure 6.** Effect of flux quantity on NiS fire assay for Pt, Pd and Rh recovery (6.36 g NiO, 5 g S, 5 g catalytic converter powder, at 950°C for 60 min)

The percent recovery increased with increasing $B_2O_3$ to $Na_2O$ ratio until 0.4 (w/w) ratios. Therefore, it is important to use 0.40 $B_2O_3$ to $Na_2O$ (w/w) ratio in fire assays if a higher recovery percentage is desired.

Slags are alloys of various oxides, which may form chemical compounds, solid and eutectic mixtures. Generally, slags may be divided into two principal groups: acid and basic slags. In metallurgy, stochiometric ratios are described by a degree of acidity or basicity. The degree of acidity n is defined as the ratio of number of atoms of oxygen, combined with silicon in silica, to the number of atoms of oxygen combined into basic oxides:

$$n = \text{Oxygen}_{SiO2} / \text{Oxygen}_{\Sigma MeO} \quad (1)$$

Acidity (n) of slag close to 1 have low viscosity and melting point, whereas acidity 2.5 to 4 a high viscosity and melting point. Additionally, Alumina ($Al_2O_3$) and other amphoteric oxides ($ZnO$,$Cr_2O_3$, $SnO_2$, $PbO$, $BeO$ etc.) are not taken into account when calculating the acidity of a slag[14].

Table 2 shows the recovery of NiS bead, amount of S in NiS bead and acidity of slag. Acidity of slag calculated using equation 1. As evidenced from the Table 2, the acidity of slag and amount of sulfur percentage in NiS bead increased with an increased amount of $B_2O_3$:$Na_2O$ ratio. However, figure 2 shows that 0.4 (w/w) ratio is optimum condition for recovery of PGMs.

Additionally, acidity of slag increases with increasing sulfur content in NiS bead because NiS matte does not dissolve in the slag. However, high acidity of slag caused NiS bead does not separate cleanly and easily from the slag. This is because acidic slags have higher viscosity[14]. Weak acidic slags result in good NiS collection and separate easily from the slag.

**Table 2.** The results of NiS bead and acidity of slag

| $B_2O_3/Na_2O$, (w/w) ratio | NiS bead$^T$ (g) | NiS bead$^R$ (g) | Recovery of NiS bead, % | Amount of S in NiS bead, % | Acidity of Slag |
|---|---|---|---|---|---|
| 0.2 | 10.00 | 6.725 | 67.25 | 23.46 | 0.88 |
| 0.3 | 10.00 | 7.245 | 72.45 | 25.82 | 0.91 |
| 0.4 | 10.00 | 7.472 | 74.72 | 26.09 | 1.15 |
| 0.5 | 10.00 | 7.107 | 71.07 | 26.51 | 1.46 |
| 0.6 | 10.00 | 7.087 | 70.87 | 26.74 | 1.73 |
| 0.7 | 10.00 | 6.897 | 68.97 | 26.91 | 1.94 |
| 0.8 | 10.00 | 7.097 | 70.97 | 27.86 | 2.34 |
| 0.9 | 10.00 | 6.823 | 68.23 | 28.07 | 2.66 |
| 1.0 | 10.00 | 6.975 | 69.75 | 28.76 | 2.94 |
| 1.2 | 10.00 | 6.954 | 69.54 | 29.14 | 3.34 |
| 1.3 | 10.00 | 5.878 | 58.78 | 29.88 | 3.72 |
| 1.4 | 10.00 | 5.884 | 58.84 | 30.05 | 4.30 |
| 1.5 | 10.00 | 5.880 | 58.80 | 30.33 | 4.57 |

*T*: Theoretical mass of NiS bead (g).
*R*: Recovered NiS bead (g).

### 3.3. Effect of Nickel Oxide Quantity and Ni:S Ratio on NiS Fire Assay

In this experimental series, the other parameters (5 g catalytic converter, 57.5 g flux, $B_2O_3$:$Na_2O$ 0.40 (w/w) ratio, 5 g S) were kept constant whereas the effect of nickel oxide quantity and nickel to sulfur ratio on the recovery percentages were investigated.

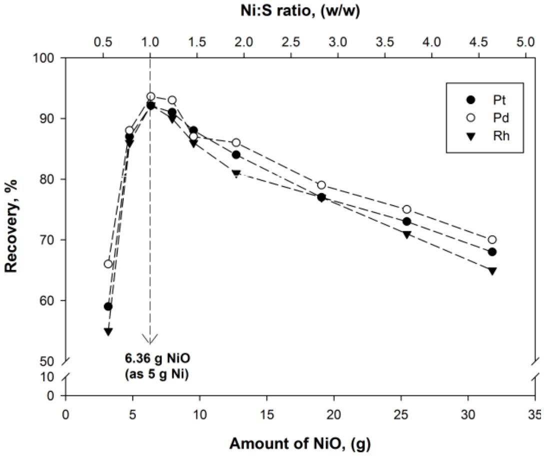

**Figure 7.** Effect of flux quantity on NiS fire assay for Pt, Pd and Rh recovery ($B_2O_3$:$Na_2O$ 0.40 (w/w) ratio, 5 g S, 5 g catalytic converter powder, at 950°C for 60 min)

As evidenced from the figure 7, an increase in Ni:S ratio from 0.5 to up to 1.0 (w/w) resulted in an increase of around 40% in recovery percentages. However, increasing the ratio produced difficulties in separating the slag from the button and decreasing the ratio (i.e. increasing S) was eventually producing a crumbly button [15].

### 3.4. Effect of Reaction Temperature on NiS Fire Assay

The effect of reaction temperature on Pt, Pd and Rh recovery was studied in the temperature range of 850−1050°C. As evident in the figure, an increase in temperature from 850°C to 975°C resulted in an increase of approximately 12% in the recovery of Pt, Pd and Rh at 60 minutes (Figure 8). Thus, increasing temperature has a clearly beneficial effective on recovery of Pt, Pd and Rh. The figure also underscores the role that temperature plays an important role in the NiS fire assay.

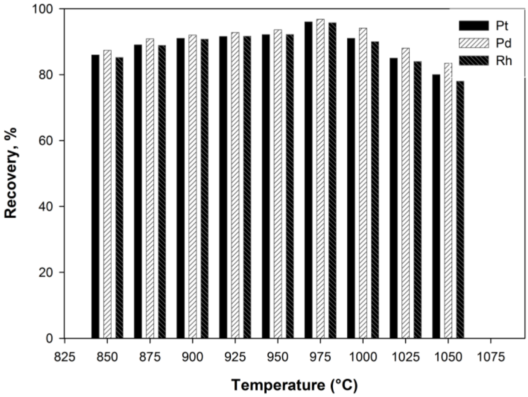

**Figure 8.** Effect of reaction temperature on NiS fire assay Pt, Pd and Rh recovery (57.5 g flux ($B_2O_3$:$Na_2O$ ratio 0.40 (w/w)), Ni:S ratio:1.0 (5g Ni and 5 g S), 5 g catalytic converter powder and 60 min)

However, at temperatures above 975°C recovery of Pt, Pd and Rh rapidly decreases, likely due to elemental sulfur oxidizing in the crucible. Hence, 975°C was selected as optimum condition for this study.

### 3.5. Effect of Reaction Time on NiS Fire Assay

The effect of reaction time on Pt, Pd and Rh recovery was studied in the time range of 30−120 min. The recovery percentage of Pt, Pd and Rh increased with increasing reaction time up to 90 minutes (Figure 9). However, above 90 minutes reaction time, the recovery percentage of Pt, Pd and Rh were decreased. This is because the melting flux does not protect the NiS in the crucible and NiS bead may become oxidizes with air[16].

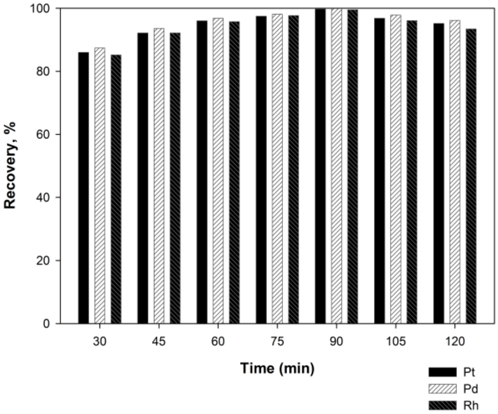

**Figure 9.** Effect of reaction time on NiS fire assay Pt, Pd and Rh recovery (57.5 g flux ($B_2O_3$:$Na_2O$ ratio 0.40 (w/w)), Ni:S ratio:1.0 (5g Ni and 5 g S), 5 g catalytic converter powder and 975°C)

### 3.6. Method Accuracy and Precision with SRM 2557 Standard Reference Material

SRM 2557 (National Institute of Standards and Technology, Gaithersburg, USA), a honeycomb type catalytic converter reference material from NIST, was used to validate the suitability and accuracy of the proposed method. Reference analyses results are shown in Table 3.

**Table 3.** Certified Value and NiS fire assay result for Pt, Pd and Rh in NIST SRM 2557

| NIST SRM 2557 | Certified Value, (ppm) | Founded result, (ppm) | Recovery, % |
|---|---|---|---|
| **Pt** | 1131.4 ± 11 | 1125.9 ± 8.8 | 99.6 |
| **Pd** | 233.2 ± 1.9 | 231.8 ± 2.4 | 99.4 |
| **Rh** | 135.1 ± 1.9 | 133.1 ± 1.1 | 99.0 |

The reference results are generally in good agreement with their certified values and published values for Pt, Pd and Rh. However, the poor Rh extractions could be due to either the oxidation of the Rh to rhodium oxide ($Rh_2O_3$), which is largely insoluble in NiS bead, or instrumental background correction.

## 4. CONCLUSIONS

When efficient production of analytical results is required, the NiS fire assay remains a practical method for the analysis of the entire set of PGMs. This study addressed the most critical parameters of the NiS fire assay with the aim of identifying optimum reaction conditions. We achieved high accuracy and precision using various mixtures of catalytic converter ((e.g., gasoline and diesel engine catalytic converters) and identified 57.5 g flux (0.40 w/w ratio, $B_2O_3$:$Na_2O$, 6.36 g NiO (as 5 g Ni) and 5 g sulfur (1.0 w/w ratio, Ni:S) for five gram of sample for 90 min at 975°C as the optimum condition for recovery of Pt, Pd and Rh; capable of recovering 99.7, 99.9 and 99.5% of Pt, Pd and Rh respectively. When using standard reference materials such as SRM 2557, our results were acceptable and consistent with certified values. We present a NiS fire method capable of recovering at least 99.0% of the Pd, Pt, and Rh present in catalytic converters and propose a fast, easy and straightforward method for the analysis of Pt, Pd and Rh in catalytic converters.

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