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## ARTICLE

- Application of two-level full factorial design and response surface methodology in the optimization of inductively coupled plasma-optical emission spectrometry (ICP-OES) instrumental parameters for the determination of platinum** 43  
Raison Mapfumo and Mark Fungayi Zaranyika

*Full Length Research Paper*

# Application of two-level full factorial design and response surface methodology in the optimization of inductively coupled plasma-optical emission spectrometry (ICP–OES) instrumental parameters for the determination of platinum

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Inductively coupled plasma optical emission spectrometry (ICP-OES) determination of platinum was optimized using 2-level, 4-factor full factorial design and response surface methodologies. Four factors, namely carrier gas flow rate, sample solution flow rate as represented by the pump speed, plasma observation height and RF power, were employed in the factorial design. Analysis of variance (ANOVA) at a p-value significance level of 0.05 was used to assess the significance of the factors on platinum analytical line emission intensity. The main effects of carrier gas flow rate and plasma power, and the interaction effect of carrier gas flow rate and plasma power, were found to be statistically significant and were varied during subsequent optimization procedure using contour map and response surface methodologies. Plasma observation height and pump speed were found to have an insignificant effect on the platinum intensity and were held constant at 10 mm above the load coil and 30 revolutions per minute, respectively during the optimization procedure. The optimized procedure comprised of a carrier gas flow rate of 0.70 L/min and plasma power of 1400 W, and was validated by analysis of Certified Reference Materials (CRMs) AMIS 0132 for low platinum grades and AMIS 0164 for high platinum grades. The instrumental limit of detection (LOD) and limit of quantization (LOQ) obtained were 0.035 µg/g Pt and 0.105 µg/g Pt, respectively, and highly precise determinations of Pt (0.21 to 0.24% RSD) were obtained when three batches of PMG ore floatation concentrates were analyzed using the optimized ICP-OES parameters.

**Key words:** Factorial experimental design, response surface methodology, optimization, inductively coupled plasma atomic optical spectroscopy, platinum.

## INTRODUCTION

Platinum ore commonly contains gold and the platinum group metals (PGMs) that is, platinum, palladium,



rhodium, iridium and ruthenium, as well as the base metals nickel, copper and cobalt. The ore is mined and processed at floatation plants into a semi-finished product which is a floatation concentrate. The concentrate is smelted to produce matte which will then be refined into individual base metals like nickel, copper, cobalt and PGMs. Thus quality control of platinum production entails monitoring the levels of several metals in geological ores, intermediate process material and final products. This calls for highly sensitive analytical techniques, capable of multi-element analysis.

Analytical techniques for the determination of precious metals in geological samples were reviewed by Hall and Bonham-Carter (1988), Reddi and Rao (1999), Balcerzak (2002), and Zhang et al. (2014). Sample decomposition and pre-concentration methods available include the lead fire assay (Pb-FA) and nickel sulfide fire assay (NiS-FA) techniques (Lenahan and Murray-Smith, 1986; Barefoot and Van Loon, 1999), chlorination and wet multi-acid digestion procedures (Reddi and Rao, 1999). Quantitative recoveries for Au, Pt and Pd are achieved using the Pb-FA method, while all the PGMs except Au are recovered quantitatively by the NiS-FA method. Chlorination is widely used for the determination of Os and Re. The wet multi-acid digestion employs mixtures of HCl, HClO<sub>4</sub>, HNO<sub>3</sub>, HBr, Br<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, etc. Wet digestion is however subject to low recoveries and poor reproducibility.

Instrumental techniques for determination of the precious metals include flame atomic absorption spectroscopy (AAS), graphite furnace atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Numerous reports have appeared in the literature on the use of flame AAS, GFAAS and ICP-MS for the geological analysis of related samples for precious metals (Reddi and Rao, 1999). Although few publications report the use of ICP-OES and ICP-OES in conjunction with Pb-FA, and aqua regia (AR) dissolution of the silver prill is widely used for the determination of Au, Pt and Pd (Reddi and Rao, 1999; Balcerzak, 2002). The major advantage of the FA procedure lies in the fact that ultra-trace amounts of precious metals in large samples, 10 to 50 g, are pre-concentrated into a small bead of metal alloys (Balcerzak, 2002).

Chung and Barnes (1988) evaluated the use of ICP-OES for the determination of Au, Pt, Pd and Ag in geological samples after separation and pre-

concentration of the metals with poly(dithiocarbamate) resin, and concluded that the technique was suitable for the determination of ultra-trace amounts of analytes from geological and related samples containing high concentrations of cations and anions, including Li, B and acetate ion. Similarly, Compennolle et al. (2011) evaluated laser ablation ICP-OES for the determination of Pd, Pt and Rh in Pb-FA buttons, and reported detection limits of between 2.5 and 12 µg g<sup>-1</sup> in the Pb-FA button.

Methods for optimizing analytical procedures fall into two classes: simplex methods and response surface methodology (RSM). Simplex optimization is a sequential procedure based on a k-factor first-order model. The response function can however not be obtained using this approach (Ferreira et al., 2003). The use of RSM enables the determination, not only the influence of the factors, but the response function as well. Chung and Barnes (1988), as well as Compennolle et al. (2011), employed simplex optimization to set the ICP-OES operating parameters. This paper reports the use of factorial experimental design and response surface methodology in the optimization of the ICP-OES parameters for the determination of Pt in platinum ore extraction plant concentrate samples, following Pb-FA sample decomposition and pre-concentration.

## Theoretical

The attributes and limitations of ICP-OES have been discussed by several authors (Kornblum and De Galan, 1977; Jarosz et al., 1978; Barnes and Boumans, 1978; Larson and Fassel, 1979; Uchida et al., 1981; Ingle and Crouch, 1988; Tripković and Holclajtner-Antunović, 1993; Galley and Hieftje, 1994; Hou and Jones, 2000; Hill, 2008; Butcher, 2010; Thompson, 2012). Critical parameters that affect the ICP-OES analytical performance and require optimization are: RF power, nebulizer gas flow rate, viewing height and sample introduction rate (Boumans, 1979; Zhaneni and Wagatsuma, 2002; Raaijmakers et al., 1983; Boumans, 1987). Traditionally, optimization of instrumental variables has been carried out by varying one variable at a time (OVAT approach). This approach is however time consuming as at least  $n^n$  experiments, where  $n$  is the number of variables, must be carried out before the optimal conditions can be identified. The alternative to the OVAT approach is the experimental design approach due to Fisher (1925). The objective of experimental

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design is to plan and conduct experiments in order to extract the maximum amount of information from the collected data in the smallest number of experimental runs (Gabrielsson et al., 2002). The basic idea is to change all the factors simultaneously over a set of planned experiments and then connect and interpret the results using mathematical models. The goals of experimental design are: (a) identifying the factors that have the largest effect on the system, (b) quantifying the effects of these factors and their interactions, and (c) finding the optimum values or conditions for these factors (optimization) (Harvey, 2000; Ferreira et al., 2002, 2003; Bruns et al., 2006; Bingol and Kuku, 2011; Candioti et al., 2014).

Several experimental designs have been developed for example, the full factorial design (FFD) (Harvey, 2000; Ferreira et al., 2003;), the Plackett-Burman design (PBD) (Tyssedal, 2008; Deng and Tang, 1999), the Box-Behnken design (BBD) (Delacroix and Porte, 1996), and the D-optimal design (DOD) (Mantre et al., 1997; Titterington, 1975; de Aguiar et al., 1995; Mitchell, 1974; Hill, 1980). In this paper the optimization of the ICP-OES parameters are reported for the determination of platinum using the 2-Level full factorial experimental design, in conjunction with response surfaces.

Response surface methodology employs mathematical and statistical models to generate response surfaces from experimental data obtained in relation to experimental designs (Bezerra et al., 2008; Sredovic Ignjatovic et al., 2015). The response surface equation is similar to the factorial design equation, but contains additional quadratic terms that allow curvature in the response, thus making response surfaces ideal for: (i) understanding how input factors influence the response, (ii) finding input factor levels that optimize the response (Hanrahan et al., 2005, 2006; Ghaseni et al., 2011; Sredovic Ignjatovic et al., 2015). The study was carried out by measuring the intensity of the Pt(1) 265.945 nm atomic line. The experimental design approach has been used previously to optimize ICP-OES with respect to sheath gas flow rate, pump speed and auxiliary gas flow rate (Bianchi et al., 2007).

The 2-Level factorial design ( $2^k$ -FD, where k is the number of factors) is the simplest and most common form of FFD design. All factors are investigated at 2 levels, Low and High, coded as + and - (or +1 and -1). When the  $2^k$ -FD is applied to ICP-OES measurements for which 4 factors must be optimized, the experimental domain involves 16 experiments, performed in random order to eliminate systematic errors. A  $2^4$ -factorial design is represented by Equation 1 (Harvey, 2000):

$$R_i = \beta_o + \beta_a A^* + \beta_b B^* + \beta_c C^* + \beta_d D^* + \beta_a \beta_b A^* B^* + \beta_a \beta_c A^* C^* + \beta_a \beta_d A^* D^* + \beta_b \beta_c B^* C^* + \beta_b \beta_d B^* D^* + \beta_c \beta_d C^* D^* \quad (1)$$

where  $\beta_o$ ,  $\beta_a$ ,  $\beta_b$ ,  $\beta_c$  and  $\beta_d$  are empirical constants given by:

$$\beta_o = \frac{1}{n} \sum R_i \quad (2)$$

$$\beta_a = \frac{1}{n} \sum A_i^* R_i \quad (3)$$

$$\beta_b = \frac{1}{n} \sum B_i^* R_i \quad (4)$$

Where  $R_i$  denotes the response measured,  $A^*$ ,  $B^*$ ,  $C^*$  and  $D^*$  are the + or - coded factors, which for the ICP are RF power, nebulizer gas flow rate, viewing height and sample introduction rate, respectively. The first 5 terms in Equation 1 represent the main effects of the respective factors, while last 6 terms represent the interaction terms. The value of  $R_i$  obtained refers to coded factors that is, + or -, and can be converted to a value based on the uncoded values of A, B, C and D used in the experiment, if need be. The effects of a given factor ( $E_i$ ) and the standard deviation (S) associated with it, are given by Equations 5 and 6, respectively:

$$E_f = \frac{(\sum R_i)_{uppercase}}{8} - \frac{(\sum R_i)_{lowercase}}{8} \quad (5)$$

and

$$S = \sqrt{\frac{2}{15} \sum E_i^2} \quad (6)$$

The statistical significance  $p$  parameter is calculated using Equation 11:

$$S^2 = Np(1-p) \quad (11)$$

Therefore

$$p = S/N \quad (12)$$

The effect obtained is significant if  $p \leq 0.05$ . Alternatively, a Pareto Chart is constructed using the Student T statistic,  $T_{(calc.)}$ , corresponding to the observed effect. The effect is significant if its  $T_{(calc.)}$  is greater than a reference line corresponding to  $t_{(critical, p = 0.05)}$  at the appropriate number of degrees of freedom (Harvey, 2000; Chang et

al., 2011; Abdel-Ghani et al., 2009; Pokhrel and Viraraghavan, 2006).

The  $2^k$ -FD is used to estimate the main effect and interaction effects. Statistical evaluation of these effects is done using analysis of variance (ANOVA) (Ferreira et al., 2003; Ignjatovic et al., 2015; Hanrahan et al., 2005; Mutihac and Mutihac, 2008). The determination of which factors and interactions have the most prominent effects on the response is achieved by comparing the statistical p-value for the estimated effects with the critical level, which is usually 0.05 (Ferreira et al., 2003). If the p-value is greater than or equal to 0.05, the effect is insignificant. If the p value is less than 0.05, the effect is significant. If the analysis suggests significant interactions, these are looked at first because a significant interaction will influence how the main effects are interpreted.

## EXPERIMENTAL

### Equipment

The instrument used was a Spectro Arcos ICP-OES manufactured by Spectro Analytical Instruments of Germany. The software on the instrument was the Smart Analyzer Vision, Version 4.02.0831. The Windows Version was Win XP (Build 2600). The radial plasma observation mode was used. The Spectro Arcos ICP-OES features a Paschen-Runge spectrometer mount, employing the proprietary Optimized Rowland Circle Alignment (ORCA) technique. It consists of two hollow section cast shells, with an optimized small volume and 32 linear CCD detectors. The wavelength range between 130 and 770 nm can be analyzed simultaneously, allowing for complete spectrum capture within two seconds. An air cooled ICP generator, based on a free running 27.12 MHz system is installed. For sample introduction, a Spectro Cross Flow nebulizer with a Scott type, double pass spray chamber is used, in conjunction with a peristaltic pump.

### Materials

The following materials were used in the study: concentrated hydrochloric acid, AR, 32%, (Merck, Darmstadt, Germany); concentrated nitric acid, AR, 55%, (Merck, Darmstadt, Germany); platinum standard solution, UltraSpec, 1000 µg/ml, 99.999% pure in 10% HCl (De Bruyn Spectroscopic Solutions, Bryanston, South Africa); scandium solution, AR, 25 µg/ml (Sigma Aldrich, Saint Louis, MO, USA); lead oxide-based flux (RO722) and lead oxide-based flux (RO712) (Proglo, Harare); silver solution, AR, 1 g/L (Sigma Aldrich, Saint Louis, MO, USA); argon, 99.999% purity (Afrox, Johannesburg, South Africa); de-ionized water, 18.2 MΩcm resistivity, produced using a Milli Q Advantage A10 water purification system (Millipore, Darmstadt, Germany); Certified Reference Materials, AMIS 0132 and AMIS 0164 (African Mineral Standards, Isando, S. Africa); PGM ore concentrate from the PGM ore concentrator plant; PGM floatation concentrate from the PGM floatation plant.

### Sample pre-treatment and preparation

The PGM ore concentrate from the PGM ore concentrator plant was

used in the optimization experiments. 50 g aliquots of the ore concentrate were mixed in a fire-clay fusion crucible with 200 g of a lead oxide based flux (RO712). 1 ml of a 1 g/L silver solution was added. The samples were fused at 1200°C for one hour. The resultant lead buttons were cupelled at 1000°C for one hour and the resultant precious metal prills were then dissolved in aqua regia. The solutions were collected and stored in a closed 2.5 L polypropylene bottle previously cleaned by soaking in aqua regia and rinsing with de-ionized water. The PGM floatation concentrate was used for precision determination and was subjected to the same sample treatment steps as the PGM ore concentrate, except that 5 g of the sample and 200 g of RO722 flux were used instead of 50 g of sample and 200 g of RO712 flux.

### Factorial designs

Optimization of the ICP-OES method for the determination of platinum was based on a 2-level full factorial experimental design for four variables affecting the platinum intensity: plasma or RF power, nebulizer or carrier gas flow rate, plasma observation height and liquid sample introduction rate as represented by the pump speed. The 4-factor 2-level full factorial design matrix is shown in the first five columns of Table 1. Table 2 shows the low and high factor levels used in the present study. These levels were selected by reference to published literature (Boumans, 1979; Skoog et al., 1998; Hou and Jones, 2000). All samples prepared were measured using the Spectro Arcos ICP-OES at the factor levels specified in Tables 1 and 2. The respective Pt 265.945 nm line intensity readings obtained are shown in Tables 1 and 2. All readings were made in triplicate and corrected for the reagent blank reading.

### Optimization strategy

The optimization process was done using the PGM ore concentrate solution prepared as described. In the factorial design, Pt line intensity readings obtained are shown in the last column of Table 1. A blank was analyzed to correct for system noise. Experimental data were processed using Minitab Release 16 software (Minitab Inc., State College, PA). Table 3 shows the estimated effects, p-values and Student T statistics for the Pt 265.945 nm intensity (Cps, coded units). Figure 1 shows the corresponding Pareto chart. Response surface designs were used in the optimization process, see Figures 2 and 3. Tables 4 and 5 show the preliminary and final design matrix, and corresponding mean Pt 265.945 nm line intensities (n = 3) used to construct the contour maps and response surfaces shown in Figures 2 and 3.

### Validation

The optimized instrumental parameters were validated by analyzing the two Certified Reference Materials (CRMs): African Mineral Standards, AMIS 0132 for low platinum grades, and AMIS 0164 for high platinum grades. Quantification was done using the calibration technique using scandium as internal standard.

## RESULTS AND DISCUSSION

### Factorial design

Table 1 shows the experimental design matrix and the



**Table 1.** 2-Level 4-Factor Factorial Design Matrix and mean Pt 265.945 nm line intensity (CPS, coded units).

Expt	A	B	C	D	I $\pm$ SD
1	-	-	-	-	1.124 $\pm$ 0.018
2	-	-	+	-	2.085 $\pm$ 0.043
3	-	-	-	+	1.124 $\pm$ 0.018
4	+	+	-	+	1.786 $\pm$ 0.014
5	+	-	+	-	52.004 $\pm$ 5.809
6	-	+	-	-	0.370 $\pm$ 0.004
7	+	-	-	-	8.435 $\pm$ 0.206
8	-	-	+	+	2.277 $\pm$ 0.010
9	+	+	+	+	4.203 $\pm$ 0.082
10	-	+	+	-	0.492 $\pm$ 0.006
11	+	-	-	+	9.409 $\pm$ 1.130
12	-	+	+	+	0.520 $\pm$ 0.002
13	+	+	-	-	1.371 $\pm$ 0.007
14	+	+	+	-	2.906 $\pm$ 0.056
15	+	-	+	+	58.208 $\pm$ 17.043
16	-	+	-	+	0.390 $\pm$ 0.004

A = Plasma gas (L/min); B = Plasma power (W); C = Plasma height (mm); D = Pump speed (rpm); SD = standard deviation.

**Table 2.** Factors and levels used in the factorial design for determination of platinum.

Variable	Low value (-)	High value (+)
Carrier gas flow rate/LMin <sup>-1</sup>	0.5	1.5
Plasma power/W	1000	1500
Plasma observation height/mm	10	30
Sample solution pump speed/rpm	15	45

results obtained from each run. Analysis of variance (ANOVA) and p-value significance at a p-value of 0.05 were used to calculate the significance of the effects as shown in Table 3. Using  $p = 0.05$ , Table 3 shows that the main effects of carrier gas flow rate and RF power, and carrier gas flow rate  $\times$  RF power interaction effect are statistically significant, that is their p-values are less than 0.05. Plasma observation height and pump speed were found to be insignificant at the levels employed in the 2-level 4-factor full factorial experimental design in Table 2. These observations are confirmed by the Pareto Chart shown in Figure 1.

#### Preliminary optimization work using contour maps and response surface methodology

Table 4 shows the preliminary design matrix that was used to construct the contour map and response surface.

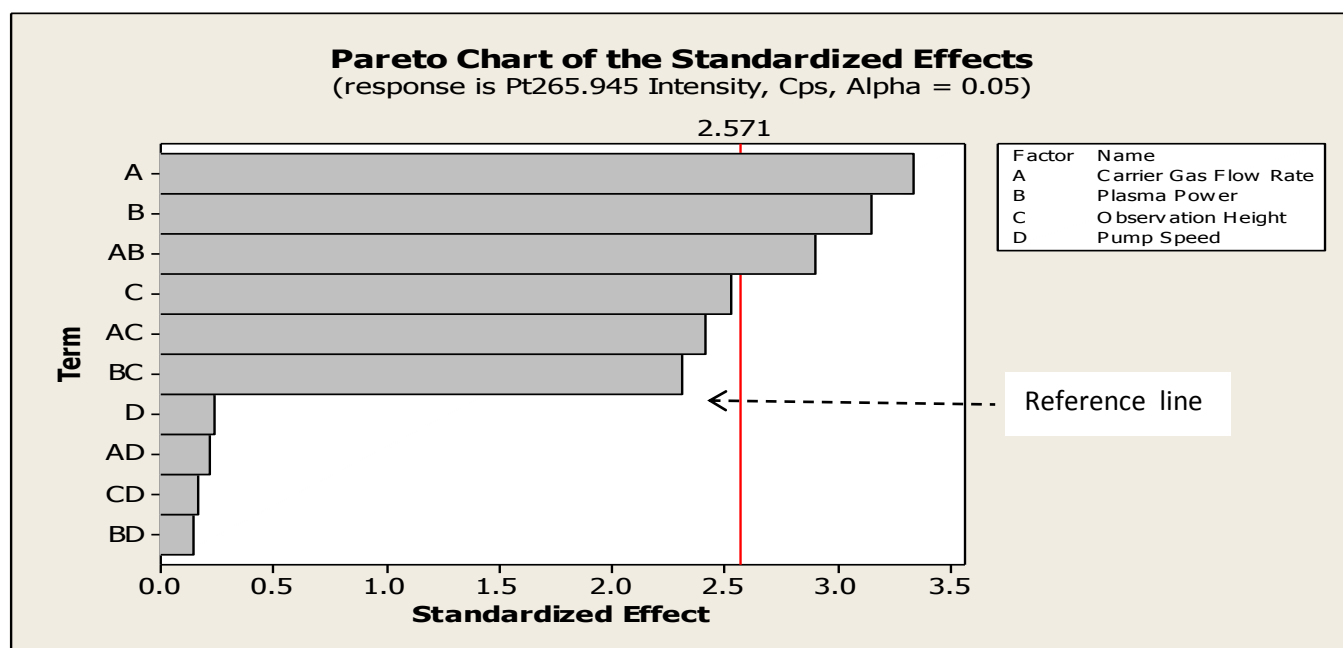
Figure 2a shows the contour map and response surface obtained for platinum intensity as a function of carrier gas flow rate and plasma power. It is apparent from Figure 2a that the region of optimum response, that is highest platinum intensity, is off-centre in the map. Similarly the response surface in Figure 2b has no sharp peak to indicate sharp optimization. As a result of this, the levels of the variables, that is plasma power and carrier gas flow rate were re-selected and the optimization process repeated.

#### Final optimization

In the final optimization experiments, pump speed was fixed at 30 revolutions per minute while plasma observation height was fixed at 10 mm above the load coil, while the design matrix employed for plasma power and carrier gas flow rate is shown in Table 5. The corresponding contour map is shown in Figure 3a, while

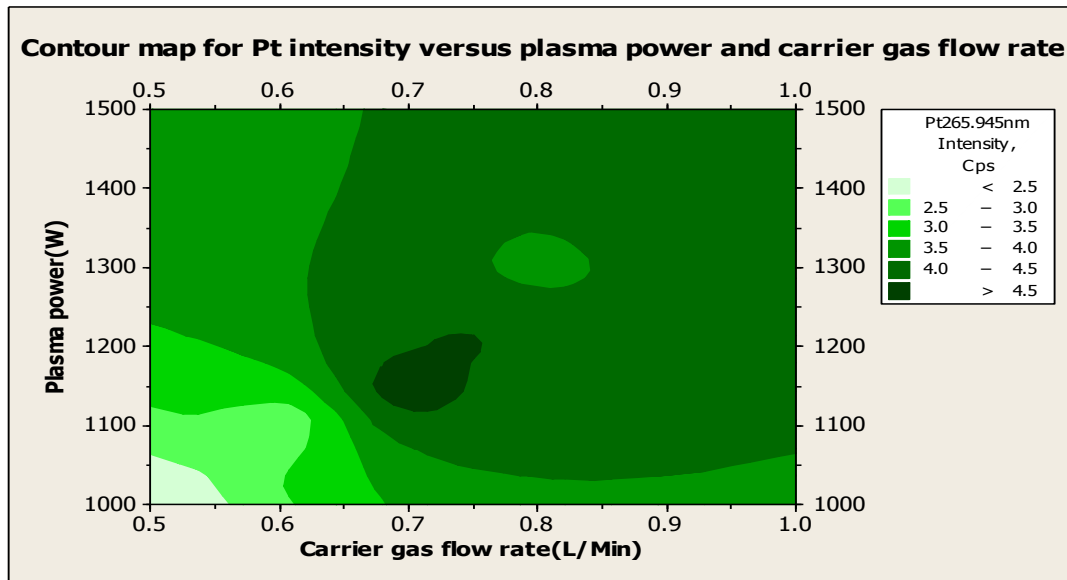
**Table 3.** Estimated Effects and p-values for Pt 265.945 nm line intensity (CPS, coded units).

Term	Effect	p-value	t statistic
Carrier Gas Flow Rate	16.242	0.021	3.33
Plasma Power	-15.329	0.025	-3.15
Plasma Observation Height	12.336	0.052	2.53
Pump Speed	1.141	0.824	0.23
Carrier Gas Flow Rate × Plasma Power	-14.119	0.034	-2.9
Carrier Gas Flow Rate × Observation Height	11.744	0.061	2.41
Carrier Gas Flow Rate × Pump Speed	1.081	0.833	0.22
Plasma Power × Observation Height	-11.285	0.068	-2.32
Plasma Power × Pump Speed	-0.701	0.891	-0.14
Observation Height × Pump Speed	0.789	0.878	0.16

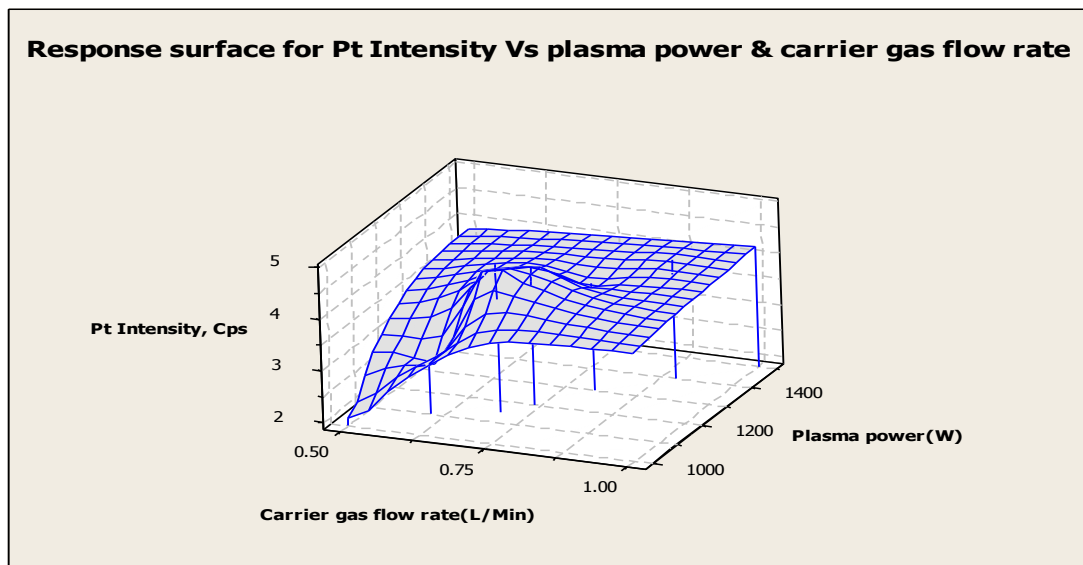
**Figure 1.** Pareto chart of the standardized effects (= t statistics).

the associated response surface is shown in Figure 3b. It is apparent from Figure 3a that the region of highest platinum intensity ( $\approx 4.5$  Cps) now lies more or less at the centre of the contour map. This is confirmed in the response surface Figure 3b which now shows a sharp peak at the optimized values of carrier gas flow rate and plasma power of 0.70 L/min and 1400 W, respectively. The optimum nebulizer gas flow rate of 0.70 L/min established for the determination of Pt using the 265.945 nm line lies close to the lower limit of 0.5 recommended by Boumans (1979), Skoog et al. (1998) and Hou and Jones (2000). The nebulizer gas flow rate directly

controls the sample transit time through the plasma, affecting the level of atomization, excitation and ionization (Todoli et al., 2002; Vanhaecke and Dams, 1993). Lower nebulizer gas flow rates increase the residence time of the analyte in the plasma, giving it longer time to acquire the energy for lines which require high excitation energies. This makes the plasma processes like atomization, ionization and excitation to be more efficient thus producing high signal intensities. The Pt 265.945 nm is a high energy line, which requires lower nebulizer gas flow rates for maximum atomization, ionization and excitation. The 0.70 L/min flow rate obtained in this



(a)



(b)

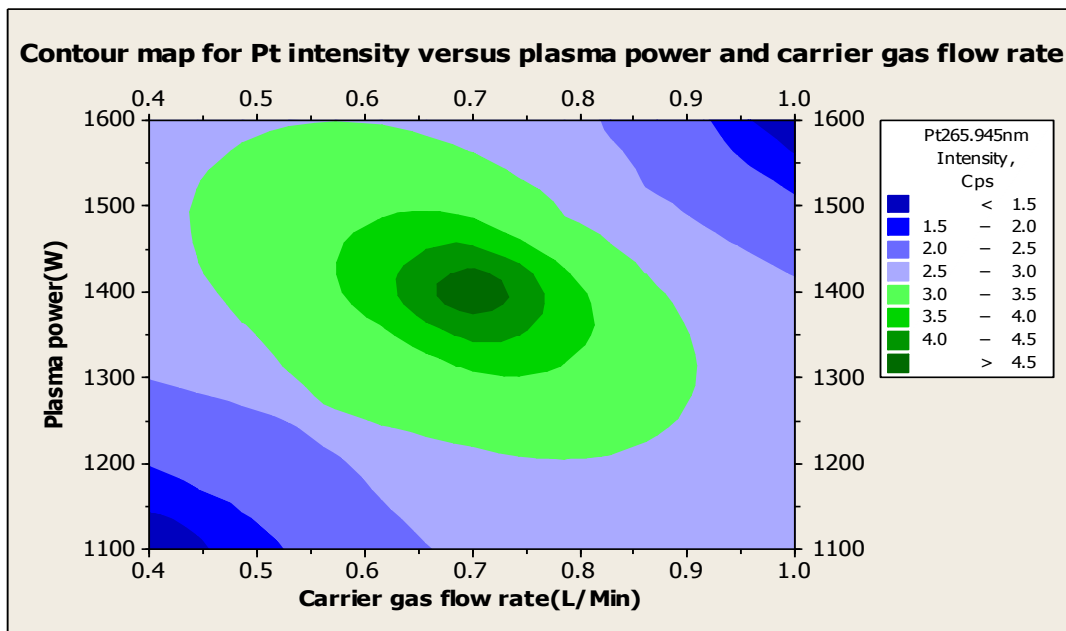
**Figure 2.** Preliminary contour map (a) and response surface (b) for platinum intensity as a function of carrier gas flow rate and plasma power. (Pump speed fixed at 30 revolutions per minute, Plasma observation height fixed at 10 mm above the load coil).

optimization exercise is consistent with this requirement.

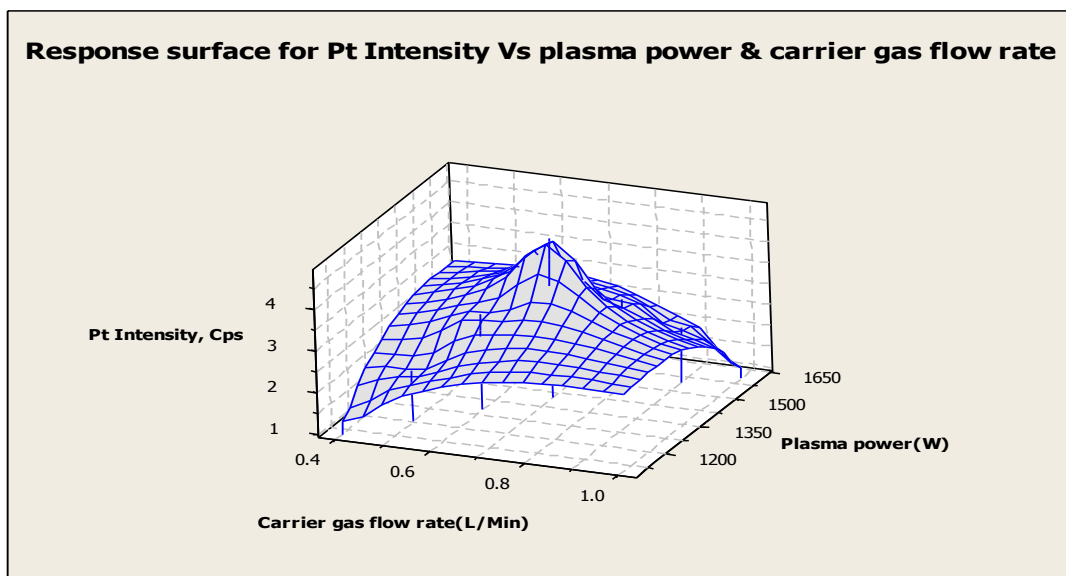
The optimum RF power (1400 W) obtained for the determination of Pt using the 265.945 nm line, lies close to the upper limit of 1.5 kW recommended by Boumans (1979) and Hou and Jones (2000). Higher plasma power conditions generate high temperature plasma conditions, and as earlier discussed for carrier gas flow rate, the Pt

265.945 nm line is a high energy line that requires high plasma power for efficient atomization, ionization and excitation.

As preliminary optimization experiments had shown that pump speed and plasma observation height had no significant effects on the intensity of the Pt 265.945 line, they were fixed at 30 revolutions per minute and 10 mm



(a)



(b)

**Figure 3.** Final contour map (a) and response surface (b) for Pt265.945 nm line intensity as a function of RF power and carrier gas flow rate. (Pump speed fixed at 30 revolutions per minute, Plasma observation height fixed at 10 mm above the load coil).

above the load coil, respectively, being the conditions used in the preliminary optimization experiments. The observation height of 10 mm above the load coil used lies at the lower limit of 10 mm recommended by Boumans(1979) and and below the lower limit of 15 mm

recommended by Skoog et al. (1998).

The plasma central channel can be divided into three different zones; a pre-heating zone (PHZ) with temperatures around 10,000 K; initial radiation zone (IRZ), with temperatures of 8000 K in which the atomic

**Table 4.** Preliminary design matrix for contour map and response surface of Pt intensity.<sup>a</sup>

Experiment No.	A <sup>b</sup>	B <sup>c</sup>	Intensity <sup>d</sup> (Cps, coded units)
1	0.50	1000	2.027±0.063
2	0.60	1100	2.805±0.012
3	0.70	1150	4.719±0.024
4	0.74	1200	4.524±0.028
5	0.80	1300	3.940±0.085
6	0.90	1400	4.166±0.049
7	1.00	1500	4.180±0.076

<sup>a</sup>Pump speed fixed at 30 revolutions per minute, and plasma observation height fixed at 10 mm above the load coil; <sup>b</sup>A = Carrier gas flow rate (L/Min); <sup>c</sup>B = RF power (W); <sup>d</sup>Mean (n = 3)

**Table 5.** Design matrix used in final optimization to construct contour map and response surface for the Pt 265.945 nm line intensity.<sup>a</sup>

Experiment	A <sup>b</sup>	B <sup>c</sup>	Intensity <sup>d</sup> (coded units)
1	0.40	1100	1.245±0.044
2	0.50	1200	2.142±0.051
3	0.60	1300	3.200±0.068
4	0.70	1400	4.719±0.073
5	0.80	1500	2.985±0.016
6	0.90	1550	2.242±0.097
7	1.00	1600	1.189±0.019

<sup>a</sup>Pump speed fixed at 30 revolutions per minute, and plasma observation height fixed at 10 mm above the load coil. <sup>b</sup>A = Carrier gas flow rate (L/Min); <sup>c</sup>B = RF power (W); <sup>d</sup>Mean (n = 3).

emission begins to be observed; and the normal analytical zone (NAZ), with temperatures of 6500 K which corresponds to the zone at which emission is produced mainly from ions (about 10 to 20 mm above the tip of the IRZ) (Hirokawa, 1980; Boss and Fredeen, 1999; Todoli et al., 2002). The IRZ extends upward to one or two mm above the load coil. The 10 mm above the load coil observation height is thus on the lower end of the NAZ. Here we expect the plasma temperature to still be high enough for efficient atomization, ionization and excitation, even for high energy lines such as the Pt 265.945 nm line.

The pump speed of 30 revolutions per minute employed in this work was chosen to lie at the centre of the range of 15 to 45 cps used in the factorial design matrix. The pump speed affects the volume of the aerosol and the efficiency of nebulization. If the sample delivery rate is too high, this may lead to the formation of large droplets in the spray chamber, resulting in an increase in the background level. The preliminary factorial design experiments showed that the pump speed had no significant effect on the Pt 265.945 nm line intensity at this level.

### Validation of the optimized ICP-OES instrumental parameters

Good agreement was obtained (0.443±0.032 µg/g (p = 0.05, n = 10) versus 0.46 µg/g) and (23.54±0.97 µg/g (p = 0.05, n = 10) versus 23.860 µg/g) when the optimized ICP-OES instrumental parameters were applied for the analysis of Certified Reference Standards AMIS 0132 and AMIS 0164 for low and high grade platinum, respectively. The Dixon Q - Test for outliers at the 95% confidence level (n = 10) showed that there were no outliers in both data sets, while the paired T-Test for means at 95% confidence level and 9 degrees of freedom confirmed that there are no significant differences between the mean of the observed platinum values and the certified values for both CRMs. The calibration curve obtained was highly linear (R<sup>2</sup> = 0.9998). The limit of detection (LOD) was calculated to be 0.035 µg/g Pt. Detection limits of 0.01 µg mL<sup>-1</sup> were reported previously for the ICP-OES determination of Pt in Pb-FA buttons by Sun et al. (2004). Although spectral and non-spectral interference effects were not evaluated in the present work, no spectral interferences from other

target elements Pd and Rh, as well as non-target elements Pb, Fe, Al and Ni, were observed previously when Pt determinations were made at the 214.423 and 265.945 nm Pt(II) emission lines (Compernelle et al., 2011).

## Application to real samples

### Determination of Pt in PGM floatation concentrates

The optimized method was applied for the determination of Pt in 3 batches of PGM floatation concentrates subjected to the same treatment employed in preparation of the PMG ore concentrate solution as earlier described. Ten samples were collected randomly from each of the three batches of PGM floatation concentrates. The results obtained were  $37.69 \pm 0.09$ ,  $37.82 \pm 0.08$  and  $37.9 \pm 0.1 \mu\text{g g}^{-1}$  ( $p = 0.05$ ,  $n = 10$ ), respectively for the three batches, showing that Pt in PMG floatation concentrates can be determined with extremely high precision (0.21 to 0.24% RSD) using the optimized ICP-OES parameters.

## Conclusion

From the foregoing discussion, it can be concluded that the critical parameters in the optimization of the ICP-OES determination of Pt using the 265.945 nm line are the carrier gas flow rate and plasma power. The optimum values for these parameter were found to be 0.70 L/min and 1400 W, respectively when optimization is carried out using the 2-Level 4-Factor full factorial experimental design in conjunction with contour maps and response surface methodology.

## CONFLICTS OF INTEREST


The authors have not declared any conflict of interest

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The background of the slide is a photograph of a stone archway in a forest. The archway is made of grey and reddish-brown stones. The ground is covered with fallen autumn leaves in shades of red, orange, and brown. There are green plants and trees in the background.

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