

SENSITIVITY AND APPLICATION TO LOW Z-ELEMENTS BY X – RAY DETECTION SYSTEM

Thet Thet Cho¹, KathiNwe²,Nyein Nyein³, KalyarThwe⁴

Abstract

The sensitivity of the X ray detection has been investigated for low Z-elements. The sample preparation and measurement were made for low Z elements to determine the influence of the pelletizing pressure on sensitivity. Depending on characteristics of SPECTRO XEPOS Spectrometer, the minimum pelletizing pressure of the sample for low Z element was determined. The results indicated that the minimum pelletizing pressure of the samples is required for the reduction of surface effect and to yield precise results. For aluminum and silicon, the minimum pressed weight of 14 ton is needed, but for potassium, a pressed weight of 12 ton is adequate. For sulfur and calcium, the pressed weight of 10 ton is sufficient. The optimized values have been tested and demonstrated on standard reference material GSR 07. It is observed that in the experimental configurations currently installed, these optimum valued allowed to determine the certified values with an accuracy of 1.33% for low-Z elements.

Key words: XRF, Low Z-element, Sensitivity

Introduction

X-ray fluorescence spectrometry is one of the most widely used routine instrumental methods of elemental analysis of biological, geological and environmental samples. Some factors that are affected on the sensitivity and accuracy of an Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer are the excitation source, the instrumental settings and the sample preparation.

In XRF measurement, sample preparation is necessary when the sample is inhomogeneous the surface layer is not representative for the whole sample. As a condition for the reliable analysis by XRF, a flat and even surface of specimen

¹. Dr, Assistant Lecturer, Department of Physics, University of Mandalay

². Dr, Professor, Department of Physics, Mandalay University of Distance Education

³. Dr, Lecturer, Department of Physics, Sagaing University

⁴. Dr, Professor, Department of Physics, University of Mandalay

is required. Particularly for the determination of light elements, the surface should be prepared mirror like, as scattering effect due to rough texture influence the results. An appropriate surface can be normally obtained by pressing the sample into pellet. Accuracy of Calibration Procedure for Energy-Dispersive X-Ray Fluorescence Spectrometry was carried by Markowicz, Haselberger and Mulenga in 1992. The Cnseten EDXRF Spectrometers – Sensitivity, Calibration and Application to Geochemistry were also researched by Rahmani and *et al.* in 2001. In this work, sample preparation has been done to study the influence of the palletizing pressure of the sample on the measurement sensitivity.

X-Ray Fluorescence Spectroscopy

For each energy region of the electromagnetic radiation, spectrometry has advanced as the associated experimental tools have been developed. The first and crudest detectors often just measure the presence of the radiation, in the second stage, they also measure the intensity of the radiation, but with only a minimum of information on its energy; and the final type measures the intensity as a function of the photon energy, i.e., they generate a spectrum. Williams (1976) give an extensive discussion of the history of spectroscopy for many of the wavelength ranges and of general and specific measurement methods. Historically, the last energy region of electromagnetic radiation to be studied was the high-energy part, the X-ray and γ -ray.

The XRF analysis has been developed by the use of primary excitation source unit, high efficiency detectors, types of spectrometer and measuring electronics. The energy dispersive spectrometers with solid-state detectors are widely used in Energy Dispersive X-ray Fluorescence Analysis.

Experimental Arrangement and Measurement

Sample Collection and Preparation

The elements from aluminum to calcium were chosen to analyze low- Z elements with XRF spectrometer system. Therefore five kinds of samples contained low Z-elements; aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), sulfur (S), potassium carbonate (K_2CO_3) and calcium oxide (CaO) were collected from Academy Chemical Group. The grade of the collected samples

is analytical reagent (AnalaR). The sample matrixes and molecular weight percentage of low- Z elements in the samples used in this experiment are presented in Table (1).

Sample preparation is an important role in XRF measurement because it is crucial to the relationship between spectral line intensity and the elemental concentration. The analysis of sample in the form of powder pellets must represent one of the simplest possible forms of sample preparation. Prepared pellets must be homogenized. If the sample is inhomogeneous, the surface layer is not representative for the whole sample. The solid samples, silicon dioxide and calcium oxide were split and milled into smaller pieces, which were then suitable for further grinding. The subsamples were ground manually with a mortar and a pestle. After grinding, the particle size distributions were determined by using sieves.

The fine powders were prepared as pellets. Then hydraulic press machine (PP-25, Retsch, GmbH) and a 32 mm diameter die set including a die body, base and two polished metal disks were used for pellet sample in our research work. Prior to pelletizing all parts of the die set were carefully cleaned with methylated spirit to prevent contamination. Initially each sample was weighed using digital balance (PW-254) to obtain the needed amount (5 g). Binding agent is added to form stable pellet of the samples. Therefore, binder (1 g) was added to the sample (5 g) and they were mixed to homogenize with each other. In this experiment, Hoechst Wax (HWC) was used as binder. After that weighed sample was poured into the mould and was pressed with 4 ton for 5 minutes by using hydraulic press machine. The pellet was then removed from the die set, taking care not to crack it in the process. For each sample the applied pelletizing pressures are 4 ton, 8 ton, 12 ton, 16 ton and 20 ton respectively. By changing the pelletizing pressure different thickness of pellets were obtained. Pressing time was taken 5 minutes for each pellet. In this procedure three replicated pellets per sample were made (Fig,1 - 5).

Table 1. Sample matrix and molecular weight percentage of low Z-elements in the samples

Sample Matrix	Element	Atomic Number(Z)	Molecular weight (%)
Al_2O_3	Al	13	52.94
SiO_2	Si	14	46.74
SO_3	S	16	40.05
$\text{K}_2\text{CO}_3 + \text{KHCO}_3$	K	19	47.81
$\text{Ca}(\text{OH})_2 + \text{CaCO}_3$	Ca	20	47.07



Figure 1. The photograph of pressed pallets of aluminum dioxide samples



Figure 2. The photograph of pressed pallets of silicon dioxide samples



Figure 3. The photograph of pressed pallets of sulfur samples



Figure 4. The photograph of pressed pallets of potassium carbonate samples

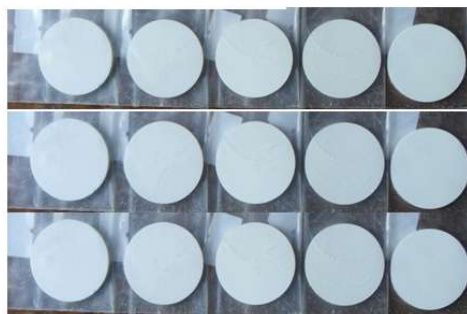


Figure 5. The photograph of pressed pellets of calciumoxide samples

X-ray Fluorescence Spectrometer

The X-ray fluorescence spectrometer used in this work is SPECTRO XEPOS spectrometer at Department of Physics, University of Mandalay. A 50 watt palladium (Pd) anode end-window X-rays tube is used to excite the samples. Three secondary targets used in this spectrometer are Highly Orient Pyrolytic Graphite (HOPG), Molybdenum (Mo) and Aluminum Oxide (Al_2O_3). They offer many different excitation conditions ensuring optimum determination of all elements from aluminum to uranium. HOPG is used for light elements and Mo is used for medium elements. For heavy elements, Al_2O_3 secondary target is applied. The XRF spectrometer consists of a Si (Li) detector with resolution of 160 eV for 5.9 keV ($\text{Mn } k_\alpha$).

X-ray Measurements

X-ray fluorescence is one of the most common techniques for the analysis of the concentrations of many elements contained in the sample by a single measurement. In this research work, all the pelletized samples were measured by using SPECTRO XEPOS spectrometer. Initially, the primary beam from the X-ray tube impinges on one of the secondary targets, molybdenum which emits almost monochromatic X-ray. The monochromatic beam is then used to excite characteristic radiation from the atoms of the sample. The emitted X-ray by the elements presented in the sample is detected by Si (Li) detector. The samples were measured three times for each pellet to determine the precision of the analysis tools. Each measurement has been

carried out for 900 seconds with three secondary targets of the XRF spectrometer system. The obtained X-ray spectra were analyzed using X-LAB Pro 4.5 software to obtain the concentration of each element in the sample. The analyzed X-ray energy range is 0-12.5 keV for light elements presented in the sample. The analyzed X-ray energy lines of the element in the samples, molybdenum target and palladium anode are listed in Table (2).

Table 2. Analyzed X-ray Emission Energies (k eV)

Atomic number	Element	X-ray energies (keV)			
		K _α	K _β	L _α	L _{β1}
13	Al	1.486			
14	Si	1.739	1.829		
16	S	2.307	2.464		
19	K	3.312	3.589		
20	Ca	3.690	4.012		
42	Mo	17.441	19.600	2.293	2.394
46	Pd	21.121	23.806	2.838	2.990

Results and Discussion

The effects of pelletizing pressure on fluorescent intensity of low-Z elements were examined to determine the sensitivity and accuracy of XRF detection system. Experimental data for average concentrations of aluminum, silicon, sulfur, potassium and calcium elements in the samples concerned with different pressed weights are presented in Table (3). The dependence of concentration on pressed weight for aluminum element is shown in Fig. (6). In this figure, for pressed weight between (4 - 12) ton, the concentration values of aluminum element are considerably increased, but for (12 - 20) ton, the concentrations do not change within the error.

For silicon element, the variation of concentration with pressed weight(Fig.7) can be seen that the concentrations are gradually increased in

the pressed weight between (4-12)ton, and then the concentrations are changed unapparently between (12 - 20) ton.

The concentration of sulfur element for five different pressed weights (Fig. 8) is obvious that the concentration values of sulfur are slightly increased in pressed weight between (4 - 8)ton. After that, they remain unchanged within the error between (8 - 20) ton.

For potassium element, the concentration values are markedly increased with an increase in pressed weight from 4 ton to 12 ton then concentrations are gradually increased between (12 - 20) ton in Fig. (9).

In Fig. (10), the concentrations of calcium are slightly increased in pressed weight between (4 - 8) ton, although they do not significantly differ between (8 - 20) ton.

From these results, it is observed that the fluorescent intensity of low- Z elements depends on the pelletizing pressure. The reason for this dependence might be surface effect of the sample.

According to the figures, we found that the minimum pelletizing pressures are 14 ton for aluminum and silicon, 12 ton for potassium and 10 ton for sulfur and calcium.

The accuracy of the XRF detection system with these optimized values was verified by measuring a certified reference material as a routine sample. The linear plots of correlation between certified and measured values of standard reference material for 0 ton to 14 ton pressed weight are also illustrated in Fig. (11)-(15). From these figures, the best value of correlation factor was 0.9829 ($R^2 = 0.9997$) which points out the pressed weight 14 ton is needed for reliable accuracy for low- Z elements in standard reference material GSR 07.

Moreover the measured values of GSR 07 for these minimum pressed weights are compared with the certified values in Table (4). The linear correlation between these values is shown in Fig. (16). The experimental results showed good agreement comparing to the given certified values. It is observed that the relative accuracy values are minimum for 14 ton pressed

weight of aluminum and silicon, 12 ton for potassium and 10 ton for sulfur and calcium.

Table 3. Concentration of low Z - element in the sample at different pressed weights

Pressed weight (ton)	Average Concentration (%)				
	Al	Si	S	K	Ca
4	44.98±2.00	34.76±1.71	36.51±0.89	27.12±0.50	46.33±0.57
8	47.13±1.43	35.60±1.70	38.22±0.62	34.00±0.60	47.46±0.42
12	51.73±2.07	36.78±1.81	38.38±0.86	40.01±0.86	47.38±0.46
16	51.99±2.30	37.12±1.70	38.62±0.67	41.00±0.48	47.48±0.61
20	51.57±2.61	37.15±1.23	38.81±0.52	42.05±0.83	47.45±0.49

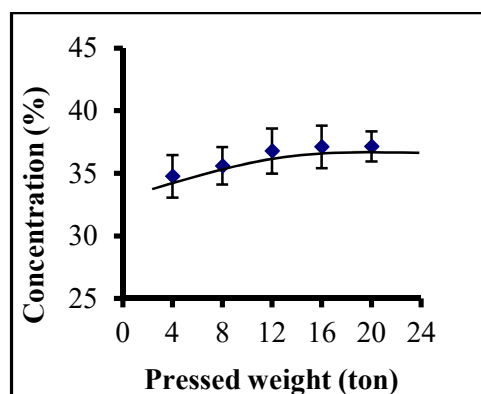
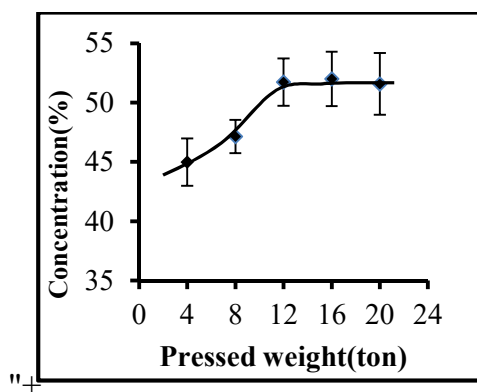


Figure 6. Concentration of aluminum element in the sample at different pressed weights

Figure 7. Concentration of silicon element in the sample at different pressed weights

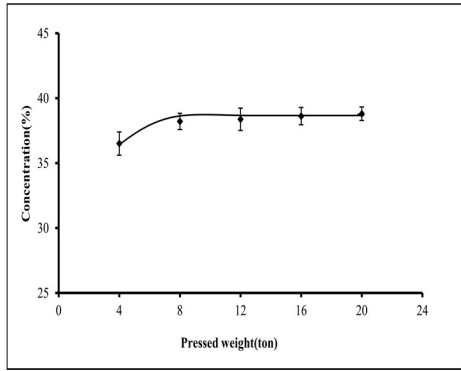


Figure 8. Concentration of sulfur element in the sample at different pressed weights

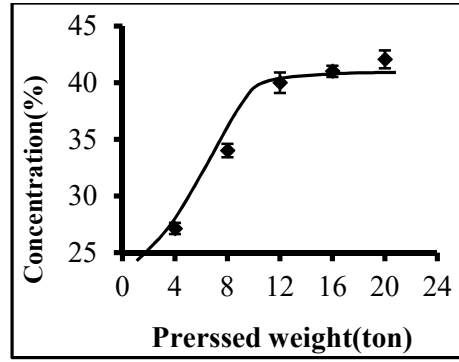


Figure 9. Concentration of potassium element in the sample at different pressed weights

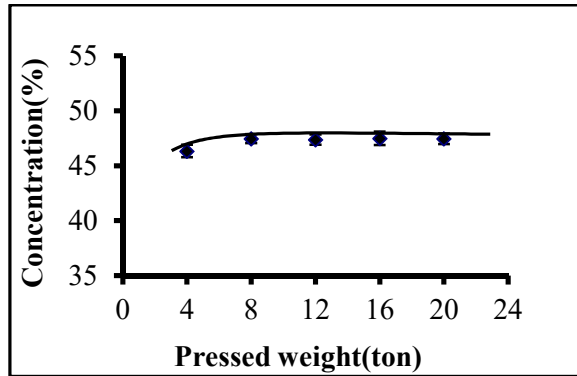


Figure 10. Concentration of calcium element in the sample at different pressed weights

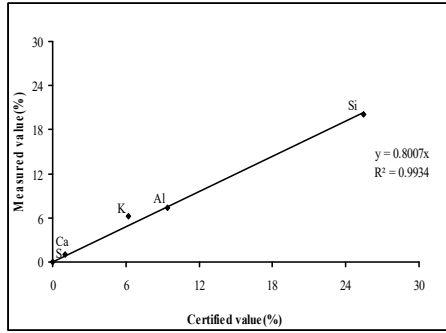


Figure 11. Correlation between certified and measured values of standard reference material GSR 07 for 0 ton pressed weight

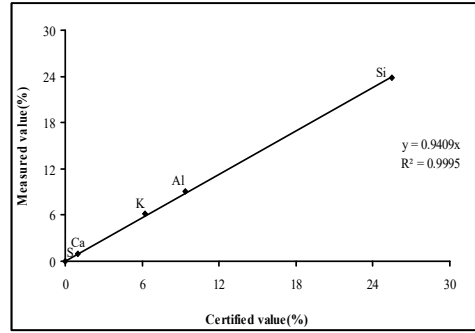


Figure 12. Correlation between certified and measured values of standard reference material GSR 07 for 8 ton pressed weight

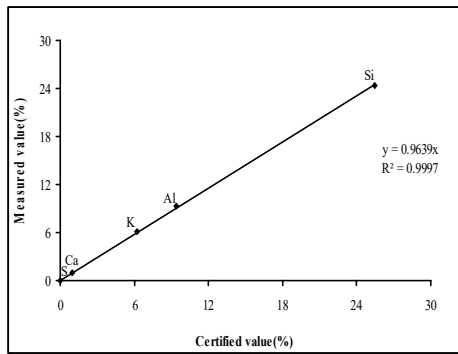


Figure 13. Correlation between certified and measured values of standard reference material GSR 07 for 10 ton pressed weight

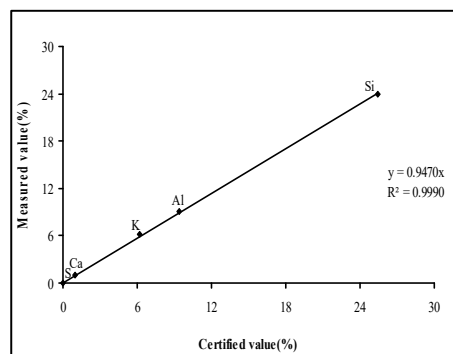


Figure 14. Correlation between certified and measured values of standard reference material GSR 07 for 12 ton pressed weight

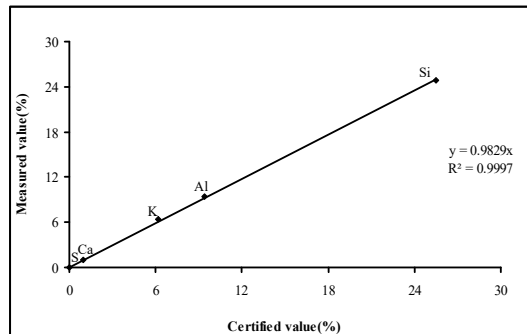


Figure 15. Correlation between certified and measured values of standard reference material GSR 07 for 14 ton pressed weight

Table 4. Analytical results compared to certified values for standard reference material, GSR 07

Element	Concentration (%)		Relative Accuracy (%)	Pressed weight (ton)
	Certified value	Measured value		
Al	9.3742	9.4020	0.2965	14
Si	25.4639	24.8600	2.3715	14
S	0.0100	0.0103	3.0000	10
K	6.2091	6.1880	0.3398	12
Ca	0.9934	0.9996	0.6241	10

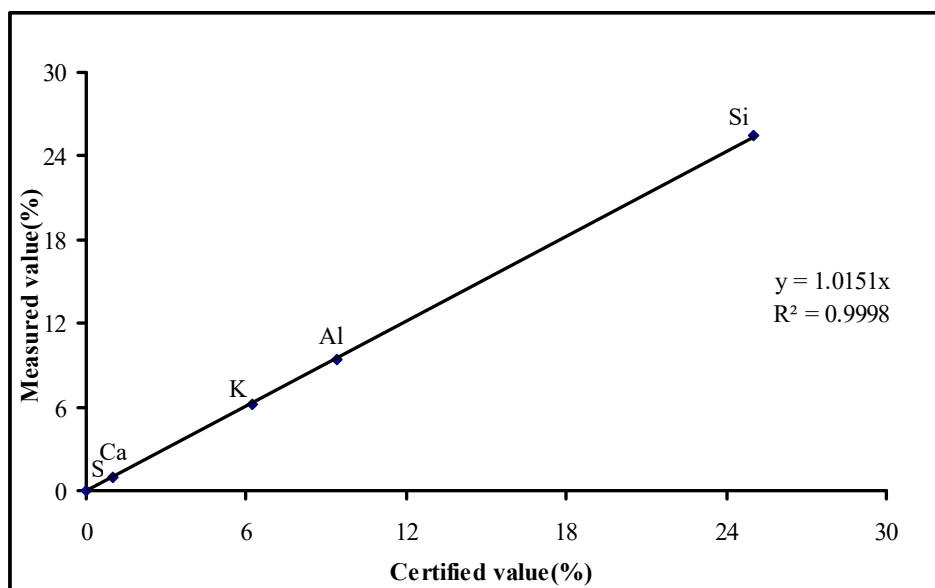


Figure 16. Correlation between certified and measured values for standard reference material GSR 07

Conclusion

The influence of the sample preparation on the elemental sensitivity value in XRF detection system has been studied for light elements. The results show that the choice of pelletizing pressure greatly influence the analysis results for low- Z elements. The results obtained from our research, it can be concluded that this minimum pelletizing pressure can reduce the surface effect. The minimum pelletizing pressure in turn affects the accuracy and precision of the XRF analysis. The correlation factor between certified and measured value of standard reference material GSR 07 with these optimized values is 1.0151. Therefore, these optimized values of pelletizing pressure could be applied and measured with the XRF spectrometer to obtain the accurate results for low- Z elements in any kinds of environmental samples.

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