

# ASSAY AND GRAPHITE FURNACE- ATOMIC ABSORBANCE SPECTROMETRY ACCURACY FOR PALLADIUM CONTENT ANALYSIS

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## ABSTRACT

Palladium is a member of the expensive Platinum Group Metals as it is indispensable for various applications of modern technology. Due to the very small number of these elements in nature, high-sensitivity analytical methods and devices are required for accurate PGM measurement. The current study aims to determine the accuracy level of the Graphite Furnace-Atomic Absorbance Spectrometry device for palladium analysis after pre-concentration through the assaying process. The studied samples were two in-house standard reference samples with stream sediment and ultramafic rock matrices. Due to the lack of certified reference material containing certain palladium compositions, the degree of accuracy was tested by the spiking method. The detection limit for Pd in this study was 11.79 ppb. Pd content in the stream sediment (17 ppb) is much lower than of the ultramafic sample (290 ppb), implying PGM association to ultramafic rock naturally. Almost all measurements have good accuracy according to spike recovery between 80-120%. Inaccurate addition process and inappropriate calibration range most probably lead to inaccuracy.

**Keywords:** palladium; GF-AAS; assay; spiking

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## INTRODUCTION

Accuracy is one component of the acceptance level of a measurement result as well as precision. Standard reference material is necessary for determining the degree of analytical accuracy, while repeated measurements are required for the precision test [1][2][3][4]. Certified Reference Material (CRM) is known as the most trusted reference material for accuracy verification. It has been tested in various certified laboratories, and the manufacturing process is supervised by an international accreditation body [5][6][7]. Various studies were carried out for CRM replacement and assistance due to its high price, small number, and limited matrix. Various laboratories generated their own in-house reference materials from their most analysed matrix [6][8][9]. The spiking method, which is attained by adding a certain amount of material, is the most adapted solution to overcome the absence of standard materials [3][10][11][12]. Spiking

accuracy simply is defined on the spike recovery as a comparison of the analyte content in the sample before and after the standard material addition.

Palladium (Pd) is classified in Platinum Group Metals (PGM) along with platinum (Pt), rhodium (Rh), osmium (Os), ruthenium (Ru), and Iridium (Ir). This group of elements is rare in nature so that it is strategic and expensive. In the earth's crust, the PGM amount is even less than the lanthanide group element, which is predicted as modern technology material. PGM is crucial in the automotive, catalyst, jewellery, electronics, and electric car industries [13][14][15]. Various usefulness of the PGM group is summarised in **Table 1**. Naturally, PGM is associated with base metals and is concentrated in ultramafic-mafic sulfide saturated igneous rocks with abundant iron (Fe)-Copper (Cu) concentrations [2][3][16]. Therefore, PGM is widely exploited in South Africa, Canada, Russia, and Zimbabwe [14][17]. In Indonesia, PGM studies were mostly

conducted in South Kalimantan, South Sulawesi, and Southeast Sulawesi because of the wide ultramafic-mafic rocks distribution in these regions [18][19].

The necessity for a high sensitivity analytical device is a consequence of measuring PGM because of the low abundance. Hence, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Instrumental Neutron Activation Analysis (INAA) were widely applied in the PGM studies [2][3][21][22][23]. Other analytical instruments are adoptable but with certain engineering such as extraction, leaching, electrowinning, assaying, and coprecipitation [14][15][24]. A combination of leaching, assaying, and ICP-MS devices were utilised in preventing analytical inaccuracies [25]. However, other analytical devices are adaptable for PGM analysis after various pre-concentration or optimisation processes. Preparation process complexity and the need for a high sensitivity analytical instrument are probably the obstacles to PGM studies in Indonesia.

North Konawe is situated in the Southeast Sulawesi Province with a wide distribution of ultramafic rocks. Olivine, pyroxene and hornblende are the main minerals in ultramafic rocks there [19]. In addition, serpentine, ilmenite, and kaolinite are accessory minerals sometimes found in altered ultramafic rocks. Although ultramafic rock exploration in North Konawe is mostly associated with nickel [19], the PGM content is worth investigating because of this metal group correlation towards the ultramafic and mafic rocks.

This study aims to determine the degree of accuracy of the Graphite Furnace-Atomic Absorbance Spectrometry (GF-AAS) method for palladium analysis after pre-concentration through the assaying process. An ultramafic rock from North Konawe and a stream sediment sample of Citarum River were selected for this study. This investigation results would support the development of palladium-associated industry in Indonesia.

**Table 1.** Platinum Group Metals sub-divisions and their industrial application [13][20].

PGM sub-group	Element	Industrial Utilities
Iridium sub-group, melting point >2000 °C	Os	Process catalyst for syn-dihydroxylation, electrical contacts, light filaments, staining agent in electron microscopy, jewellery, fountain pen points.
	Ir	Coating of dimensionally stable anodes (DSA), Process catalyst (for hydrogenation, acetic acid synthesis, and hydroformylation), jewellery fabrication, catheters.
	Ru	chlor-alkali industry, ammonia synthesis, hydrocarbon synthesis, hydroformylation, computer hard drive, anti-corrosion piping, dentistry.
Platinum sub-group, melting point <2000 °C	Rh	The alloying agent with Pt in thermocouples, sliding and pressure contacts, jet engine glow plugs, electroplating, ammonia catalytic oxidation.
	Pd	Multilayer ceramic capacitors (MLCC), hybrid integrated circuits, plating connectors, lead-frames, oxygen sensors, petroleum refinery, exchange-traded funds (as coins).
	Pt	Jewellery fabrication, dental alloys, biomedical devices, anticancer drugs, reforming and isomerisation in petroleum refinery, optical glass, thermocouples, contact materials, varistors, and bond wires.

## MATERIALS AND METHODS

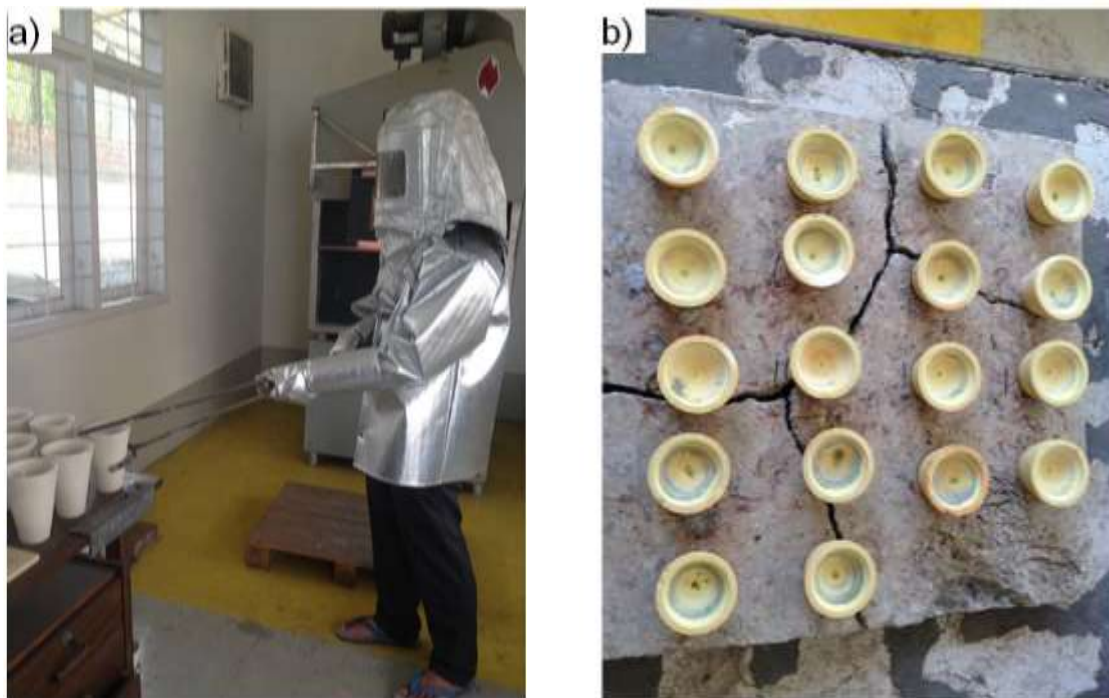
The two in-house reference materials for which Pd composition was measured in this study are called Citarum 3 and Serpentine. Citarum 3 is stream sediment of the Citarum River from the Bandung Regency area. The rock types traversed by the Citarum River are majorly andesitic to dacitic tuff [26]. Conventional gold mining was conducted in several places along with the river flow. PGM is sometimes correlated with gold [19]. Therefore, Citarum River flow sediments might also contain PGM. The Serpentine was attained from ultramafic rock domains in North Konawe Regency. Those samples were deemed suitable as studied materials due to their strong association of ultramafic rock to PGM.

Atomic Absorption Spectrometry (AAS) instrument works based on the absorption of radiation absorbance by free atoms of an element at a certain frequency and wavelength. This device is commonly used for base metals and precious metals studies, such as Ca, Pb, Cu, Cr, Mn, Ag, and Au [27][28][29]. Basically, atomisation in the AAS is carried out using two options, namely flame atomisation and graphite furnace atomisation. The first option uses a flame burner, while the other one adopts a graphite cylinder connected to electrodes at both ends.

Flame atomisation is commonly applied to analyse high concentration metals at a low cost due to the low-temperature requirement of <3,000 °C and a short residence time [30]. However, this option is not sensitive enough for trace elements or volatiles measurements.

Although strong electric power is required in the graphite furnace atomisation process, this alternative is preferred for PGM analysis [31] that the option applied in this study.

The samples were crushed and ground in gaining particle size of -200 mesh to accelerate the preparation process. A standard solution containing 1,000 ppm Pd (produced by Spex CertiPrep, Germany) was diluted stratified to obtain a calibration curve and to calculate the detection limit. A fire-assaying scheme that separates metals and impurities based on their melting point [3][32] was carried out to support the analytical device sensitivity. Special protective apparel during the assaying scheme is useful to protect the operator from the furnace's high combustion temperature **Figure 1a**. The fire-assaying process consists of three stages: flux mixing, fusion reaction, and coupling [3][19]. The selected sample was put together with the flux components (60 g of Na<sub>2</sub>CO<sub>3</sub>, 40 g of PbO, 20 g of SiO<sub>2</sub>, 25 g of Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, 10 g of CaF<sub>2</sub>, and 5 g of flour) in polyethylene plastic. For fusion reaction, the furnace was set at 1100°C for one hour while the coupling was carried out at 850°C for 45 minutes as described in the previous study [3]. The coupling plates of this study are shown in **Figure 1b**. Prill (Au + PGM) resulted from the assaying process then was separated from the lead button as a compound of impurities before preparation and measurement using the GF-AAS. Entire pre-concentration, preparation, and analysis using GF-AAS steps were worked at the Laboratory of Center for Geological Survey, Bandung.



**Figure 1.** Supporting tools of this study: a) Unique apparel to protect the operator from working in high temperature; b) coupling plates utilised at the end of the fire-assaying process.

The spiking technique was adapted because of no CRM containing guaranteed PGM composition available at the Laboratory of Center for Geological Survey. The accuracy of a spiking method is represented on the spike recovery value ( $S_R$ ), which is calculated according to **Equation 1** below:

$$SR\% = \frac{(C_{spike} - C_{smp})}{C_{lar}} \times 100\% \quad (1)$$

$C_{spike}$ ,  $C_{smp}$ ,  $C_{lar}$  is the concentrations after spiking, before spiking, and spike solution, respectively. Standard solutions, which contain 2,500 ppb, 5,000 ppb, and 7,500 ppb of Pd were added to the sample to gain 10 ml final solutions.

## RESULTS AND DISCUSSION

### A. Limit of Detection

Four levels of Pd-containing calibration solutions (blank, 50 ppb, 100 ppb, and 150 ppb) were measured to draw a calibration curve. The analysis results are then input in linear regression.

calculation in **Equation 2** to obtain the standard deviation ( $S_{y/x}$ ) applying equation (3) below:

$$y = ax + b \quad (2)$$

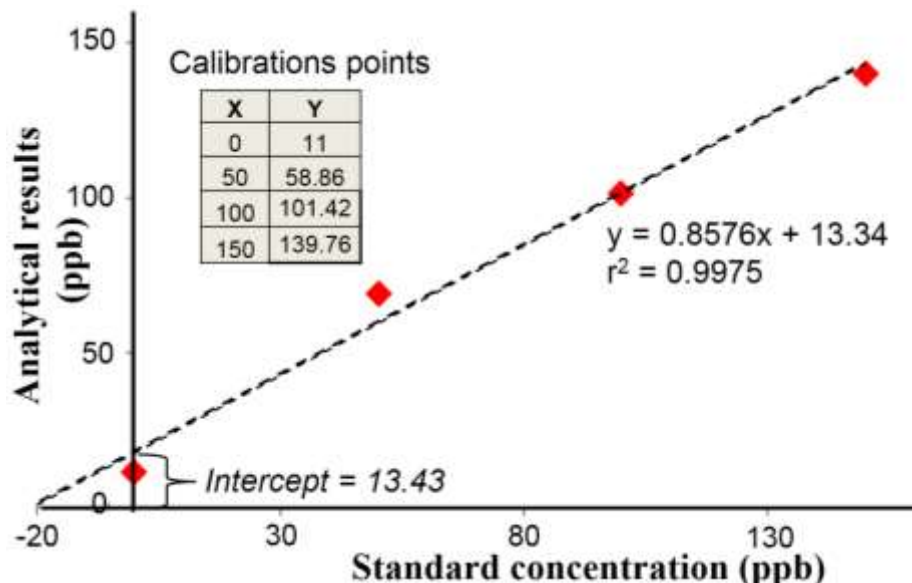
$$S_{y/x} = \sqrt{\frac{\sum_i^n (x_i - x_R)^2}{n - 2}} \quad (3)$$

The  $y$ ,  $x$ ,  $a$ , and  $b$  parameters in **Equation 2** are the measured concentration, the theoretical concentration, the slope of the curve, and the intercept, respectively. Moreover,  $x_i$ ,  $x_R$ , and  $n$  in **Equation 3** refer to analytical results, mean concentration, and the number of analyses. Pd limit of detection of this study is three folds of the standard deviation, as illustrated in **Equation 4**. The curve-based Pd limit of detection of this study is three folds of the standard deviation, as illustrated in **Equation 4**. Thus the final LOD was calculated using **Equation 5**.

$$y_{LOD} = 3S_{y/x} \quad (4)$$

$$LOD = \frac{3S_{y/x} - b}{a} \quad (5)$$

The calibration curve for the Pd analysis of this study is shown in **Figure 2**.



**Figure 2.** Calibration series measurement results after input in the calibration curve. The intercept is 13.43.

Positive intercept implies that the analytical settings are adequate to detect the lowest analyte content in the solution. On the other hand, a negative intercept suggests that the previous detection limit level is not sufficient to measure analyte abundance [3][19]. So that a negative intercept is considered influential, but the positive one is ignorable. The intercept of the calibration curve is positive **Figure 2**, so that it was negligible in LOD calculation. Based on **Equation 2 - Equation 5**, the detection limit for Pd using the GF-AAS method in this study was

11.79 ppb. A very strong positive correlation between the concentration of the prepared standard values theoretically with the analytical results was amplified by the strong calibration coefficient ( $r^2 = 0.9975$ ). However, this limit is not as good as a previous study on Pd measurement using ICP-MS device with LOD 2.29 ppb [3]. This difference proves the higher ICP-MS sensitivity than AAS even though modified with graphite furnace atomisation. Pd measurement results in this study are summarised in **Table 2**.

**Table 2.** Pd measurement results of the two in-house reference materials in this study.

Sample Codes	Pd content (ppb)	Spike recovery (%)
Citarum 3	17	-
Serpentine	290	-
Citarum 3 + Pd 2500 ppb	2817	112
Citarum 3 + Pd 5000 ppb	5280	105
Citarum 3 + Pd 7500 ppb	9007	119
Serpentin + Pd 5000 ppb	3428	125
Serpentin + Pd 7500 ppb	4717	89
Serpentin + Pd 2500 ppb	7852	101

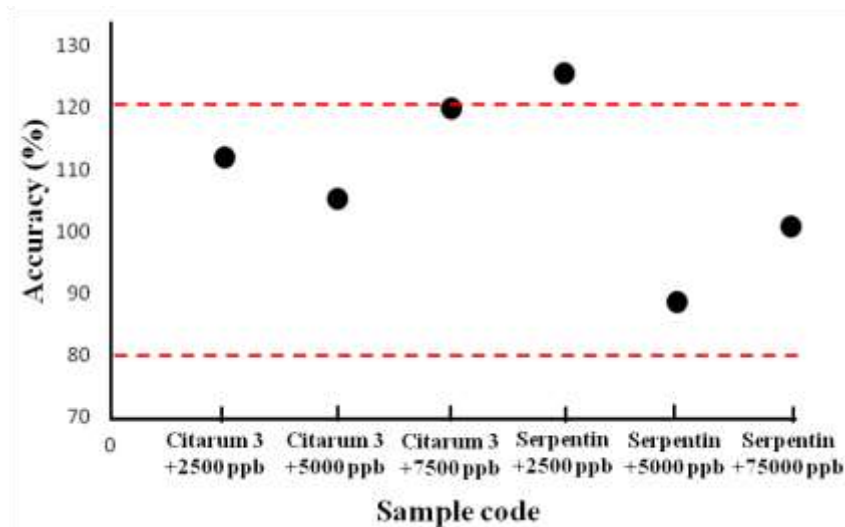
### B. Pd content comparison

Palladium abundance of the Citarum 3 (17 ppb) is much lower in comparison to the Serpentine (290 ppb). As a stream-sediment origin sample, the chemical content of Citarum 3 represents the eroded material from the higher ground and draws the material composition of the catchment area. The Citarum River majorly flows through andesitic and dacitic rocks, which are uncommon as PGM-bearing material [26]. Although conventional gold mining was conducted in the vicinity of this river flow, the mineralisation unlikely correlated to PGM. On the other hand, Serpentine was obtained from an ultramafic outcrop that most possibly correlated to PGM according to the previous reports [2][3][16][19]. Thus the high Pd contents in Serpentine reflect its parent rock composition.

After spiking and calculation using Equation 1, the accuracy of the test method is in a fairly wide range of 89% to 125% Figure 3. The degree accuracy of the research considered good with a spike recovery of 100

± 20% as described in the previous studies [3][32][33]. However, the result of Serpentine + 2,500 ppb Pd is below the acceptance criteria (spike recovery ≈ 125%), which might be because of some inaccuracy during standard Pd addition. PGM analysis was worked at a high sensitivity level as a consequence of its very low concentration in nature. A slight mismatch during spiking should have a significant impact on the final measurement result.

Studied samples were diluted 250 times through pre-concentration and preparation sequences. The lowest concentration for the calibration series is 0 ppb (blank) and the highest at 150 ppb, implying that the resulting curve should be most valid for a concentration range of up to 37,500 ppb. On the other hand, the upper limit is too far for sample measurement with a maximum content of 7,852 ppb Table 2. Future improvement could be carried out using a lower concentration series for calibration. Then, repeatability and reproducibility works would strengthen this study on the method robustness.



**Figure 3.** The accuracy of the spiking method was determined from the spike recovery in this study. Most of the analysis shows acceptable accuracy with spike recovery between 80% to 120%.

### CONCLUSION

The palladium concentration of two in-house reference materials was analysed using the GF-ASS device after pre-concentration by assaying process. The limit of detection was 11.79 ppb that obtained from the measurement on a series of calibration solutions. Pd content in the stream sediment sample from Bandung (17 ppb) was less than the one originated from ultramafic rock

in North Konawe (290 ppb). These results reflect PGM natural association with ultramafic to mafic rocks. Almost analysis shows good accuracy with spike recovery between 80-120%. The inaccuracy of one analysis should be caused by errors during Pd addition and/or inappropriate calibration range. Repeatability and reproducibility tests would improve the proposed method to enhance Pd exploration in Indonesia.

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