

Accuracy and Precision of Energy Dispersive X-Ray Fluorescence (EDXRF) Analysis of Trace and Major Elements in Rock Standard Reference Materials Using Fine Powder

Jean Faustin Sabouang*, Jean Félix Beyala Ateba, Cebastien Joel Guembou Shouop, Josue Maya, Cedric Tayou Kamkumo, Lawan Loubou Mohamadou, Augustin Simo

National Radiation Protection Agency, Yaounde, Cameroon

Email: *sabouang2000@yahoo.fr

How to cite this paper: Sabouang, J. F., Ateba, J. F. B., Shouop, C. J. G., Maya, J., Kamkumo, C. T., Mohamadou, L. L., & Simo, A. (2023). Accuracy and Precision of Energy Dispersive X-Ray Fluorescence (EDXRF) Analysis of Trace and Major Elements in Rock Standard Reference Materials Using Fine Powder. *Journal of Geoscience and Environment Protection*, 11, 83-95.

<https://doi.org/10.4236/gep.2023.116006>

Received: May 23, 2023

Accepted: June 23, 2023

Published: June 26, 2023

Copyright © 2023 by author(s) and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

In this work the performance of a screening analytical method for Energy Dispersive X-Ray Fluorescence (EDXRF) analysis in terms of accuracy and precision was evaluated through analysis of rock standard reference materials. The method allowed the division of elements into four groups taking into account the excitation energies and measurement conditions of the sample. Two standard reference materials were used and 15 sample replicates were prepared and analyzed, then statistics were applied to assess the precision and accuracy of analytical results. The obtained results show that major compounds or elements (SiO_2 , P_2O_5 , K_2O , CaO , Fe_2O_3 , Ti) can be determined in fine powder sample with a deviation lower than 15%, and a relative standard deviation in the range (1 - 10)%. The deviation was found to be lower than 5% for major compounds such as K_2O , and CaO , which suggest that the EDXRF is accurate in evaluating major elemental concentrations in rock samples. It was also found that the method seems to be more accurate and precise for major elements than for trace element investigation. This screening analytical method can be used for routine analysis with acceptable results, even though the method should be optimized to increase its precision and accuracy.

Keywords

ED-XRF, Screening Method, Rock Material, Accuracy, Precision

1. Introduction

Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometry is a useful analyt-

ical technique for elemental analysis of a wide range of materials. A wide variety of sample types (solids, liquids and even gases) can be analyzed by X-ray spectrometry. It should be noted that the use of XRF techniques for analysis of gases is not widespread but it has been demonstrated by Knöchel et al. (Injuk & Van Grieken, 1993). Many authors have reported interesting results on the method to evaluate the elemental content. Saini et al. have published analytical results of 15 trace elements in soil and sediment samples, using EDXRF method (Saini et al., 2002). Prior to this report, he detailed the analysis of major oxides in rocks using EDXRF (Saini et al., 2000). In that study, pressed powder pellets were prepared for analysis of rock reference materials to investigate accuracy and precision of analytical results using EDXRF. Analytical results were obtained with reasonably good accuracy (DEV of $\pm 21\%$) and precision (RSD in the range 0% - 17%), depending upon the elemental abundance, analyzed matrix and analytical conditions.

Mannee et al. (Croffie et al., 2020) conducted a comparison study of different sample preparation methods for the analysis of a standard soil reference material using loose powder, pressed powder pellets and pressed pellets with a wax binder by calculating the recoveries of 13 elements. This study shows that pressed powder pellet with binder is more suitable for multi-elemental analysis of different soils compared to loose powder and pressed powder pellet method (Croffie et al., 2020). For XRF analysis of minerals, samples are generally prepared in the form of glass disc or pressed pellets depending on the objective of the elements investigated (trace or major elements) (Duchesne & Bologne, 2009; Guembou et al., 2019). It should be noted that the preparation of pressed pellets may take more time than using directly powder material for XRF analysis, no matter the fact that pellets are durable and could be used for repetitive measurements over a longer period of time. If powder specimen is used for XRF analysis, the powder must be ground finely enough in order to have homogeneous sample (Injuk & Van Grieken, 1993).

The direct elemental composition analysis on powder samples could be viewed by many as an issue as the technique is relatively new compared to other sample types used (glass discs and pressed pellets) and the high risk of equipment contamination due to the ventilation of dust from the powder samples (Kimura & Yamada, 1996; Nakayama & Nakamura, 2005; Orihashi & Hirata, 2003; Xue et al., 2022). It is, therefore, crucial to evaluate the precision and accuracy of the method in comparison to other techniques to leverage or clear up any ambiguity related to this topic (Akbulut et al., 2014; Orihashi & Hirata, 2003). As the method makes it possible to obtain reliable data of the surface composition object non-destructively, its sensitivity and simplicity are competitive with other techniques as the atomic absorption and neutron activation: the investigation on the accuracy and precision is therefore a relevant topic to be addressed (Akbulut et al., 2014; Enzweiler & Webb, 1996; Krishna et al., 2016; Lundblad et al., 2008; Lutz & Pernicka, 1996).

For routine analysis, using samples in the form of powder saves time. In the present work we are focused on the performance in term of accuracy and precision related to analysis of rock materials in the form of fine powder instead of pressed pellets, using EDXRF technique. Precision is defined as the reproducibility of a set of measurements or the extent to which results agree with one another. Precision usually is reported as a standard deviation, which alternatively can be expressed as the percent relative standard deviation (RSD). Accuracy is how close a measurement is to its desired or theoretical value, and usually is reported as a percent error. This work aims to determine precision and accuracy levels of analytical results of rock samples in the form of fine powder, using a screening analytical method based on EDXRF.

2. Materials and Methods

2.1. Sample Preparation

The samples considered in this study are made of rock standard reference materials (NCS DC 71301 and NCS DC 7 3305) which are delivered in fine powder form. Each standard was analyzed once per month during 15 consecutive months. Preparation for analysis consisted to simply fill a sample cup approximately 3/4 full. The sample cup is a finite polyethylene cylinder cover on the top, with the bottom cover with polypropylene film of 4 μm thick. Fifteen samples (designated S1 to S15) made of standard material labelled NCS DC 71301 were prepared monthly for analysis. The same process was done for the standard material labelled NCS DC 7 3305 (designated S'1 to S'15).

2.2. ED-XRF Equipment

The equipment used in this study is an energy dispersive bench-top X-ray fluorescence spectrometer for multi-element analysis. It is well suited to the analysis of elements between sodium and uranium in concentrations from 100% down to ppm levels. The analysis of solids and powdered samples can be done with little or no sample preparation using this equipment. The excitation system is made of an X-ray tube with thick binary Pd/Co alloy anode with air-cooling, max voltage 50 kV, including adaptive excitation system with optimized filters. The adaptive excitation offers different excitation conditions ensuring optimum determination of elements in the range from Na to U. The detector is a state-of-the-art silicon drift detector with large area. The spectral resolution (Full Width at Half Maximum—FWHM) of the detection system is 130 eV for Mn K-alpha (5.9 keV). The method uses 4 different excitation conditions as described in **Table 1**. For the analysis, sample cups of 32 mm diameter are used.

2.3. Method Summary

Radiation from an electrically excited X-ray tube is used to generate characteristic X-ray emissions from elements in a sample. The X-ray tube used for analysis operates at differing voltage and current settings to optimize excitation of spe-

cific elements. Accordingly, elements are divided into four groups with determined exciting conditions for each one. Thus a specific set of primary X-rays excite a corresponding range of elements in a sample. Fluorescent and backscattered X-rays from the sample enter through the detector window and are converted into electric pulses in the detector. For each group of elements considered, a specific filter is used. Each sample is measured four times and the overall measurement time is 600 s. Instrumental conditions for determination of different elements are summarized in **Table 1**.

2.4. Calibration

Concerning Energy Dispersive X-Ray Fluorescence analysis Remya Devi et al. (Remya et al., 2015) write chemical composition of the matrix severely affects the measured analyte line intensity during XRF measurements (Absorption and fluorescence by the matrix) and hence matrix matched standards are required for accurate and precise determination. The concentration of a particular element is calculated from a calibration line obtained by measuring a set of standards with known composition and fitting a least squares regression line through the data. Three calibration procedures are considered for quantification in this work: Mass Attenuation Coefficient (MAC) calibration, Compton peak ratio or normalization method, and Fundamental parameters calibration.

The MAC calibration is done through measurement of a set of standards to obtain a graph showing the Compton intensity or Compton/Rayleigh ratio versus mass attenuation coefficient. The standard samples used for this calibration are (GSR 10, BIR-1a, PM-S, GMO-02, AGV-2, GSR-09, AN-G, GSR-08, GSR-02, UB-N, GSR-04).

For Compton calibration, a set of standards are measured to obtain a graph showing the given element concentration versus the calculated concentration. Offset and slope of the calibration line are determined via regression. The Compton calibration curve is plotted for each element.

Table 1. Instrumental conditions for determination of different elements.

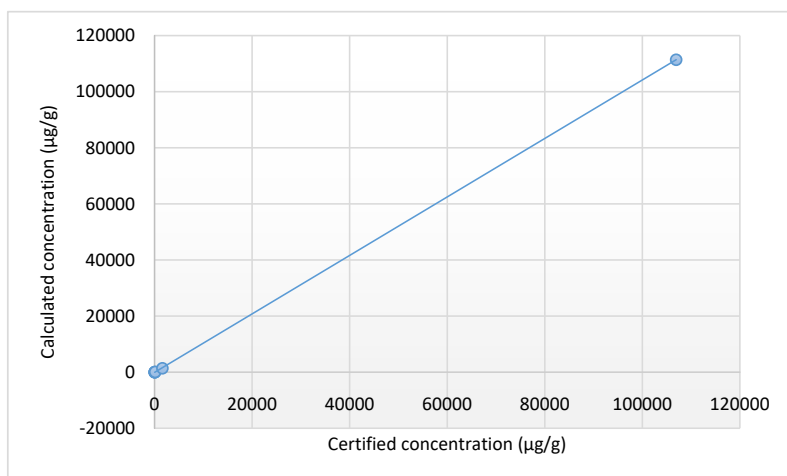
| Elements | Excitation conditions | | Measurement conditions | | |
|--|-----------------------|--------------|------------------------|------------|----------|
| | Voltage (kV) | Current (mA) | Filter | Line | Time (s) |
| Mg, Al, Si, P, S, Cl | 22.5 | 1.777 | none | K α | 150 |
| K, Ca, Ti, V, Cr, Mn | 22.5 | 1.777 | Fe | K α | 150 |
| Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo | 45 | 0.888 | Pd | K α | 150 |
| Hf, Ta, W, Au, Hg, Tl, Pb, Bi, Th, U | | | | La | |
| Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce | 50 | 0.800 | Mo, Ta | K α | 150 |

The fundamental parameters approach to calibration in X-ray fluorescence is based upon the theoretical relationship between measured X-ray (K, L, or M) intensities and the concentrations of elements in a sample. This theoretical relationship is based upon X-ray physics and the measured values of fundamental atomic parameters in the X-ray region of the electromagnetic spectrum. Fundamental parameter calibration graph is plotted for each element by considering K and L X-Ray emission lines. Offset and slope of the calibration line are determined via regression. Linear calibration curves for all elements were accomplished. Depending on the range of concentration of the element to measure, different standards are used for Compton and Fundamental parameter calibrations.

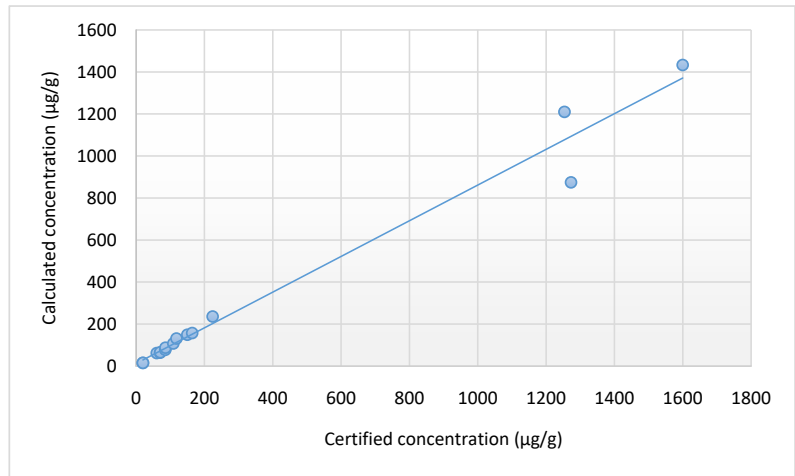
As an example 6 standards (GSR 01, GSR 04, GSR 06, N3 ICP, NOD P1, GBM 309-16) covering a concentration range between 20 $\mu\text{g/g}$ - 106,947 $\mu\text{g/g}$ are used for Compton calibration for the determination of Zn concentration, while 16 (GSR 04, AN-G, PN-S, BIR-1a, GSR 02, UB-N, GSR 09, AGV-2, GMO-02, GSR 10, GSR 03, GSR 08, AC-E, NIST 2782, NIST 2781, NOD P-1) covering a concentration range between 20 $\mu\text{g/g}$ - 1600 $\mu\text{g/g}$ are used for fundamental parameter calibration for determination of the same element. Compton and fundamental calibration graphs obtained for Zn are presented in **Figure 1(a)** and **Figure 1(b)**.

3. Results and Discussion

Results of this study are interpreted in terms of precision and accuracy. The certified reference materials used to check the accuracy of the method are Biotite granite and Olivine basalt referenced respectively as GSR 01 and GSR 03. Results are given as concentrations of chemical element or certain oxides. For each element, the deviation of determined concentration values from certified values is calculated. The results are presented in **Table 2**. The deviation is calculated as given in relation (2) where actual value means the measured value and expected value is the certified value.



(a)



(b)

Figure 1. (a) Compton calibration graph for Zn; (b) Fundamental calibration graph for Zn.

Table 2. Analytical results of standards GSR 01 and GSR 03.

| Element | GSR 03 | | | GSR 01 | | |
|------------------------------------|----------------|---------------|---------|----------------|---------------|---------|
| | Certified Val. | Meas. Val. | Dev (%) | Certified Val. | Meas. Val. | Dev (%) |
| Al ₂ O ₃ (%) | 13.83 ± 0.07 | 13.62 ± 0.01 | 1.5 | 13.40 ± 0.04 | 13.03 ± 0.01 | 2.7 |
| SiO ₂ (%) | 44.64 ± 0.06 | 38.62 ± 0.01 | 13.5 | 72.83 ± 0.06 | 76.28 ± 0.2 | -4.7 |
| P ₂ O ₅ (%) | 0.95 ± 0.01 | 1.023 ± 0.002 | -7.4 | 0.093 ± 0.002 | 0.102 ± 0.001 | -11.1 |
| K ₂ O (%) | 2.32 ± 0.03 | 2.079 ± 0.002 | 10.4 | 5.01 ± 0.03 | 5.197 ± 0.002 | -3.7 |
| CaO (%) | 8.81 ± 0.01 | 8.010 ± 0.003 | 9.1 | 1.55 ± 0.02 | 1.628 ± 0.001 | -5.0 |
| Fe ₂ O ₃ (%) | 13.40 ± 0.03 | 13.11 ± 0.01 | 2.2 | 2.14 ± 0.02 | 2.258 ± 0.002 | -5.5 |
| MnO (ppm) | 1700.09 | 1505 ± 2 | 11.5 | 598 ± | 502.6 ± 0.7 | 16.0 |
| Ti (ppm) | 14,200 ± 200 | 12,670 ± 10 | 10.8 | 1720 ± 30 | 1531 ± 2 | 11.0 |
| V (ppm) | 167 ± 5 | 162.5 ± 2.4 | 2.7 | 24 ± 1 | 25.45 ± 0.82 | -6.0 |
| Zn (ppm) | 150 ± 4 | 150 ± 1 | 0.0 | 28 ± 1 | 29.6 ± 0.4 | -5.7 |
| Ga (ppm) | 24.8 ± 0.6 | 24.05 ± 0.45 | 3.0 | 19 ± 1 | 21.20 ± 0.33 | -11.6 |
| Rb (ppm) | 37 ± 2 | 40.76 ± 0.31 | -10.2 | 466 ± 10 | 509.7 ± 0.6 | -9.4 |
| Sr (ppm) | 1100 ± 30 | 1272 ± 1 | -15.6 | 106 ± 3 | 122.2 ± 0.3 | -15.3 |
| Y (ppm) | 22 ± 1 | 25.05 ± 0.28 | -13.9 | 62 ± 2 | 72.27 ± 0.39 | -16.6 |
| Zr (ppm) | 277 ± 10 | 319.8 ± 0.8 | -15.5 | 167 ± 5 | 192.7 ± 0.4 | -15.4 |
| Nb (ppm) | 68 ± 4 | 79.51 ± 0.42 | -16.9 | 40.0 ± 1.4 | 42.24 ± 0.28 | -5.6 |
| Mo (ppm) | 2.6 ± 0.1 | 2.45 ± 0.51 | 5.7 | 3.5 ± 0.1 | 2.80 ± 0.35 | 19.9 |
| Sn (ppm) | 2.0 ± 0.3 | 1.73 ± 0.89 | 13.5 | 12.5 ± 1.0 | 14.87 ± 0.85 | -19.0 |
| La (ppm) | 56 ± 2 | 41 ± 6 | 26.2 | 54 ± 2 | 68.7 ± 6.5 | -27.3 |
| Hf (ppm) | 6.5 ± 0.4 | 4.99 ± 0.88 | 23.2 | 6.3 ± 0.5 | 8.96 ± 0.77 | -42.2 |
| Ta (ppm) | 4.3 ± 0.4 | 4.3 ± 1.5 | -0.3 | 7.2 ± 0.4 | 7.37 ± 0.96 | -2.4 |
| Th (ppm) | 6.0 ± 0.5 | 6.89 ± 0.54 | -14.9 | 54.0 ± 1.3 | 60.22 ± 0.41 | -11.5 |
| U (ppm) | 1.4 ± 0.2 | 1.1 ± 0.0 | 21.4 | 18.8 ± 1.0 | 25 ± 1 | -33.2 |

Results in **Table 2** show that trace elements (Mn, V, Zn, Ga, Rb, Sr, Y, Zr, Nb, Sn, Ta, Th) can be analyzed with accuracy in terms of deviation of $\pm 20\%$, while for major elements (Al, Si, P, K, Ca, Fe, Ti) the deviation is $\pm 15\%$. A deviation exceeding $\pm 20\%$ is observed for U, Hf, and La elements. The method seems to be more accurate for determination of major elements compared to trace elements.

Before calculating the precision and accuracy of implemented method for analysis of samples considered for this study, a statistical test based on Student's *t* distribution is done on measurements to find outliers. For that purpose, the mean and standard deviation of a set of results are calculated, then a factor (*t* factor) is used to determine the minimum and maximum value of interval for a desired confidence level. The values outside the confidence interval may be considered as outliers. The confidence level used for this calculation is 95% ($P = 0.05$) and *t* values are given by Fisher. The analytical results of samples from NCS standards together with the 95% confidence interval are presented in **Table 3** and **Table 4**. It can be observed from these tables that very few results can be considered as outliers at $P = 0.05$. Those results are not rejected considering that they are not observed in the same sample. The precision of measurement was evaluated through determination of relative standard deviation calculated as follows.

Table 3. Analysis results of NCS DC 71301 (Compounds from Al_2O_3 to Fe_2O_3 in % while all the remaining in ppm).

| Elt | S1 | S2 | S3 | S4 | S5 | S6 | S7 | S8 | S9 | S10 | S11 | S12 | S13 | S14 | S15 | \bar{x} . | SD | 95% conf. interval | |
|-------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------------|-------|-------------------------|--------|
| | | | | | | | | | | | | | | | | | | Min | Max |
| | | | | | | | | | | | | | | | | | | Al_2O_3 | 24.79 |
| SiO_2 | 63.33 | 63.58 | 63.38 | 63.36 | 62.82 | 62.96 | 63.08 | 63.7 | 63.67 | 63.79 | 62.95 | 63.17 | 63.59 | 63.77 | 64.02 | 63.41 | 0.36 | 62.64 | 64.18 |
| P_2O_5 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| K_2O | 7.714 | 7.716 | 7.785 | 7.883 | 8.137 | 7.927 | 7.721 | 7.405 | 7.687 | 7.524 | 8.042 | 7.856 | 7.766 | 7.771 | 7.419 | 7.76 | 0.20 | 7.33 | 8.19 |
| CaO | 1.446 | 1.433 | 1.47 | 1.484 | 1.537 | 1.516 | 1.47 | 1.407 | 1.469 | 1.452 | 1.536 | 1.532 | 1.496 | 1.507 | 1.435 | 1.48 | 0.04 | 1.39 | 1.57 |
| Fe_2O_3 | 6.686 | 6.634 | 6.744 | 6.927 | 7.004 | 7.156 | 6.912 | 6.432 | 6.702 | 6.512 | 7.071 | 6.903 | 6.339 | 6.81 | 6.538 | 6.76 | 0.24 | 6.25 | 7.27 |
| MnO | 1014 | 1015 | 1045 | 1048 | 1117 | 1089 | 1046 | 1007 | 1049 | 1028 | 1106 | 1090 | 1041 | 1067 | 1009 | 1051.40 | 35.52 | 975.2 | 1127.5 |
| Ti | 2742 | 2717 | 2811 | 2834 | 2955 | 2868 | 2759 | 2704 | 2799 | 2752 | 2968 | 2931 | 2875 | 2865 | 2756 | 2822.40 | 85.78 | 2638.4 | 3006.4 |
| V | 175.9 | 172.5 | 177.2 | 181.7 | 188.6 | 185.1 | 178.6 | 169.1 | 177.7 | 174.4 | 187.5 | 185.8 | 176.9 | 182.9 | 173.5 | 179.16 | 5.86 | 166.59 | 191.73 |
| Zn | 100.4 | 99.45 | 101.3 | 105 | 106.6 | 111.3 | 108.1 | 96.55 | 100.5 | 97.3 | 108.3 | 102.8 | 90.13 | 103 | 98.27 | 101.93 | 5.43 | 90.28 | 113.58 |
| Ga | 32.15 | 31.89 | 32.15 | 33.56 | 33.91 | 34.34 | 33.06 | 30.88 | 31.18 | 30.53 | 34.19 | 32.53 | 29.25 | 32.4 | 30.62 | 32.18 | 1.49 | 28.98 | 35.38 |
| Rb | 110.2 | 109.6 | 111.3 | 115.6 | 115.4 | 119.1 | 114.3 | 105.1 | 108.8 | 104.4 | 115.6 | 111.6 | 100.3 | 109.9 | 104.7 | 110.39 | 5.17 | 99.30 | 121.48 |
| Sr | 1058 | 1055 | 1073 | 1118 | 1117 | 1158 | 1109 | 1015 | 1051 | 1010 | 1110 | 1089 | 961 | 1064 | 1016 | 1066.93 | 51.96 | 955.5 | 1178.4 |
| Y | 24.42 | 24.14 | 24.81 | 26.1 | 26.04 | 27.33 | 26.01 | 23.05 | 23.74 | 23.27 | 25.19 | 24.85 | 22.68 | 24.15 | 23.55 | 24.62 | 1.32 | 21.79 | 27.45 |
| Zr | 1246 | 1240 | 1266 | 1315 | 1306 | 1361 | 1300 | 1196 | 1217 | 1174 | 1286 | 1248 | 1087 | 1242 | 1176 | 1244.00 | 68.25 | 1097.6 | 1390.4 |
| Nb | 57.41 | 57.15 | 58.22 | 60.88 | 60.36 | 63.18 | 60.3 | 54.46 | 56.32 | 54.53 | 60.46 | 58.2 | 51.58 | 57.05 | 54.81 | 57.66 | 3.06 | 51.10 | 64.22 |
| Mo | 1.00 | 1.01 | 1.01 | 1.02 | 1.01 | 1.03 | 1.01 | 0.98 | 0.95 | 0.95 | 1.00 | 0.96 | 0.88 | 0.97 | 0.95 | 0.98 | 0.04 | 0.89 | 1.07 |
| Sn | 3.97 | 3.91 | 5.622 | 4.552 | 5.043 | 4.461 | 5.062 | 3.685 | 4.862 | 5.074 | 5.74 | 5.982 | 4.299 | 5.726 | 5.591 | 4.91 | 0.74 | 3.32 | 6.50 |
| Ta | 2.60 | 2.63 | 2.64 | 2.69 | 2.67 | 2.64 | 2.61 | 2.61 | 2.30 | 2.54 | 2.60 | 2.19 | 3.63 | 2.56 | 2.45 | 2.62 | 0.31 | 1.96 | 3.28 |
| Th | 71.48 | 71.39 | 72.43 | 76.65 | 74.66 | 78.8 | 76.11 | 66.47 | 70.03 | 67.62 | 73.83 | 73.16 | 63.43 | 71.68 | 68.02 | 71.72 | 4.13 | 62.86 | 80.58 |

Table 4. Analysis results of NCS DC 73305 (Compounds from Al₂O₃ to Fe₂O₃ in % while all the remaining in ppm).

| Elt | S'1 | S'2 | S'3 | S'4 | S'5 | S'6 | S'7 | S'8 | S'9 | S'10 | S'11 | S'12 | S'13 | S'14 | S'15 | \bar{x} | SD | 95% conf. interval | |
|--------------------------------|-------|-------|-------|-------|-------|-------|-------|--------|-------|-------|-------|-------|-------|-------|-------|-----------|-------|--------------------------------|-------|
| | | | | | | | | | | | | | | | | | | Min | Max |
| | | | | | | | | | | | | | | | | | | Al ₂ O ₃ | 25.4 |
| SiO ₂ | 64.29 | 64 | 64.12 | 64.19 | 64.44 | 64.28 | 64.33 | 64.29 | 65.72 | 65.96 | 65.48 | 65.61 | 65.68 | 65.59 | 63.99 | 64.80 | 0.76 | 63.17 | 66.43 |
| P ₂ O ₅ | 0.13 | 0.13 | 0.11 | 0.13 | 0.12 | 0.15 | 0.16 | 0.13 | 0.16 | 0.14 | 0.14 | 0.14 | 0.15 | 0.16 | 0.13 | 0.14 | 0.02 | 0.10 | 0.18 |
| K ₂ O | 4.23 | 4.42 | 4.37 | 4.48 | 4.41 | 4.31 | 4.41 | 4.35 | 4.23 | 4.12 | 4.06 | 4.10 | 4.07 | 3.94 | 3.84 | 4.22 | 0.19 | 3.81 | 4.63 |
| CaO | 0.58 | 0.61 | 0.60 | 0.61 | 0.62 | 0.60 | 0.62 | 0.59 | 0.58 | 0.57 | 0.56 | 0.56 | 0.56 | 0.56 | 0.52 | 0.58 | 0.03 | 0.52 | 0.64 |
| Fe ₂ O ₃ | 6.57 | 6.95 | 6.88 | 7.16 | 6.89 | 6.78 | 6.97 | 6.83 | 6.14 | 6.02 | 5.80 | 5.89 | 5.90 | 5.68 | 5.39 | 6.39 | 0.58 | 5.15 | 7.63 |
| MnO | 178.6 | 202.5 | 184.2 | 191.7 | 195.4 | 180.6 | 185 | 184.8 | 183.3 | 183.3 | 169.3 | 187.8 | 165.7 | 166.8 | 154.8 | 180.92 | 12.38 | 154.4 | 207.5 |
| Ti | 3758 | 4016 | 3893 | 4033 | 3947 | 3913 | 4013 | 3885 | 3746 | 3681 | 3572 | 3650 | 3634 | 3474 | 3390 | 3774 | 203.8 | 3337 | 4211 |
| V | 82.4 | 88.28 | 87.4 | 89.69 | 87.73 | 83.73 | 87.53 | 85.97 | 81.57 | 80.27 | 78.33 | 78.81 | 78.8 | 74.59 | 74.28 | 82.63 | 5.04 | 71.82 | 93.44 |
| Zn | 44.4 | 47.79 | 47.27 | 48.91 | 44.15 | 45.55 | 44.44 | 45.33 | 39.59 | 36.77 | 34.84 | 37.72 | 32.71 | 36.36 | 30.81 | 41.11 | 5.88 | 28.50 | 53.72 |
| Ga | 20.59 | 22.21 | 21.93 | 22.94 | 21.79 | 20.78 | 21.75 | 20.15 | 17.99 | 17.54 | 16.64 | 16.25 | 16.01 | 15.18 | 13.81 | 19.04 | 2.97 | 12.67 | 25.41 |
| Rb | 160.5 | 174.4 | 171.8 | 181 | 172.6 | 170.6 | 176.8 | 171.3 | 141 | 136.9 | 132.8 | 135.7 | 133.7 | 127.8 | 120.6 | 153.83 | 21.39 | 108.0 | 200.0 |
| Sr | 73.88 | 79.65 | 78.83 | 83.35 | 79.52 | 78.62 | 81.44 | 78.71 | 64.06 | 62.64 | 60.96 | 61.86 | 61.13 | 57.97 | 55.08 | 70.51 | 10.06 | 48.93 | 92.09 |
| Y | 20.8 | 22.18 | 21.99 | 23.25 | 21.99 | 21.89 | 22.58 | 21.88 | 17.66 | 17.44 | 16.81 | 16.74 | 16.84 | 15.9 | 15.04 | 19.53 | 2.91 | 13.29 | 25.77 |
| Zr | 71.84 | 77.21 | 80.29 | 83.29 | 82.34 | 78.98 | 82.99 | 79.81 | 58.79 | 59.59 | 51.17 | 53.49 | 56.79 | 54.41 | 45.07 | 67.74 | 13.78 | 38.18 | 97.30 |
| Nb | 8.82 | 9.58 | 9.34 | 9.85 | 9.60 | 9.39 | 9.80 | 9.55 | 7.20 | 7.13 | 6.75 | 7.15 | 6.97 | 6.91 | 6.19 | 8.28 | 1.37 | 5.34 | 11.22 |
| Mo | 0.59 | 0.61 | 0.61 | 0.62 | 0.61 | 0.61 | 0.62 | 0.61 | 0.51 | 0.50 | 0.48 | 0.50 | 0.49 | 0.48 | 0.46 | 0.55 | 0.06 | 0.42 | 0.68 |
| Sn | 1.291 | 1.071 | 1.084 | 1.078 | 1.087 | 1.373 | 1.81 | 0.9914 | 1.802 | 2.562 | 1.522 | 1.902 | 1.844 | 1.579 | 1.348 | 1.49 | 0.43 | 0.57 | 2.41 |
| Ta | 3.16 | 3.29 | 3.27 | 3.36 | 3.30 | 3.25 | 3.27 | 3.23 | 2.71 | 2.69 | 2.59 | 2.71 | 2.61 | 2.58 | 2.43 | 2.96 | 0.34 | 2.23 | 3.69 |
| Th | 9.67 | 9.94 | 10.03 | 11.44 | 10.38 | 9.93 | 10.19 | 9.68 | 7.7 | 7.684 | 7.76 | 7.77 | 7.82 | 7.21 | 6.91 | 8.94 | 1.42 | 5.89 | 11.99 |

$$RSD = (SD/\bar{X}) \times 100(\%) \quad (1)$$

where SD is the standard deviation and \bar{X} is the mean result.

Results in **Table 5** show that for most elements, RSD values are less than 20%. A RSD > 20% is obtained for one element (Sn) in NCS DC 73305. It should be noted that in environmental geochemical analysis programme, a precision in terms of relative standard deviation of 5% - 25% is acceptable (Saini et al., 2002). Results in **Table 5** show that a good precision is obtained for the majority of elements, nevertheless compared to results reported by Saini et al. (Saini et al., 2002) in the case of analysis of pellets, better precision can be achieved using EDXRF technique.

The accuracy of measurements in terms of percent error or deviation (DEV) is calculated as follows:

$$DEV = ((X_a - X_e)/X_e) \times 100(\%) \quad (2)$$

where: X_a is the actual value.

X_e is the expected value.

Table 5. Precision and accuracy of analytical results for NCS 73 305 and NCS 71 301^a.

| Element | NCS DC 73 305 (shale) | | | | NCS DC 71 301 (syenite) | | | |
|------------------------------------|-----------------------|--------|---------|---------|-------------------------|---------|---------|---------|
| | CV | MV | RSD (%) | DEV (%) | CV | MV | RSD (%) | DEV (%) |
| Al ₂ O ₃ (%) | 18.82 | 25.06 | 0.67 | -33.2 | 17.72 | 24.55 | 0.90 | -38.5 |
| SiO ₂ (%) | 59.23 | 64.80 | 1.17 | -9.4 | 54.48 | 63.41 | 0.57 | -16.4 |
| P ₂ O ₅ (%) | 0.16 | 0.14 | 10.86 | 12.5 | 0.018 | - | - | - |
| K ₂ O (%) | 4.16 | 4.22 | 4.59 | -1.4 | 7.48 | 7.76 | 2.63 | -3.7 |
| CaO (%) | 0.60 | 0.58 | 4.71 | 3.3 | 1.39 | 1.48 | 2.75 | -6.5 |
| Ti (%) | 0.40 | 0.38 | 5.40 | 5.0 | 0.29 | 0.28 | 3.04 | 3.45 |
| Fe ₂ O ₃ (%) | 7.60 | 6.39 | 9.02 | 15.9 | 6.04 | 6.76 | 3.55 | -11.9 |
| MnO (ppm) | 223.38 | 180.92 | 6.84 | 19.0 | 1200 | 1051.40 | 3.38 | 12.4 |
| V (ppm) | 87.00 | 82.63 | 6.10 | 5.0 | 179 | 179.16 | 3.27 | -0.1 |
| Zn (ppm) | 55.00 | 41.11 | 14.29 | 25.3 | 112 | 101.93 | 5.33 | 9.0 |
| Ga (ppm) | 25.60 | 19.04 | 15.60 | 25.6 | 35.8 | 32.18 | 4.63 | 10.1 |
| Rb (ppm) | 205.00 | 153.83 | 13.90 | 25.0 | 130 | 110.39 | 4.68 | 15.1 |
| Sr (ppm) | 90.00 | 70.51 | 14.26 | 21.7 | 1160 | 1066.93 | 4.87 | 8.0 |
| Y (ppm) | 26.00 | 19.53 | 14.90 | 24.9 | 24.7 | 24.62 | 5.36 | 0.3 |
| Zr (ppm) | 96.00 | 67.74 | 20.35 | 29.4 | 1540 | 1244.00 | 5.49 | 19.2 |
| Nb (ppm) | 14.30 | 8.28 | 16.60 | 42.1 | 66.9 | 57.66 | 5.31 | 13.8 |
| Sn (ppm) | 2.00 | 1.49 | 29.19 | 25.5 | 6.50 | 4.91 | 15.05 | 24.5 |
| Th (ppm) | 12.80 | 8.94 | 15.89 | 30.2 | 79.3 | 71.72 | 5.76 | 9.6 |

^aAbbreviation: CV: Certified Value; MV: Measured Value.

The expected value refers to the certified value of an element in the sample made of certified reference material. Concerning the calculation of concentration deviation for certain elements, the analytical result given for the molecular concentration is converted to elemental concentration taking into consideration the stoichiometric coefficients. Results presented in **Table 5** show that accuracy in terms of deviation is not identical for the same element in different samples. Accuracy in terms of deviation in the range $\pm 15\%$ was obtained for some major elements which are: SiO₂, P₂O₅, K₂O, CaO, Ti and Fe₂O₃. This observation is similar to the one obtained above after analysis of GSR 01 and GSR 03 to check the accuracy of the method.

For the analytical method used in this work the instrumental limit of detection defined by Richard (Rousseau, 2001) as the minimum net peak intensity of an analyte, expressed in concentration unit, that can be detected by an instrument in a given analytical context with a 99.95% confidence level, is given for some elements in **Table 6**.

Results of EDXRF analysis of two standard reference materials made by rock material including precision and accuracy are presented in **Table 5**.

Deviation of analytical results obtained in this study is either positive or negative, suggesting that a systematic error may not be responsible of that deviation. Obtained results are compared with reported values of the concentrations of major oxides in rock reference material analyzed in the form of pressed pellets. This study reported by Saini (Saini et al., 2002) was made using reference rock materials STM-1 (Syenite) and SCO-1 (Shale), while the present study made use of reference rock materials GSR-5 (Shale) and GSR-7 (Syenite). Both studies use the same material, but the source of reference materials in Saini's report is USGS (United States Geological Survey, Denver, USA) and for the present study reference materials are from National Research Center for CRMs in China. **Table 7** presents the variation in accuracy when analyzing rock samples in the form of fine powder or pressed pellets.

Table 6. Limit of detection for some major and trace elements.

| | Element | Limit of detection ($\mu\text{g/g}$) |
|----------------|---------|--|
| Major elements | Al | 2.0 |
| | Si | 1.0 |
| | P | 0.3 |
| | K | 0.9 |
| | Ca | 0.8 |
| | Fe | 2.0 |
| Trace elements | Ti | 0.3 |
| | V | 0.2 |
| | Mn | 0.2 |
| | Zn | 0.5 |
| | Ga | 0.4 |
| | Rb | 0.2 |
| | Sr | 0.2 |
| | Y | 0.2 |
| | Zr | 0.2 |
| | Nb | 0.2 |
| | Mo | 0.2 |
| | Sn | 0.3 |
| | La | 1.5 |
| | Hf | 1.0 |
| | Ta | 0.8 |
| Th | 0.3 | |
| U | 0.3 | |

Table 7. Accuracy of EDXRF analytical results of rock material (shale and syenite) using powder or pressed pellets.

| Oxide | Shale | | | | Syenite | | | |
|--------------------------------|---|---------------|---------------------|---------------|---|---------------|---------------------|-------|
| | SCO-1 (pressed pellets) (Saini et al., 2002) | | GSR-5 (fine powder) | | STM-1 (pressed pellets) (Saini et al., 2002) | | GSR-7 (fine powder) | |
| | Certified Value (%) | Deviation (%) | Certified Value (%) | Deviation (%) | Certified Value (%) | Deviation (%) | Certified Value (%) | |
| Al ₂ O ₃ | 13.6 | -7.5 | -33.2 | 18.82 | 18.5 | -3.5 | -38.5 | 17.72 |
| SiO ₂ | 62.6 | 2.7 | -9.4 | 59.23 | 59.6 | 2.0 | -16.4 | 54.48 |
| P ₂ O ₅ | 0.23 | 13.0 | 12.5 | 0.16 | 0.16 | 18.8 | - | 0.018 |
| K ₂ O | 2.75 | -3.3 | -1.4 | 4.16 | 4.3 | 1.9 | -3.7 | 7.48 |
| CaO | 2.61 | -10.3 | 3.3 | 0.6 | 1.1 | -3.6 | -6.5 | 1.39 |
| MnO | 0.05 | -40.0 | 19 | 0.02 | 0.23 | -4.3 | 12.4 | 0.12 |
| Fe ₂ O ₃ | 5.14 | -8.4 | 15.9 | 0.00076 | 5.21 | -6.3 | -11.9 | 6.04 |

Table 7 shows that analyzing rock samples in the form of pressed pellets give more accurate results. Nevertheless, while preparing samples in the form of fine powder, some major compounds as SiO₂, P₂O₅, K₂O, CaO and Fe₂O₃ can be determined with a deviation less than 15%, which suggest that the method presented in this study should be optimized to achieve more accurate results. The result obtained for K₂O suggests that for this major compound a deviation lower than 5% can be obtained while using EDXRF for analysis of rock samples in the form of either fine powder or pressed pellets.

4. Conclusion

Standard reference materials in the form of fine powder were used in this study to investigate the precision and accuracy of analytical results obtained by Energy Dispersive X-Ray Fluorescence using a screening analytical method. The precision in terms of relative standard deviation and the accuracy in terms of deviation of obtained analytical results using the screening method are comparable to some values reported in the literature for the analysis of rocks by EDXRF. This study suggests that the EDXRF method presented in this work can be used for routine analysis with acceptable results. Globally for major compounds as SiO₂, P₂O₅, K₂O, CaO, Fe₂O₃ and Ti, the deviation was found to be lower than 15%. It was also found that the method seems to be more accurate and precise for major elements than for trace element investigation.

Acknowledgements

The EDXRF equipment used in this study was received by the National Radiation Protection Agency (NRPA) of Cameroon through technical cooperation with the International Atomic Energy Agency (IAEA).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- Akbulut, S., Cevik, U., Van, A. A., De Wael, K., & Van Grieken, R. (2014). Precision and Accuracy of ST-EDXRF Performance for As Determination Comparing with ICP-MS and Evaluation of As Deviation in the Soil Media. *Chemosphere*, *96*, 16-22. <https://doi.org/10.1016/j.chemosphere.2013.06.086>
- Croffie, M. E. T., Williams, P. N., Fenton, O., Fenelon, A., Metzger, K., & Daly, K. (2020). Optimising Sample Preparation and Calibrations in EDXRF for Quantitative Soil Analysis. *Agronomy*, *10*, Article No. 1309. <https://doi.org/10.3390/agronomy10091309>
- Duchesne, J. C., & Bologne, G. (2009). XRF Major and Trace Element Determination in Fe-Ti Oxide Minerals. *Geologica Belgica*, *12*, 205-212.
- Enzweiler, J., & Webb, P. C. (1996). Determination of Trace Elements in Silicate Rocks by X-Ray Fluorescence Spectrometry on 1:5 Glass Discs: Comparison of Accuracy and Precision with Pressed Powder Pellet Analysis. *Chemical Geology*, *130*, 195-202. [https://doi.org/10.1016/0009-2541\(96\)00022-8](https://doi.org/10.1016/0009-2541(96)00022-8)
- Guembou, J. C. S., Moyo Ndontchueng, M., Mekongtso Nguelem, J. E., Chene, G., Motapon, O., Kayo, S. A., & Strivay, D. (2019). Determination of the Natural Radioactivity, Elemental Composition and Geological Provenance of Sands from Douala in the Littoral Region of Cameroon Using X-Ray and γ -Ray Spectrometry. *Applied Earth Science*, *128*, 167-180. <https://doi.org/10.1080/25726838.2019.1637656>
- Injuk, J., & Van Grieken, R. E. (1993). Sample Preparation for XRF. In *Handbook of X-Ray Spectrometry Methods and Techniques* (p. 658). Marcel Dekker, Inc.
- Kimura, J., & Yamada, Y. (1996). Evaluation of Major and Trace Element XRF Analyses Using a Flux to Sample Ratio of Two to One Glass Beads. *Journal of Mineralogy, Petrology and Economic Geology*, *91*, 62-72. <https://doi.org/10.2465/ganko.91.62>
- Krishna, A. K., Khanna, T. C., & Mohan, K. R. (2016). Rapid Quantitative Determination of Major and Trace Elements in Silicate Rocks and Soils Employing Fused Glass Discs Using Wavelength Dispersive X-Ray Fluorescence Spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *122*, 165-171. <https://doi.org/10.1016/j.sab.2016.07.004>
- Lundblad, S. P., Mills, P. R., & Hon, K. (2008). Analysing Archaeological Basalt Using Non-Destructive Energy-Dispersive X-Ray Fluorescence (EDXRF): Effects of Post-Depositional Chemical Weathering and Sample Size on Analytical Precision. *Archaeometry*, *50*, 1-11.
- Lutz, J., & Pernicka, E. (1996). Energy Dispersive X-Ray Fluorescence Analysis of Ancient Copper Alloys: Empirical Values for Precision and Accuracy. *Archaeometry*, *38*, 313-323. <https://doi.org/10.1111/j.1475-4754.1996.tb00779.x>
- Nakayama, K., & Nakamura, T. (2005). X-Ray Fluorescence Analysis of Rare Earth Elements in Rocks Using Low Dilution Glass Beads. *Analytical Sciences*, *21*, 815-822. <https://doi.org/10.2116/analsci.21.815>
- Orihashi, Y., & Hirata, T. (2003). Rapid Quantitative Analysis of Y and REE Abundances in XRF Glass Bead for Selected GSJ Reference Rock Standards Using Nd-YAG 266 nm UV Laser Ablation ICP-MS. *Geochemical Journal*, *37*, 401-412. <https://doi.org/10.2343/geochemj.37.401>
- Remya, D. P. S., Trupti, A. C., Nicy, A., Dalvi, A. A., Swain, K. K., Wagh, D. N., & Verma, R. (2015). Evaluation of Uncertainty in the Energy Dispersive X-Ray Fluorescence Determination of Platinum in Alumina. *Analytical Methods*, *7*, 5345-5351. <https://doi.org/10.1039/C5AY00547G>
- Rousseau, R. M. (2001). Detection Limit and Estimate of Uncertainty of Analytical Results. *The RIGAKU Journal*, *18*, 33-47.

- Saini, N. K., Mukherjee, P. K., Rathi, M. S., & Khanna, P. P. (2000). Evaluation of Energy-Dispersive X-Ray Fluorescence Spectrometry in the Rapid Analysis of Silicate Rocks Using Pressed Powder Pellets. *X-Ray Spectrum*, *29*, 166-172.
[https://doi.org/10.1002/\(SICI\)1097-4539\(200003/04\)29:2<166::AID-XRS411>3.0.CO;2-L](https://doi.org/10.1002/(SICI)1097-4539(200003/04)29:2<166::AID-XRS411>3.0.CO;2-L)
- Saini, N. K., Mukherjee, P. K., Rathi, M. S., Khanna, P. P., & Purohit, K. K. (2002). Trace Element Estimation in Soils: An Appraisal of ED-XRF Technique Using Group Analysis Scheme. *Journal of Trace and Microprobe Techniques*, *20*, 539-551.
<https://doi.org/10.1081/TMA-120015615>
- Xue, D. S., Tian, H. C., Zhang, D. P., Liu, Y. H., Sun, J. F., Wu, S. T., Liu, S. K., Guo, S., & Wan, B. (2022). Quantitative Verification of 1:35 Diluted Fused Glass Disks with 10 mg Sample Sizes for the Wavelength-Dispersive X-Ray Fluorescence Analysis of the Whole-Rock Major Elements of Precious Geological Specimens. *Spectrochimica Acta Part B: Atomic Spectroscopy*, *193*, Article ID: 106433.
<https://doi.org/10.1016/j.sab.2022.106433>