

# Validation and performance assessment of a WD-XRF fused bead method for accurate quantification of scandium in nickel laterite deposits

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**Abstract.** This study focuses on the validation and performance assessment of the Wavelength Dispersive X-ray Fluorescence (WD-XRF) fused bead method for scandium quantification in nickel laterite ores. The calibration of the instrument showed a high correlation ( $R^2 = 0.9962$ ), with a Limit of Detection (LoD) of 20 ppm and a precision of 1.28% RSD. Accuracy was confirmed with good recoveries ranging from 98.05% to 101.46%. The relative expanded uncertainty was calculated at 5.89%. Method and instrumental reproducibility were confirmed by quality control (QC) Chart monitoring using certified reference materials (CRMs) and by relative error (RE) values below 10% for duplicate pulverized samples. The mode of scandium concentration in the samples was found to be 140 ppm. Overall, these results demonstrate that the WD-XRF fused bead method shows good validation performance, with excellent linearity, precision, accuracy, reproducibility, low expanded uncertainty and a low LoD for scandium quantification in complex matrices such as nickel laterite ores.

## 1 Introduction

Nickel laterite ores are one of the most imperative global incomes not only for nickel (Ni), iron (Fe) and cobalt (Co) [1], but also for critical rare elements such as scandium (Sc) [2], which has growing technological importance in advanced alloys, fuel cells, radionuclides for diagnostic imaging optical and aerospace applications [3]. The strategic value of Sc has prompted significant research into its exploration, mining [3], extraction [4], and reliable quantification from complex lateritic matrices [5]. Accurate determination of scandium assay in nickel laterite is crucial to support both resource evaluation and mineral downstream processing strategies [6].

WD-XRF spectroscopy has long been applied as a fast and non-destructive analytical method for minor, major, and trace elements in ores, with extensive applications in nickel ore characterization [5,7,8]. However, the accuracy and precision of XRF strongly depend on sample preparation techniques and matrix effects [9]. Among various methods, the fused bead method has been recognized as a robust preparation technique to minimize mineralogical heterogeneity and surface irregularities that often compromise pressed powder analysis [7].

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In the face of the increasing use of WD-XRF fused bead techniques in geological analysis [5,8], comprehensive method validation for scandium determination in nickel laterite is still limited. Previous researches have primarily focused on the geochemical characterization of laterite deposits containing scandium [2] or on extraction and recovery processes [4,6], but systematic validation studies addressing accuracy, precision, linearity, detection limits, and robustness in WD-XRF fused bead analysis remain scarce.

Accordingly, we validate and performance assessment of the WD-XRF fused bead method for scandium quantification in nickel laterite deposits through systematic evaluation of analytical parameters, namely linearity, precision, accuracy, LoD, limit of quantification (LoQ), and expanded measurement uncertainty and therefore confirming its reliability for scandium quantification in laterite deposits and related industrial applications.

## 2 Experimental

### 2.1 Materials

All reagents were of analytical grade and high purity. Fusion flux (12:22) and ammonium iodide tablets were supplied by XRF Scientific. CRMs (OREAS 180, 197 – 198; scandium mineralised laterite) were used for calibration, precision, accuracy validation, and monitor instrumental performance. In addition, representative nickel laterite ores from Obi Island, Indonesia, with scandium target values determined by a KAN-accredited laboratory, were included as calibration materials to provide traceable benchmarks for method validation.

### 2.2 Sampel preparation

Nickel laterite samples were prepared by weighing 0.5 g of sample and mixing it with 8 g of fusion flux (12:22). The mixture was fused using a Modutemp electric fusion machine (XRF Scientific, Australian) to produce homogeneous fused beads. During ignition, an ammonium iodide tablet was added as a release agent to reduce surface tension and ensure smooth bead formation.

### 2.3 Instrument condition

The analysis of scandium in nickel laterite samples was conducted using a WD-XRF Zetium spectrometer (Malvern Panalytical, The Netherlands) equipped with the SuperQ software application for data acquisition and processing. The instrument was operated under optimized analytical settings to ensure reliable detection of scandium in lateritic matrices.

The spectrometer was operated in WD-G measurement mode, employing a flow detector without tube filter, and measurements were carried out under a vacuum atmosphere to reduce absorption effects. A LiF200 crystal was used as the analysing crystal, with a 150  $\mu\text{m}$  collimator and a 37 mm mask to optimize resolution and signal quality. The X-ray tube was operated at 60 kV and 55 mA, providing sufficient excitation for scandium and other trace elements. The pulse height distribution (PHD) was set in the range of 26–71 to improve the signal-to-noise ratio. For scandium quantification, the measurement focused on the Sc  $K\alpha_{1,2}$  fluorescence line of 4.087 keV [5], which offers high sensitivity and specificity for Sc detection.

## 3 Result and Discussion

### 3.1 Method Validation

#### 3.1.1 WD-XRF instrument calibration

The calibration of the WD-XRF instrument was established using a series of CRMs OREAS 180, 197, 198, and 199, which represent scandium-mineralized laterite ores. These CRMs provided a wide compositional range suitable for constructing reliable calibration curves. The calibration was further supported by local nickel laterite samples from Obi Island with scandium values determined independently by a KAN-accredited laboratory, ensuring traceability and method validation.

The calibration curve for scandium showed excellent linearity across the concentration range from 10 to 591 ppm (figure 1), with a coefficient of determination ( $R^2$ ) of 0.9962 above 0.9950, indicating a strong correlation between measured intensities and certified values. A linear correlation between XRF Intensity and scandium assay was established, described by the calibration equation of  $Y = 0.00057[\text{Sc assay}] - 0.00273$ . The signal sensitivity for the Sc  $K\alpha_{1,2}$  fluorescence line was determined as  $0.00057 \text{ kcps.ppm}^{-1}$ .

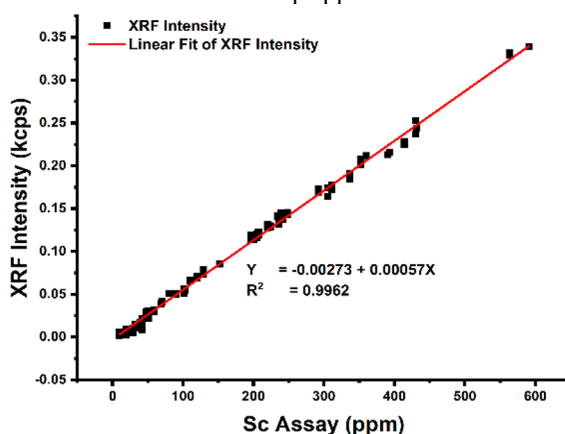


Fig. 1. Linear calibration curve of scandium assay obtained with the WD-XRF fused bead method

#### 3.1.2 Limit of detection and quantification

The Values of LoD and LoQ were evaluated using blank fused bead samples consisting solely of fusion flux, with the results presented in Table 1. The LoD was calculated as 20 ppm based on the mean blank signal of 12 ppm with a standard deviation (SD) of 3 ppm ( $\text{LoD} = \text{mean} + 3\text{SD}$ ), indicating the lowest detectable concentration of scandium above the background signal in the blank sample. The LoQ was found to be 38 ppm using the same dataset ( $\text{LoQ} = \text{mean} + 10\text{SD}$ ), representing the lowest concentration for reliable quantification with acceptable precision.

#### 3.1.3 Precision and accuracy method

The precision and accuracy of the WD-XRF fused bead method for scandium determination were evaluated using repeated measurements of CRM OREAS 197 under identical analytical conditions were showed in Tabel 2. Ten replicate analyses were performed, yielding scandium concentrations ranging from 201 to 208 ppm with an average value of 204 ppm, compared to the certified reference value of 205 ppm. The precision assessment showed a SD of 2.60 ppm and a

relative standard deviation (RSD) of 1.28%. Since this value is greatly lower than the Horwitz coefficient of variation (CV Horwitz) criterion ( $0.67 \times CV$  Horwitz of 4.81%) [10,11], the method demonstrates excellent repeatability.

The calculated percent recovery was 99.46%, which falls well within the acceptable range of 90–107% as specified by the Association of Official Analytical Chemists (AOAC) Criteria [10], thereby confirming the accuracy of the method. The good recovery, indicating strong agreement between the measured and certified values. These results demonstrate that the WD-XRF fused bead method provides accurate quantification of scandium in lateritic matrices and meets internationally recognized validation requirements [5,10,12].

**Table 1.** LoD and LoQ for scandium measurement using WD-XRF fused bead method

Replicates	XRF Intensity (kcps)	Sc Assay (ppm)
Blank - 1	0.001	8
Blank - 2	0.004	12
Blank - 3	0.001	8
Blank - 4	0.003	10
Blank - 5	0.005	14
Blank - 6	0.003	10
Blank - 7	0.004	13
Blank - 8	0.004	13
Blank - 9	0.006	16
Blank - 10	0.004	13
Average (X)		12
SD		3
LoD = X + 3SD		20
LoQ = X + 10SD		38

**Table 2.** Precision and accuracy of replicate analyses of CRM OREAS 197 for Sc

Sampel Replicates	XRF Intensity (kcps)	Sc Assay (ppm)	%Recovery
OREAS 197 - 1	0.116	204	99.51%
OREAS 197 - 2	0.116	205	100.00%
OREAS 197 - 3	0.118	208	101.46%
OREAS 197 - 4	0.115	203	99.02%
OREAS 197 - 5	0.114	201	98.05%
OREAS 197 - 6	0.114	201	98.05%
OREAS 197 - 7	0.118	208	101.46%
OREAS 197 - 8	0.114	202	98.54%
OREAS 197 - 9	0.114	202	98.54%
OREAS 197 - 10	0.116	205	100.00%
Average (X)		204	99.46%
Certified reference value of Sc		205	-
SD		2.60	-
%RSD		1.28	-
0.67 CV Horwitz		4.81	-

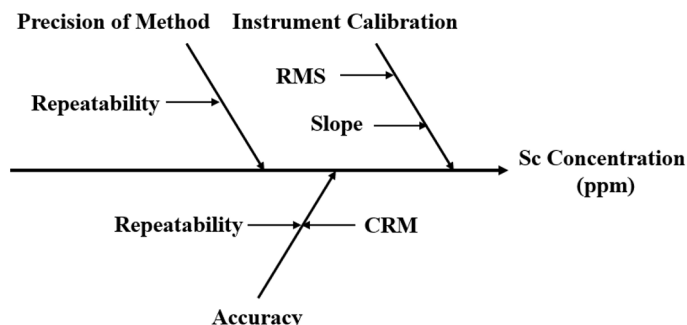
### 3.1.4 Estimation of uncertainty

The measurement uncertainty of scandium was evaluated based on both instrumental calibration and methodological factors related to precision and accuracy. An Ishikawa (cause-and-effect) diagram was employed to identify and visualize the major sources of uncertainty and their relationships to the final scandium concentration, as illustrated in Figure 2. This approach enables a structured assessment of how individual uncertainty components propagate and interact within the overall analytical process [13].

Calibration uncertainty arises from the regression parameters of the calibration curve, including the slope and residual dispersion between measured and predicted intensities [13]. In this study, the calibration curve yielded a root mean square (RMS) of 0.00407 kcps and slope of 0.00057 kcps.ppm<sup>-1</sup>, indicating low dispersion between measured and predicted intensities. The absolute uncertainty of the calibration curve ( $\mu_{\text{curve}}$ ) was estimated at 15 ppm for a scandium concentration of 591 ppm, corresponding to a relative calibration uncertainty ( $\mu_{\text{curve}}/X$ ) of 2.53%. This component represents the dominant contribution associated with WD-XRF instrumental response and calibration model fitting for scandium quantification in nickel laterite matrices.

Precision uncertainty refers repeatability of the method and is associated with random variations in repeated measurements under identical conditions. It was evaluated by calculating the SD values divided by square root of the number of replicates [13]. The precision uncertainty ( $\mu_{\text{precision}}$ ) was calculated as 1 ppm for the average Sc measurement of 204 ppm from OREAS 197, corresponding to a relative precision uncertainty ( $\mu_{\text{precision}}/X$ ) of 0.40%.

Accuracy uncertainty accounts for systematic bias and was evaluated using CRMs data [13]. The accuracy uncertainty ( $\mu_{\text{accuracy}}$ ) was calculated by dividing the uncertainty of the CRM measurement of 1 ppm by the CRM target value was 3 ppm from a SD of 6 ppm, with coverage factor ( $k=2$ ). When normalized to the CRM recovery (%R = 99.46%), this resulted in an accuracy uncertainty of 1.58%, corresponding to a relative accuracy uncertainty ( $\mu_{\text{accuracy}}/\%R$ ) of 1.60%.



**Fig. 2.** Ishikawa diagram of uncertainty measurement for scandium quantification

The combined uncertainty is the overall uncertainty of the measurement, considering the contributions from calibration uncertainty, precision uncertainty, and accuracy uncertainty, as shown in Tabel 3. The combined relative uncertainty ( $Uc/Sc$ ) (1) is calculated as follows:

$$\frac{Uc}{Sc} = \sqrt{\left(\frac{\mu_{\text{curve}}}{X}\right)^2 + \left(\frac{\mu_{\text{precision}}}{X}\right)^2 + \left(\frac{\mu_{\text{accuracy}}}{\%R}\right)^2} \quad (1)$$

**Table 3.** The combined uncertainty of scandium measurement, considering calibration, precision, and accuracy uncertainties.

Source of uncertainty	unit	x	$\mu_x$	$\mu_x/X$	$(\mu_x/X)^2$
Instrument calibration	ppm	591	15	0.0253	0.00002
Precision of Method	ppm	204	1	0.0040	0.00026
Accuracy	%	99.46	1.58	0.0160	0.00064
The combined uncertainty	ppm	204	6	0.0302	0.00091

The expanded uncertainty (U) is calculated by multiplying the combined uncertainty (Uc) by a coverage factor ( $k=2$ ) to achieve a 95% confidence interval. For the scandium measurement, with a concentration of 204 ppm, the combined uncertainty was calculated as 6 ppm. Therefore, the expanded uncertainty is 12 ppm, and the relative expanded uncertainty is 5.89%. This results in a valid scandium concentration range from 191 ppm to 217 ppm, ensuring that the measurement is reliable and providing a high degree of confidence in the results.

### 3.2 Monitor Instrumental Performance

To monitor instrumental performance over a period of 7 days, CRMs OREAS 180 (Figure 3a), OREAS 197 (Figure 3b), OREAS 198 (Figure 3c), and OREAS 199 (Figure 3d), was regularly tested for scandium quantification using WD-XRF fused bead method. These CRMs provided known concentrations of scandium, which were used to validate the instrument's performance and ensure the accuracy of the results. Each CRM's scandium measurement was compared against its certified value, and the results were plotted on the QC charts. These charts allowed for real-time tracking of the instrument's performance by comparing measured values against certified values.

The QC Chart displayed the Upper Control Limit (UCL), Upper Warning Limit (UWL), Target, Lower Warning Limit (LWL), and Lower Control Limit (LCL), providing a comprehensive view of the instrument's accuracy and precision [14]. UCL and LCL indicate the threshold beyond which the measurements are considered out of control, signalling potential instrument malfunction or calibration drift. UWL and LWL are set closer to the target, allowing early detection of trends that may eventually lead to measurements exceeding the control limits. The target represents the ideal or expected value, which in this case is the certified value for scandium concentration in the CRM.

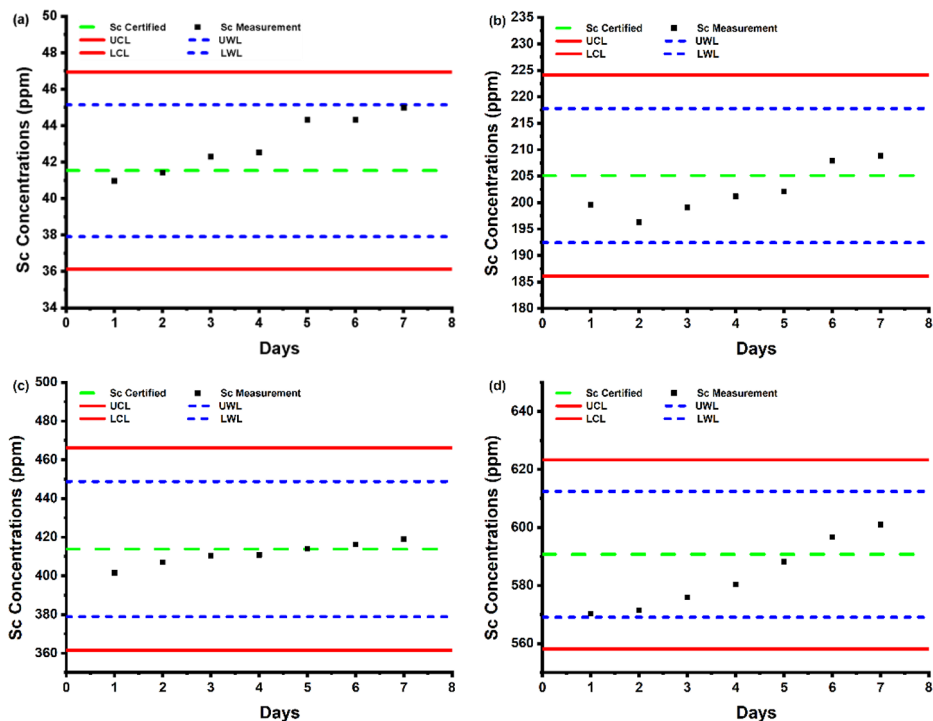


Fig. 3. QC Charts for scandium detection of CRMs OREAS 180 (a), 197 (b), 198 (c), and 199 (d).

Over the 7-day period, the results showed that the instrument's measurements remained within the acceptable range, consistently staying between the UWL and LWL, and close to the Target. The UCL and LCL were not exceeded, indicating stable instrument performance with minimal bias. This monitoring approach helped detect any anomalies early, ensuring reliable data for scandium quantification in nickel laterite ores.

### 3.3 Sample Measurement

The scandium content in nickel laterite ore was measured twice (original and duplicate) using pulverized samples on different days over a period of several months to evaluate method consistency and long-term reproducibility. A strong correlation of 0.9994 was attained from 335 test data points (Figure 4a), indicating excellent reproducibility and reliability for scandium quantification in lateritic ores. To further assess method accuracy and sample homogeneity, the RE between duplicate and original measurements were calculated and visualized in the Cumulative Frequency Chart (Figure 4b). Based on commonly applied homogeneity criteria, RE values of < 2% indicate excellent homogeneity, 2–5% good homogeneity, 5–10% acceptable homogeneity, and > 10% rejected homogeneity [15]. The results show that the majority of RE values remains below 10%, demonstrating that the samples exhibit acceptable to excellent homogeneity and that the method consistently produces good reproducibility. Additionally, the scandium concentration distribution was evaluated using a histogram, as shown in Figure 4c. The histogram revealed that the mode of the scandium concentration was approximately 140 ppm, with the peak clearly visible in the distribution, indicating that the majority of the samples fall within this concentration range.

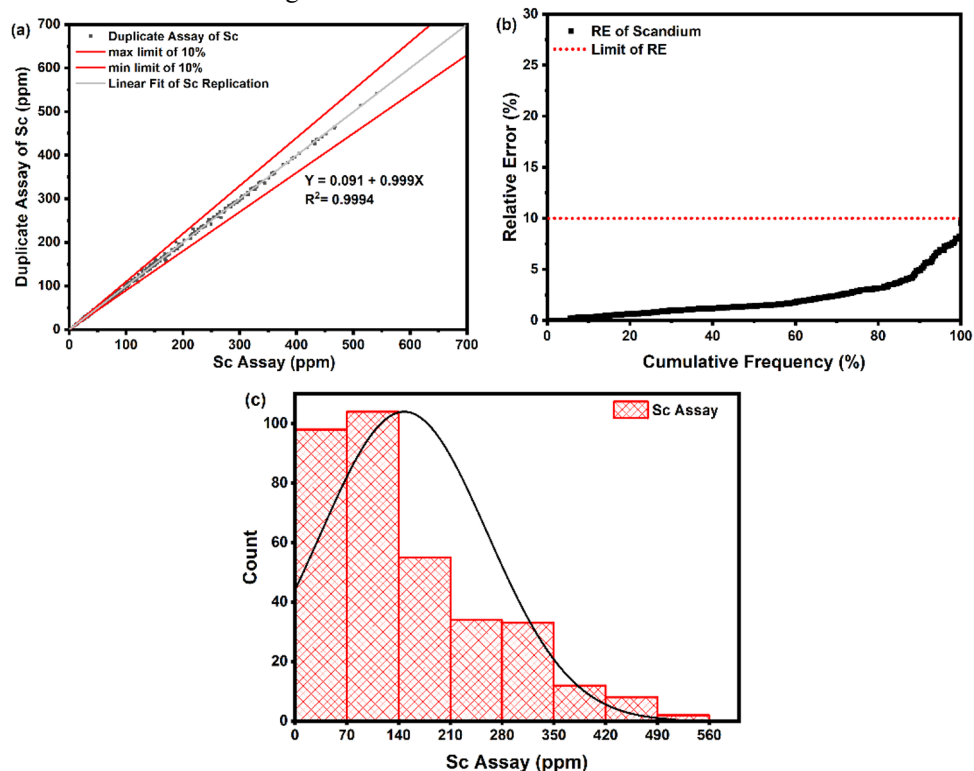


Fig. 4. Sc quantification: (a) Duplicate correlation, (b) RE frequency, and (c) Sc assay histogram.

### 4 Conclusion

The instrument calibration exhibited a strong correlation of 0.9962, exceeding the 0.9950 threshold, with a LoD of 20 ppm and excellent precision (1.28% RSD), well below the 2/3 CV Horwitz value of 4.81%. Accuracy reached from 98.05% to 101.46%, within the tolerable 90–107% range. The relative expanded uncertainty was 5.89%, indicating reliable quantitative performance of the method. Monitoring instrumental performance using the QC Chart showed

scandium measurements consistently within the UWL and LWL for all CRMs. Nickel ore tests exhibited good reproducibility, with RE below 10% and a Sc mode of 140 ppm obtained from 335 data points, demonstrating acceptable to excellent sample homogeneity for scandium measurements.

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## References

1. T. H. Gultom, IOP Conference Series: Earth and Environmental Science **1422**, (2024)
2. J. M. Supit, A. Idrus, H. T. B. M. Petrus, I. G. Sukadana, dan F. Pratiwi, Indonesian Journal on Geoscience **12**, 175 (2025)
3. A. Maulana, K. Sanematsu, dan M. Sakakibara, Indonesian Journal on Geoscience **3**, 139 (2016)
4. Y. Chen, H. Wu, B. Xu, dan W. Zhang, RSC Advances **15**, 2250 (2025)
5. M. Guitouni, Analytical Science and Technology **37**, 315 (2024)
6. A. D. Salman, T. Juzsakova, S. Mohsen, T. A. Abdullah, P.-C. Le, V. Sebestyen, B. Sluser, dan I. Cretescu, Materials **15**, 2376 (2022)
7. S.-I. Yamasaki, H. Yamagishi, dan N. Tsuchiya, Sustainable Environment **9**, (2023)
8. E. Marguí, I. Queralt, dan E. de Almeida, Chemosphere **303**, 135006 (2022)
9. A. Rohiman dan A. S. Arifin, Indonesian Journal of Physics **31**, 24 (2020)
10. G. W. Latimer, editor, in *Official Methods of Analysis of AOAC INTERNATIONAL*, 22nd ed. (Oxford University Press, New York, 2023)
11. J. M. Syukur, A. R. Sanjaya, I. Rahmawati, dan M. Ridwan, Environmental and Materials **3**, 1 (2025)
12. American Standard Testing and Material, *Guide for Elemental Analysis by Wavelength Dispersive X-Ray Fluorescence Spectrometry* (ASTM International, West Conshohocken, PA, 2022)
13. S. Supriyono, M. Fitrillah, dan A. P. Putra, Jurnal Kimia Sains dan Aplikasi **23**, 177 (2020)
14. A. Alaeddini, M. Ghazanfari, dan M. Amin, Information Sciences **179**, 1769 (2009)
15. A. M. Idris, BMC Chemistry **13**, 1 (2019)