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Evaluation of Uncertainty in the Energy Dispersive X-Ray Fluorescence Determination of Platinum in Alumina

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Evaluation of uncertainty in the Energy Dispersive X-Ray Fluorescence (EDXRF) Spectromteric determination of platinum in alumina catalyst is discussed. Pressed pellets of platinum standard and catalyst sample were prepared by using microcrystalline cellulose powder as the base material. A linear calibration of the X-ray fluorescence spectrometer was obtained in the range 0.1 - 3 mg g^{-1} of platinum using pellets of matrix matched synthetic standards. The calibration function was obtained through bivariate least square fitting, in conjunction with weighted regression of the residuals. The EDXRF results were compared with those obtained by instrumental neutron activation analysis and inductively coupled plasma optical emission spectrometry. Analysis of variance established the statistical parity of the results obtained by all the three techniques. A comprehensive evaluation of the various sources of uncertainty in the complete measurement process was carried out using the bottom-up approach. The main source of uncertainty was identified as the calibration of the EDXRF spectrometer, in which the major share was attributed to the intercept of the calibration function.

Keywords: EDXRF, platinum, alumina, bivariate least squares fitting, uncertainty, bottom-up approach, analysis of variance

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Introduction

Platinum group metals (PGMs) are widely used as catalysts in chemical processes [1]. Most of the conventional oxidation catalysts are based on either platinum (Pt) or palladium (Pd) on alumina support. Platinum based catalytic converters are used in automobiles [2]. Platinum-alumina catalysts have been reported for the decomposition of sulphuric acid [3].

The efficiency and cost of the catalyst depends upon the concentration of PGM and hence their accurate and precise determination is essential. Several solution sampling techniques viz. atomic absorption spectrometry (AAS), graphite furnace atomic absorption spectrometry (GF-AAS) [4, 5], inductively coupled plasma - mass spectrometry (ICPMS) [6] and spectrophotometry [7] have been reported for the determination of Pt in catalysts. These determinations put forward the inevitability of a validated analytical method with established precision, as dictated by economic considerations [8]. Appropriate analytical techniques are chosen, depending on the concentration of Pt as well as the nature of the substrate material used in these catalysts [9]. A method that requires the sample to be dissolved, encounters certain difficulties during sample processing [10]. The dissolution of alumina is difficult, due to its refractory nature. Hence, wet chemical routes are tedious and are not generally recommended for the analysis of alumina. In order to achieve complete dissolution of alumina matrix, microwave assisted aqua-regia dissolution can be adopted [11]. However, this process is tedious and time consuming. Cyanide leaching was reported for the beneficiation of spent hydrogenation catalyst by Shams et al [12]. This process is not practically adoptable since it generates hazardous cyanides as the by-products. Considering these practical difficulties, a purely instrumental method, which does not require sample dissolution, is desirable for the determination of Pt in the refractory alumina matrix. X-ray fluorescence (XRF) [8, 13, 14] and neutron activation analysis (NAA) [10, 15] have been established as very efficient and versatile analytical techniques for the direct analysis of solids. Determination of Pt in analysis by NAA technique has been reported from our laboratory [16]. Even though NAA is non-destructive, availability of nuclear reactor is indispensable for performing the analysis.

Energy dispersive X-ray fluorescence (EDXRF) spectrometry is a common solid sampling technique and is extensively used in industrial laboratories. The advantages of this technique include non-destructive nature, simplicity, minimum sample preparation and fast operation. The chemical composition of the matrix severely affects the measured analyte line intensity during XRF measurements and hence matrix matched standards are required for accurate and precise determination. Thus, EDXRF technique can be used when either matrix matched standard is available commercially or it is possible to prepare it synthetically. X-ray fluorescence methods have been reported for determination of Pt in alumina catalyst using commercial and synthetic standards [8, 13]. High Energy-Polarized beam-EDXRF technique was used for determination of Pt, Pd and Rh in cordierite [14].

The performance of a particular method is evaluated in terms of precision as well as trueness of the results. Recently, emphasis on the measurement precision has greatly increased, as it is one of the most important parameters for assessing the quality of results. Precision of an analytical measurement is best represented in terms of measurement uncertainty, encompassing all probable sources alongwith their contribution, during the complete measurement process [17]. For evaluating the uncertainty associated with the complete measurement process, either the bottom-up or the top-bottom approach can be adopted [18].

Uncertainty evaluation during EDXRF measurements have been reported in literature [19, 20]. The present report describes the evaluation of uncertainty during the EDXRF determination of Pt in alumina catalysts, adopting the bottom-up approach. Matrix-matched synthetic standards were used for calibration. Calibration, being one of the fundamental steps during the calculation of the concentration of analyte, is discussed in detail in the present manuscript. Generally, ordinary least square (OLS) fitting is adopted to arrive at the calibration function, which takes into account the error in the dependent variable only. However, there may be non-negligible errors associated with the preparation of calibration standards [21]. In such cases, bivariate least squares (BLS) fitting can be used, which takes into account the errors in both axes [22]. In the present work, the calibration function was derived, considering uncertainties in both the axes, alongwith heteroscedasticity in the instrumental response (i.e., unequal variances) at each point. Sources of uncertainty in the complete measurement process were identified and the combined uncertainty was evaluated systematically. In the absence of suitable reference material, EDXRF results were validated using NAA and Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) techniques.

Experimental

Regents and Chemicals

All reagents were of analytical reagent grade. Solutions were prepared using de-ionized water (Conductivity = 0.05 µS cm^{-1}). Microcrystalline cellulose powder, (particle size ≤ 75 µm, Merck), and high purity alumina (Norton, USA) were used as the base materials for preparing pellets of calibration standards. Pt solution (1 mg mL^{-1}) from Merck was used as stock-standard for Pt.

EDXRF determination of platinum in alumina

Preparation of Pt-standard pellets for calibration High purity alumina (~ 0.2 g) was mixed thoroughly with micro-crystalline cellulose powder (~ 0.8 g) in the ratio 1:4 (w/w) in a Teflon dish. A known volume of Pt-standard solution was added to the above mixture (~ 1 g), dried under I.R. lamp and mixed thoroughly. Pellets were prepared using an automatic KBr press (AP-15, Technosearch Instruments), at a pressure of 10 tons. All pellets had identical dimensions (diameter = 2.5 cm and thickness = 0.2 cm).

Alumina sample pellets Pt-alumina catalyst samples (fresh and used) were obtained from Chemistry Division, Bhabha Atomic Research Centre, Mumbai. The used catalyst was the one employed for decomposition of sulphuric acid at 800 ^{o}C for prolonged period. Both fresh and used alumina samples were crushed, sieved through 200-mesh and used for analysis. The ratio of alumina catalyst sample to cellulose was also maintained at 1:4 (w/w). Pellets having dimensions identical to that of the standard pellets, were made in triplicate for each sample.

EDXRF Instrumentation and Measurement Procedure

XRF measurements were made using an EDXRF spectrometer (EX-3600 M, Jordan Valley, Israel; Resolution: 145 eV for the 5.9 keV Mn KL_{III} X-rays) and the experimental conditions are summarized in Table 1. Six replicate measurements were made on each standard pellet and the X-ray fluorescence intensities of Pt were obtained. Calibration was done by plotting the intensity of fluorescent X-rays against the concentration of Pt in the standards. Each sample pellet was measured twice (both sides). Analytical lines of Pt were the characteristic $L_{III}M_V$ (9.439 keV) and $L_{II}M_{IV}$ (11.073 keV) [23].

NAA determination of platinum in alumina

Determination of Pt was carried out by NAA using two different nuclear reactors, independently.

Neutron irradiations for 1 min duration were carried out in the Pneumatic Carrier Facility (PCF) of Dhruva reactor, Trombay, Mumbai, India [24] in a neutron flux was ~ 10^{13} cm^{-2} s^{-1}. About 1 - 2 mg of the samples, Pt-standards (evaporated on filter paper) and alumina blank were heat-sealed in polyethylene separately and irradiated in a polypropylene capsule. Most of the matrix activity (^{28}Al: $t_{1/2}$ = 2.24 min) decayed within 15 min after irradiation. The gamma ray measurements were carried out, after 1 d cooling, using high purity germanium detector (45 % relative efficiency, Resolution: 1.9 keV at 1332 keV, Canberra) coupled to 8k-channel analyzer. Characteristic gamma ray of ^{199}Au ($t_{1/2}$ = 3.13 d; 158.4 keV), the daughter of ^{199}Pt ($t_{1/2}$ = 30.8 min) was used for the quantification of Pt. Relative method of NAA was used for calculating the concentration.

The graphite reflector position of Advanced Heavy Water Reactor Critical Facility (AHWR CF) reactor, Trombay, Mumbai, India [25] was also utilized for neutron irradiation. About 500 mg of the alumina samples, along with Pt standards and blanks were heat-sealed separately in polyethylene and irradiated for 4 h in a neutron flux of ~ 10^8 $cm^{-2}s^{-1}$. The pellets used for EDXRF measurements were also heat-sealed in polyethylene and irradiated along with the above samples. Gamma ray measurements were carried out as described above.

ICPOES determination of Pt in alumina

Microwave-assisted digestion procedure was adopted for bringing alumina sample into solution. Approximately 0.2 g of accurately weighed sample was dissolved in 10 mL of aqua-regia in microwave sample digestion system (ETHOS One, Milestone). The procedure was repeated twice, with fresh aqua regia each time, for complete dissolution of the sample. The solutions were evaporated nearly to dryness and made up to 50 mL, maintaining 5 % acidity with respect to HNO_3.

These solutions were analyzed using inductively coupled plasma optical emission spectrometer (JY 2000, Jobin YVON, Horiba Scientific). Calibration was carried out using Pt-standard solutions (5, 10, 20 mg L^{-1}), which were prepared by dilution of the Pt-stock solution (1 mg mL^{-1}, Merck). Characteristic emission lines of Pt (214.120, 224.552 and 265.945 nm) were measured and concentration of Pt in the samples was obtained using the calibration plot.

Results and discussion

A non-destructive EDXRF methodology was used, which obviates the need for sample dissolution, the most time consuming step. Pressed pellet and fusion bead are the methods for sample preparation in XRF measurements. Samples prepared by fusion bead method have better homogeneity. However, there is a risk of loss / contamination from platinum crucible which is used in fusion bead method. Hence, pressed pellet method was adopted for sample preparation, during the present work. Microcrystalline cellulose powder was used as the base material for preparing all pressed pellets, owing to the ease of preparation, mechanical strength and X-ray absorption/fluorescence characteristics. The optimized ratio between alumina and cellulose, during the present determinations was 1:4 (w/w). Alumina as well as cellulose, being comprised of low-Z elements, is practically transparent to the excitation source (mass absorption coefficient, μ = 0.96 for 20.22 keV) and characteristic X-ray of Pt (μ = 6.55 for 9.44 keV). Sensitivity for determination of Pt is high due to high mass absorption coefficient of Pt for the source X-rays (μ = 75.74 for 20.22 keV) [26] and the fluorescence yield (ω_L = 0.35) [23].

EDXRF spectrum of a typical fresh Pt-alumina catalyst (Fig. 1) shows that both the characteristic lines of Pt (i.e., $L_{III}M_V$ and $L_{II}M_{IV}$) have similar intensities and can be utilized for measurements.

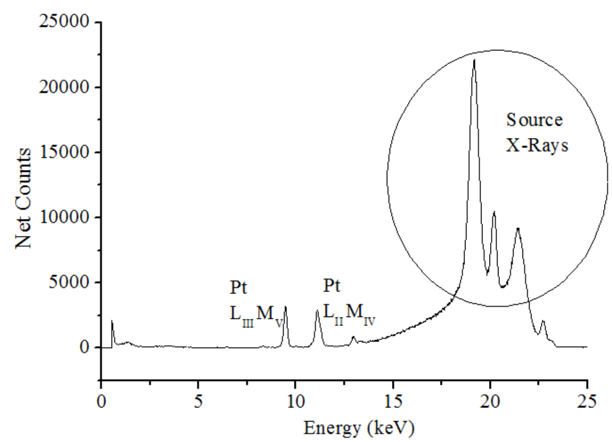

Fig. 1: EDXRF spectrum for fresh Pt-alumina sample

Calibration using platinum standard pellets

The quantification methodology in EDXRF analysis is usually different for thin, intermediate thickness and infinitely thick samples [19, 27]. All the pressed pellets (both sample and standard) used during this work could be categorized as intermediate thickness samples, since they satisfy the condition: $m_{thin} < m < m_{thick}$, where m is the mass per unit area of the sample and m_{thin} and m_{thick} are given by equations 1 and 2 [19, 27].

$$m_{thin} \le \frac{0.1}{[\mu(E_0)\csc\theta_1 + \mu(E_i)\csc\theta_2]} \quad (1)$$

$$m_{thick} \ge \frac{4.61}{[\mu(E_0)\csc\theta_1 + \mu(E_i)\csc\theta_2]} \quad (2)$$

where μ is the mass absorption coefficient, E_0 is the energy of source X-rays, E_i is the energy of characteristic X-rays, θ_1 and θ_2 are the incident and take-off angles respectively. The energy of source X-rays was considered as ~ 20 keV for the sample thickness calculations, based on the characteristics of X-ray tube [28] used in the spectrometer. Table 2 summarizes the corresponding values of the parameters in equations 1 and 2. A number of approaches have been developed for quantification in XRF analysis of intermediate-thickness samples [27, 29]. In the present work, the calibration-standards approach was adopted due to the superior accuracy [29].

Calibration is the primary step in most of the instrumental analytical techniques [21]. When the random uncertainties associated with each of the dependent variable viz. the net counts, are not constant (designated as heteroscedasticity), the fitting should be done using the weighted regression method, instead of the most common ordinary regression.

Since in the present calibration procedure, both the axes contribute to the final uncertainty, Bivariate Least Squares (BLS) fitting is the most appropriate regression method. Among all the regression techniques which consider uncertainty in both axes, the BLS technique more readily provides the regression coefficients as well as their associated variances [22]. The BLS method calculates the coefficients of the straight line by taking into account the individual heteroscedastic random uncertainties in both the axes. Herein, the sum of the weighted residuals, S, is minimized as shown in equation 3.

$$S = \sum_{j=1}^{n}\left(\frac{N_j - \hat{N}_j}{w_j}\right) \qquad (3)$$

where n is the number of experimental data pairs, $\hat{N}_j$ is the fitted value of N_j (net counts) and w_j is the weighting factor that corresponds to the variance of the j^{th} residual, represented by equation 4.

$$w_j = s_{e_j}^{\,2} = s_{N_j}^{\,2} + b_1^2 s_{C_j}^{\,2} - 2b_1 \operatorname{cov}(C_j, N_j) \qquad (4)$$

where s_{ej}^2 is the variance for the j^{th} residual, s_{Cj}^2 and s_{Nj}^2 are the experimental variances for the concentration and net counts for Pt in the standard pellets, b_1 is the slope of the calibration function, $\operatorname{cov}(C_j, N_j)$ is the covariance between the two variables, which is normally set at zero. Root mean square of the residuals (RMS), in the linear least squares fitting was calculated using equation 5.

$$RMS = \sqrt{\frac{\sum_{j=1}^{n}\left(\frac{N_j - \hat{N}_j}{w_j}\right)^2}{n}} \qquad (5)$$

where n is the number of data points in the linear least squares fitting for calibration. In the present work, five standards were used for calibration. The values of N_j, $\hat{N}_j$ and w_j for the calibration standard pellets are listed in Table 3. The slope, b_1 = 31633; intercept, b_0 = 1707 and the RMS = 3.94 were obtained from the calibration.

Least squares fitting could be applied to get the calibration function, since the variance in the instrument response (viz. the net counts for Pt) for each data point was much larger than the product of the slope and the variance in the concentration of Pt [21]. The Pearson's correlation coefficient, (r = 0.9997) between the instrument response and the concentration of Pt in the pellets was greater than 0.995, further confirming the linear relationship between the two [30]. Fig. 2 depicts the linear calibration obtained for the Pt-standard pellets during EDXRF analysis. The linear calibration range of the instrument was 0.1 - 3 mg g^{-1} for Pt in the standard pellets.

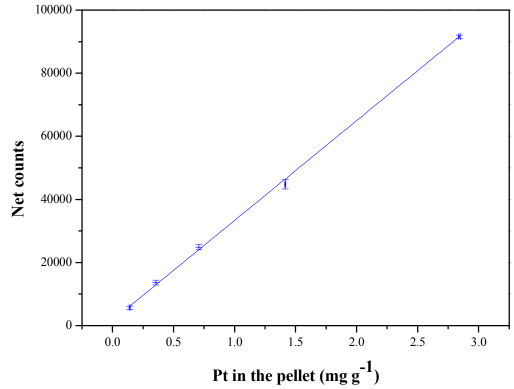

Fig. 2: Calibration plot for Pt using EDXRF spectrometer

The reliability of results depends on the extent of correlation between the measured X-ray fluorescence intensities of the samples and calibration standards, in EDXRF spectrometry. Errors are likely to arise when the matrices of sample and standard are not identical. During the present measurement, matrix effect was overcome by maintaining identical matrices (1: 4 w/w of alumina and cellulose) for all the samples and standards. The characteristic X-ray intensities in the samples were used for calculating the Pt concentrations by means of equation 6, viz. the calibration equation.

$$C_{Pt,sam} = \frac{N_{sam} - b_0 - RMS}{b_1} \times \frac{m_{pellet}}{m_{sam\ in\ pellet}} \qquad (6)$$

where $C_{Pt,sam}$ is the concentration of Pt in the sample (mg g^{-1}), N_{sam} is the net counts for Pt in the sample, b_0 and b_1 are the intercept and slope of the calibration respectively, RMS is the root mean square of the residuals obtained on least squares fitting, m_{pellet} is the weight of the sample pellet, $m_{sam\ in\ pellet}$ is the weight of sample (i.e., alumina) in the pellet.

The advantage of using calibration method during EDXRF includes short analysis time (~ 15 - 20 min for each sample; after the calibration has been performed) compared with the other methods, which require the tedious sample dissolution step. The limits of detection (LOD) and quantitation (LOD) were 2 and 7 mg kg^{-1} respectively, calculated as per the guidelines given by IUPAC and ACS [31, 32]. However, LOD and LOQ, calculated using the method of error propagation [33] were 10 and 35 mg kg^{-1} respectively. The method of error propagation considers the uncertainty in all the parameters and hence provides the practical limit of detection. The calibration standards, once prepared, can serve the purpose for all future determinations, provided that they are preserved appropriately.

Comparison of EDXRF results with NAA and ICPOES

The results obtained by EDXRF, NAA and ICPOES techniques are given in Table 4. All the results are rounded off according to the rules described in ASTM E29-13 [34, 35]. The measurement repeatability of each method is given as one standard deviation of n numbers of replicate samples. Analysis of variance (ANOVA) was carried out to compare the results obtained by the three techniques. Calculated F values for fresh ($F_{3,12,cal.}$ = 1.79) and used ($F_{3,14,cal.}$ = 0.86) catalyst samples were less than the critical F values ($F_{3,12,crit.}$ = 3.49 and $F_{3,14,crit.}$ = 3.34) [36] respectively, at 95 % confidence level. Thus, statistically, there is no difference, at 95 % confidence level, among the mean values obtained by EDXRF, NAA (both PCF and CF) and ICPOES techniques.

Comparison of Pt concentration in fresh and used catalyst samples using ANOVA ($F_{7,26,cal.} = 0.97$ and $F_{7,26,crit.} = 2.39$) [36] established that the fresh and used samples are statistically indistinguishable.

Evaluation of uncertainty in the EDXRF determination of Platinum in alumina

Analytical results should always be expressed alongwith the corresponding uncertainty and the evaluation of uncertainty is an essential part of quantitative analysis [17]. Top-down and bottom-up are the two methods adopted for arriving at the combined uncertainty [18]. In the bottom-up approach of uncertainty evaluation, the analytical method is divided into sequential steps, various uncertainty sources are identified, quantified and combined appropriately [37]. Basic equations of measurement uncertainty for linear calibrations in chemical analysis are presented and comprehensively discussed in the Eurachem-CITAC Guide, Appendix E [17]. We have adopted the bottom-up approach of uncertainty evaluation.

Sources of uncertainty In the present EDXRF determinations, three main sources of uncertainties could be identified viz. (i) preparation of samples / standards (ii) counting statistics and (iii) calibration of the XRF spectrometer. Instability of the EDXRF spectrometer was assumed to be negligible [19], since the samples and standards were counted under identical conditions. Matrix effects could be surmounted by preparing the standard pellets of Pt in alumina-cellulose mixtures, whose mass ratio was maintained identical to that of sample pellets. The relevant uncertainty sources contributing to the final combined uncertainty for complete measurement process are depicted in the cause and effect diagram (Fig. 3).

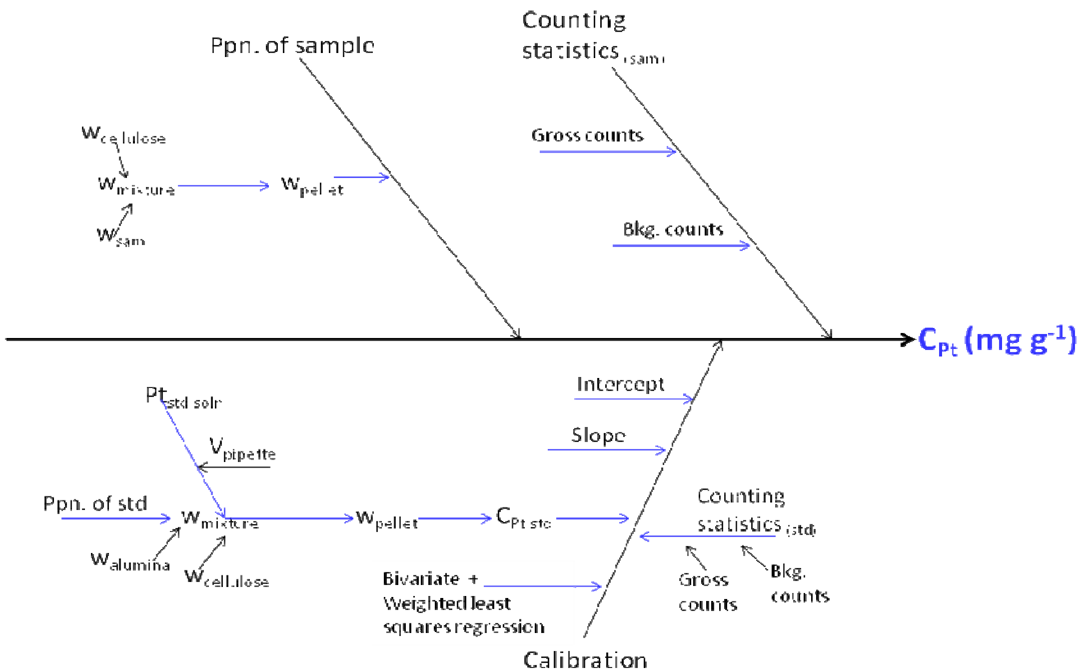

Fig. 3 Cause and effect diagram: EDXRF determination of Pt

Uncertainty in the preparation of samples/standards arises mainly during weighing (i.e., the least count of the weighing balance, in the calculations) and pipetting of the Pt- standard solution. Contribution from counting statistics was considered in the usual manner as shown in equation 7 [38],

$$u_{net}^2 = u_{gross}^2 + u_{background}^2 \qquad (7)$$

The net counts were derived from the relation,

$$(\text{net counts}) = (\text{gross counts}) - (\text{background counts}) \qquad (8)$$

The uncertainty associated with counting is given by [38]

$$u_{count} = \sqrt{\text{counts}} \qquad (9)$$

Uncertainty contribution from the slope and intercept of the calibration plot were obtained on curve fitting, using origin software, through the standard procedure. The uncertainty from the linear least squares calibration was obtained using the RMS of the residuals [19] as shown in equation 10.

$$RMS_{uncertainty} = \frac{RMS}{b_1}\sqrt{\frac{n}{(n-2)}} \qquad (10)$$

where b_1 is the slope of the calibration curve, n is the number of data pairs used for the instrument calibration, (n - 2) is the number of degrees of freedom for the calibration function and RMS value was calculated using equation 5. $RMS_{uncertainty}$ was found to be 1.6 x10^{-3}.

Contribution of uncertainty from each source was evaluated, converted to the standard uncertainty and combined to get the final uncertainty in the determination of Pt using EDXRF method. By applying the law of uncertainty propagation, the combined standard uncertainty was obtained as 0.090 mg g^{-1}. Uncertainty contribution from each source for fresh sample is illustrated in Fig. 4. It is evident from Fig. 4 that the calibration is the major contributor to uncertainty, which is manifested in terms of slope and intercept of the fitted line. The fractional contribution from counting statistics was found to be 0.032 mg g^{-1}. The expanded uncertainty, calculated from the combined standard uncertainty using the coverage factor, k = 2 [17] was 0.18 mg g^{-1}.

It was concluded that the sample was homogeneous at the sample size of 0.2 g as the standard deviation for the six replicate samples (s = 0.060 mg g^{-1}) was less than the combined standard uncertainty (u = 0.090 mg g^{-1}) [39].

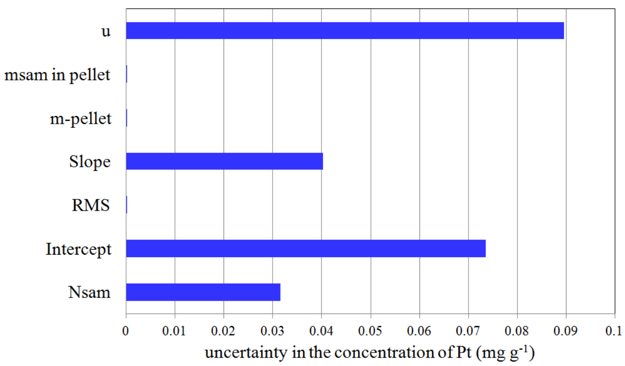

Fig. 4 Uncertainty contribution from each source in the EDXRF determination of Pt

Conclusion

Systematic evaluation of uncertainty during the EDXRF determination of Pt in alumina was carried out by way of the bottom-up approach. The calibration constants, viz. the slope and intercept were found to bear the major share of uncertainty. By taking careful precautions in the above step, the overall uncertainty in the quantification procedure can be controlled to a large extent. Calibration function of the EDXRF spectrometer was derived through bivariate least square fitting, in combination with weighted regression of the residuals. ANOVA revealed the statistical equivalence of the results obtained by EDXRF, NAA and ICPOES techniques. EDXRF is a fast, precise and accurate technique and hence can used for quality control during the determination of Pt in alumina.

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Table 1: Optimized parameters for EDXRF determination of Pt

Parameter	Value
Voltage (kV)	35
Current (µA)	160
Filter	Rh
Counting time (s)	200
Acquisition medium	Air

Table 2: Basis for categorization of the present pellets as intermediate thickness samples for EDXRF measurements

Composition of the pellet	Effective µ(E_0) [for E_0 = 20.22 keV]#1	Effective µ(E_{Pt}) [for E_{Pt} = 9.44 keV] #2	Ψ1 = Ψ2 = (radians)	m, mass per unit area of the pellets (g cm^{-2})	m_{thin} (using equation 2) (g cm^{-2})	m_{thick} (using equation 3) (g cm^{-2})
Alumina (Pt) + Cellulose	1.032	6.662	0.78	0.204	0.009	0.424

#1: Energy of the source X-rays was assumed = 20.22 keV, as reported in the literature [28].
#2: Energy of the characteristic X-ray $L_{III}M_V$ for Pt = 9.44 keV [23].

Table 3: Parameters used for least squares fitting in EDXRF calibration

Pt in the standard pellets (mg g^{-1})	N_j	$\hat{N}_j$	w_j
0.1411	5728	5286	33425
0.3547	13638	14348	29914
0.7077	24846	25595	37853
1.4153	44768	43056	73328
2.8414	91592	91592	181711

Table 4: Results for EDXRF, NAA and ICPOES analyses of Pt-alumina samples

	Concentration of Pt (mg g^{-1})$^{\#}$			
	EDXRF	**NAA(PCF)**	**NAA (CF)**	**ICPOES**
Fresh	4.71 ± 0.060 (n = 6)	4.9 ± 0.27 (n = 3)	4.62 ± 0.17 (n = 3)	4.77 ± 0.18 (n = 4)
Used	4.63 ± 0.070 (n = 6)	4.7 ± 0.24 (n = 4)	4.7 ± 0.38 (n = 4)	4.50 ± 0.18 (n = 4)

#Values are rounded off as per the ASTM E 29-13 guidelines [34].

Evaluation of Uncertainty in the Energy Dispersive X-Ray Fluorescence Determination of Platinum in Alumina

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Uncertainty, the most important characteristic of an analytical result, has been evaluated using bottom-up approach during EDXRF determination of Pt in alumina. Calibration function of the EDXRF spectrometer was derived through bivariate least square fitting, in combination with weighted regression of the residuals.

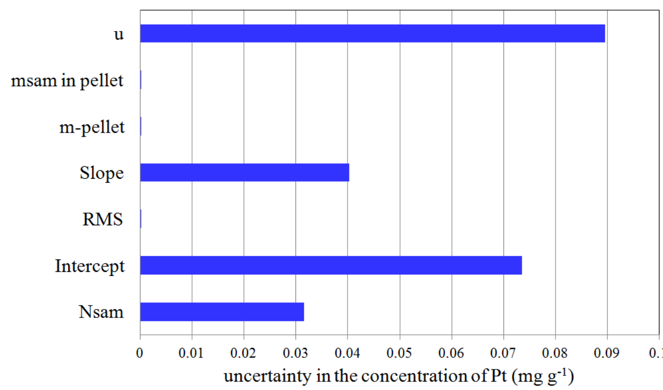

Fig: Contribution of various parameters towards combined uncertainty during determination of Platinum in Alumina