

# Implication Of X-Ray Path, Region Of Interest, Tube Current And Voltage In Calibration Of X-Ray Fluorescence Instrument: A Case Study Of X-Supreme 8000

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**Abstract:** This report unveils the measures taken to calibrate the newly installed x-ray fluorescence instrument (X-Supreme 8000) in Multi-User Science Research Laboratory, Ahmadu Bello University, Zaria. Precision and accuracy is dependent on appropriate method set up and suitable analyte conditions. The tube current was set to achieve 20% dead time for silicon drift detector (SDD). The tube voltage setting with at least twice line energy of elements aided method set up for spectrum scan from which region of interest (ROI) was utilized to check interferences and matrix effect. Air readily absorb low energy x-ray, thus the analysis chamber was evacuated with helium for low Z elements up to Niobium (Nb). Direct proportional relationships occur between concentration of analytes and detector count per seconds (cps). The standard error of mean of given and calculated concentration of standard reference materials (SRM) range between 0.001 – 0.013wt%. A relatively low standard deviation and repeatability of results confirms good precision and accuracy of the instrument.

**Keywords:** calibration of XRF, compton scattering, interferences, region of interest, tube current, tube voltage, x-ray path

## 1 INTRODUCTION

### 1.1 X-ray Fluorescence Technique

X-ray fluorescence (XRF) has been proven to be a very useful technique for elemental analysis of materials. The benefits of using XRF rather than a traditional analysis method are that it is quick, non-destructive, and versatile [1].

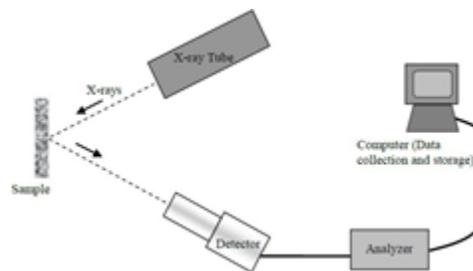
### 1.2 Basic XRF setup

The setup of XRF instrumentation generally consists of four basic components [2]:

- An excitation source
- A sample
- A detector
- A data collection and analyzing system

The excitation source is typically an x-ray tube, but a radioactive isotope may also be used; the X-Supreme 8000 XRF instrument uses an x-ray tube.

The x-ray tube sends a beam of x-rays with various energies to the sample, and the sample absorbs and emits the x-rays to the detector. The detector senses each impinging x-ray and sends electrical pulses to the data collection and analyzing system. The analyzing system categorizes each x-ray by its energy. Then, the data is collected and stored; this is typically done with a computer (Fig. 1). An XRF measurement essentially gives two pieces of information: The energy of an x-ray, and how many x-rays were received (count number or intensity for that energy). When graphed in a spectrum, the energy of the x-rays is the independent variable, and the count number is the dependent variable. A typical spectrum of such data will show one or more peaks for each element present in the sample [3]. While the XRF method is very quick and efficient, it can also give very inaccurate results if the instrument is not calibrated correctly. This is a result of two particular systematic errors: First, the instrument is not perfect and tends to drift from previous calibrations, and second, characteristic x-ray energies are not totally unique to an element and often overlap with other characteristic x-rays [1]. These two errors can be resolved by implementing a good calibration program and using it as often as necessary. Present work focuses on the measures taken to appropriately calibrate the X-Supreme 8000 XRF instrument in Multi-User Science Research Laboratory, Ahmadu Bello University, Zaria (Fig. 2).



**Fig 1:** The components of basic XRF instrumentation setup

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Fig. 2: The X-Supreme 8000 XRF instrument

## 2. XRF THEORY

### 2.1 Elastic and Inelastic X-ray Scattering

The two most common interactions of x-ray with materials are elastic and inelastic scattering. Scattering refers to the dispersed radiation that comes as a result of these interactions (Jenkins 1999). Elastic scattering, also referred to as coherent or Rayleigh scattering occurs when an x-ray collides with an electron in an atom and no energy is lost in the collision. In this case, the x-ray is best thought of as an electromagnetic wave. An electron in the atom is oscillated in this wave, and the oscillating electron will radiate an electromagnetic wave of the exact same energy as the incident x-ray. Inelastic scattering also referred to as incoherent or Compton scattering, occurs when an x-ray collides with an electron in an atom and its energy is transferred, in whole or in part, to the electron. In this case, the x-ray is best thought of as a photon. This photon can either bump the electron into higher orbital energies or eject the electron completely from the atom. The incident x-ray photon will then deflect away from the atom with a corresponding loss of energy.

### 2.2 Characteristic Radiation and its Measurement

Every element has a set of characteristic x-rays. A characteristic x-ray has a very specific energy that is unique to an element. Therefore, a characteristic x-ray can be thought of as an element's "thumbprint" [5]. Incident x-ray of sufficient energy will eject an electron from an atom, leaving a vacancy. The atom will then adjust its electron configuration to be in the lowest energy state; in other words, an electron in a higher shell will drop down to fill the vacancy. The process of an electron filling the vacancy creates an x-ray which is characteristic of a specific electron transition for that element (Fig. 3).

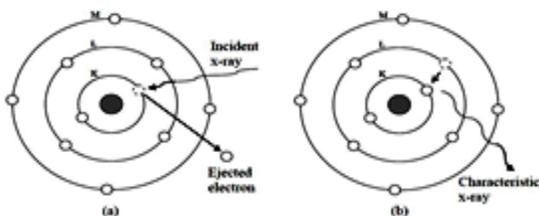


Fig. 3: (a) Incident x-ray ejects the K-shell electron. (b) Atom returns to ground state by transitioning an L-shell electron to the K-shell.

Typically, most electron transitions occur from the L-shell to the K-shell, which is classified as a  $K\alpha$  transition. The second

most common electron transition occurs from the M-shell to the K-shell, which is classified as a  $K\beta$  transition [1]. Two other common transitions are the  $L\alpha$  and  $L\beta$  transitions (a transition from the M-shell to the L-shell, and from the N-shell to the L-shell, respectively). When an atom returns to its ground state, it typically does so using more than one electron transition. As shown in Fig. 5, XRF measurements are mainly concerned with these four transitions (Fig. 4). Other transitions have characteristic energies that are out of the detectable range of the X-Supreme 8000 XRF instrument.

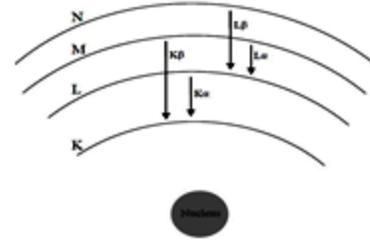


Fig. 4: Four common electron transitions used in XRF measurements

Characteristic x-ray energies of  $K\alpha$  and  $L\alpha$  energies for many elements are very similar. For example, the  $K\alpha$  energy of titanium (4.510 keV) is very close to the  $L\alpha$  energy of barium (4.467 keV); this introduces a difference of only 0.043 keV [6]. Thus, a need arises for better calibration in order to resolve overlapping energies.

### 2.3 Continuous Radiation

In every XRF measurement where an x-ray tube is used for the excitation source, a broad range of energies is observed, producing a non-linear background noise in the spectrum. The radiation that causes this is called continuous radiation or *bremstrahlung* (German for "braking radiation"). In the x-ray tube, electrons are accelerated over a large potential difference, followed by rapid deceleration at the anode. From this, a continuous range of x-rays are produced that may provide for excitation of many different atoms [7]. The noise created from continuous radiation does not impede measurements, providing the peaks of interest are relatively more intense than the noise (Fig. 5).

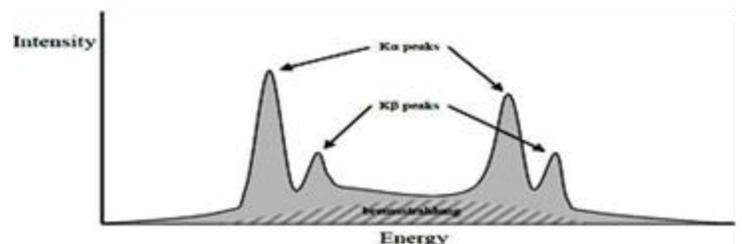


Fig. 5: A spectrum with peaks from two elements. Typically, each element in the sample will have pronounced  $K\alpha$  and  $K\beta$  peaks. The continuous radiation of noise in the spectrum is called *bremstrahlung*.

## 3. METHODOLOGY

This essentially include an extensive review of literature on XRF theory to enhance background knowledge, detailed study of manual to develop standard operating procedure, practical

calibration program which include spectrum scan and calibration with of standard reference material (polyvinyl chloride) for chlorine, potassium, calcium, manganese, iron and zinc.

**3.1 Standard Reference Materials (SRMs)**

Polyvinyl chloride (PVC) with a blank and others with concentration range between 0.01 to 13.60wt% were used. The analyte concentration SRMs are presented in Table 1 below:

Table 1: Contents of analytes in certificate of analysis of PVC SRM

Analyte	PVC Standard Reference Material (wt%)								
	1	2	3	4	5	6	7	8	9
Cl	0.00	13.60	13.10	13.00	12.70	12.60	13.00	0.00	12.70
Ca	0.00	2.42	3.40	1.93	0.97	2.92	0.97	3.37	1.41
Cr	0.00	0.10	0.13	0.15	0.02	0.03	0.01	0.17	0.08
Zn	0.00	0.01	0.01	0.02	0.02	0.10	0.01	0.03	0.02

**3.2 Spectrum Scan**

Spectrum Scan helped to develop empirical methods (calibrations). It was used to experiment and select the best measurement conditions for elements. The conditions and spectrum are shown in Fig. 6 and 7.

**3.2.1 Measurement condition**

Prior to acquisition of a spectrum, the following parameters were set to discern acquisition conditions.

**a. Detector selection**

The X-Supreme 8000 is preinstalled with silicon drift detector (SDD). The SDD detector can be used to analyse elements Na to U.

**b. Tube voltage (kV)**

The tube voltage is the energy required to excite the element lines of interest. As a simple rule of thumb the tube voltage required for a particular element line is approximately twice the line energy for that element. Therefore, the tube voltage was set to cater for elements within a narrow range of line energy.

**c. Path**

Low-energy X-ray lines are absorbed by air. Helium is used to purge the detection area of air for low Z elements so that low-energy X-rays reach the detector as vacuum does not absorb x-ray. Helium may also be needed for higher-energy X-rays because, without the helium, the argon peak from the air may overlap the element lines of interest and make detection difficult.

**d. Tube current (µA)**

An increase in x-ray tube current will increase the number of counts per second (cps) that a detector receives. The tube current was promptly set to reach dead time limit of 20% during which the detector sought earlier detected counts to reduce spectra overlap (matrix effect).

**e. Measurement time(s)**

Precision and measurement time are intimately related. To improve the precision of a measurement at a particular concentration level, the measurement time must be increased by the square of the improvement required. Measurement time 60 seconds were used.

**f. Spinner**

The spinner was enabled to ensure uniformity of the SRMs during analysis. A close reproducible result with pelletized sample confirms the reliable function of spinner for powdered sample.

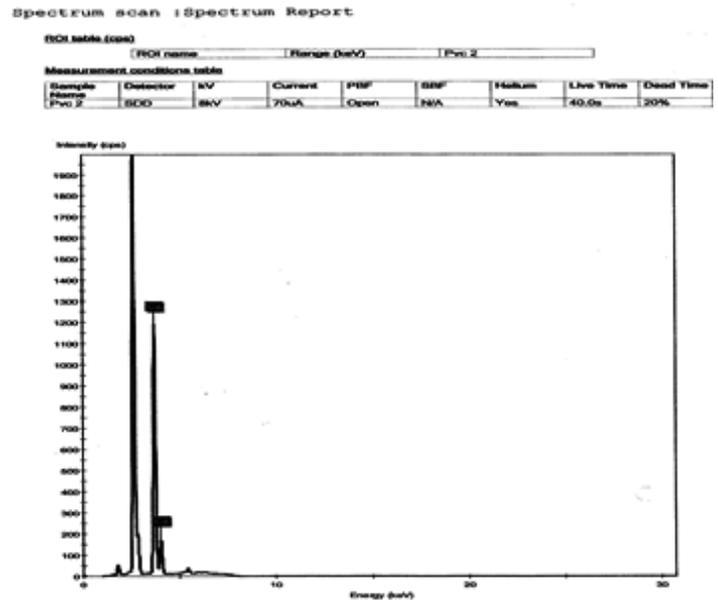


Fig. 7: Spectrum and measurement conditions of PVC 2

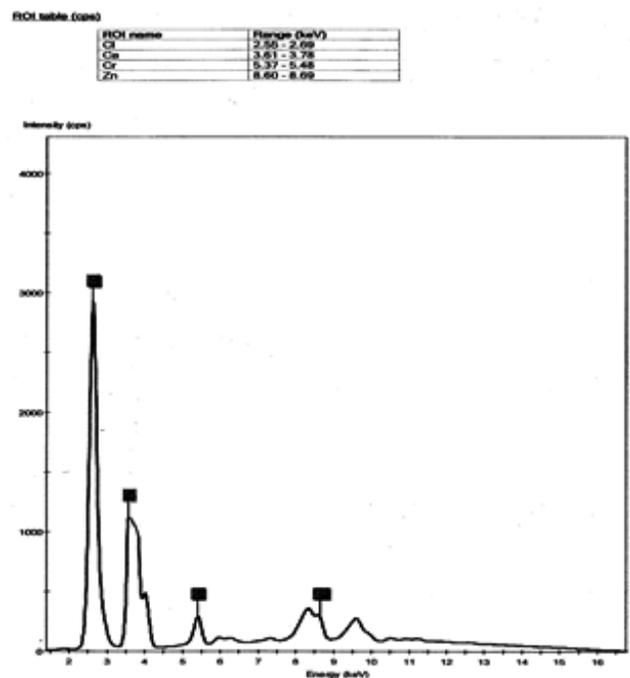


Fig. 8: Elemental peaks from spectrum scan for analytes in PVC 6

Consequently, spectra for each of the samples using various measurement conditions were attempted. The result gives element peak intensity (qualitative concentration). Direct proportional relationships occur between concentration of analytes and detector count per seconds (cps) (Fig. 8). Peaks are identified and region of interest that covers energy of  $K\alpha$  and  $K\beta$  are painted to reduce interferences and matrix effects.

**3.3 Empirical Method Set-up**

Minimum of six SRMs are required for accurate calibration program.

**3.3.1 Standard measurement and regression**

In this study, nine calibration standards that are representative of sample's matrix to minimise inaccuracies caused by matrix effects were used. The analytes (Cl, Ca, Cr and Zn) were selected and named with appropriate units of measurements. Specific measurement conditions from spectrum scan with characteristic ROI to check interferences/overlaps were noted. Regression was performed on the results obtained from measuring a series of calibration standards before the calibration method was validated for routine analysis. Regression helps to correct raw count per seconds (cps) in order to enhance proximity to SRMs concentration. The results of measured standard and regression are presented in Table 2 to 5 and Fig. 9 below:

Table 2: Standard line of Chlorine in PVC

Standard	Raw cps	Corrected cps	Known (wt%)	Calculated (wt%)	Diff
PVC 1	246.4	264.2	0.00	0.00	0.00
PVC 2	6199.7	6199.7	13.60	13.64	0.04
PVC 3	6066.9	6065.5	13.10	12.92	-0.18
PVC 4	5822.6	5810.1	13.00	13.03	0.03
PVC 5	5743.3	5600.0	12.70	12.59	-0.11
PVC 6	5768.2	5794.4	12.60	12.89	0.29
PVC 7	5966.8	5966.8	13.00	12.91	-0.09
PVC 8	346.7	347.4	0.00	0.01	-0.01
PVC 9	5986.5	5986.3	12.70	12.81	0.11

Standard Error = 0.013wt%  
Correlation coefficient = 0.999

Table 3: Standard line of Calcium in PVC

Standard	Raw cps	Corrected cps	Known (wt%)	Calculated (wt%)	Diff
PVC 1	348.2	342.1	0.00	0.03	-0.03
PVC 2	4132.7	4130.7	2.42	2.42	0.00
PVC 3	4822.8	4820.8	3.40	3.48	0.08
PVC 4	4001.3	4045.6	2.92	3.01	0.09
PVC 5	2142.3	2124.8	0.97	0.99	0.02
PVC 6	4420.1	4450.3	2.92	2.89	-0.03
PVC 7	1986.8	2014.6	0.97	1.14	0.07
PVC 8	4735.3	4735.0	3.37	3.21	-0.16
PVC 9	3023.4	3023.2	1.41	1.47	0.06

Standard Error = 0.004wt%  
Correlation coefficient = 0.996

Table 4: Standard line of Chromium in PVC

Standard	Raw cps	Corrected cps	Known (wt%)	Calculated (wt%)	Diff
PVC 1	198.6	198.0	0.00	0.00	0.00
PVC 2	1090.1	1095.8	0.10	0.08	0.02
PVC 3	1322.7	1322.4	0.13	0.12	0.01
PVC 4	1280.4	1289.6	0.15	0.14	-0.01
PVC 5	864.5	800.2	0.02	0.01	0.01
PVC 6	902.1	887.4	0.03	0.03	0.00
PVC 7	883.8	769.9	0.01	0.01	0.00
PVC 8	1324.3	1324.2	0.17	0.14	0.03
PVC 9	901.4	901.4	0.08	0.10	0.02

Standard Error = 0.002wt%  
Correlation coefficient = 0.979

Table 5: Standard line of Zinc in PVC

Standard	Raw cps	Corrected cps	Known (wt%)	Calculated (wt%)	Diff
PVC 1	96.2	90.0	0.00	0.00	0.00
PVC 2	1132.7	1011.3	0.01	0.01	0.00
PVC 3	1822.8	1643.6	0.01	0.00	-0.01
PVC 4	1001.3	996.4	0.02	0.03	0.01
PVC 5	842.3	842.2	0.02	0.02	0.00
PVC 6	1420.1	1320.9	0.01	0.00	-0.01
PVC 7	786.8	776.4	0.10	0.20	0.01
PVC 8	1735.3	1678.3	0.03	0.02	-0.01
PVC 9	923.4	920.8	0.02	0.02	0.00

Standard Error = 0.001wt%  
Correlation coefficient = 0.982

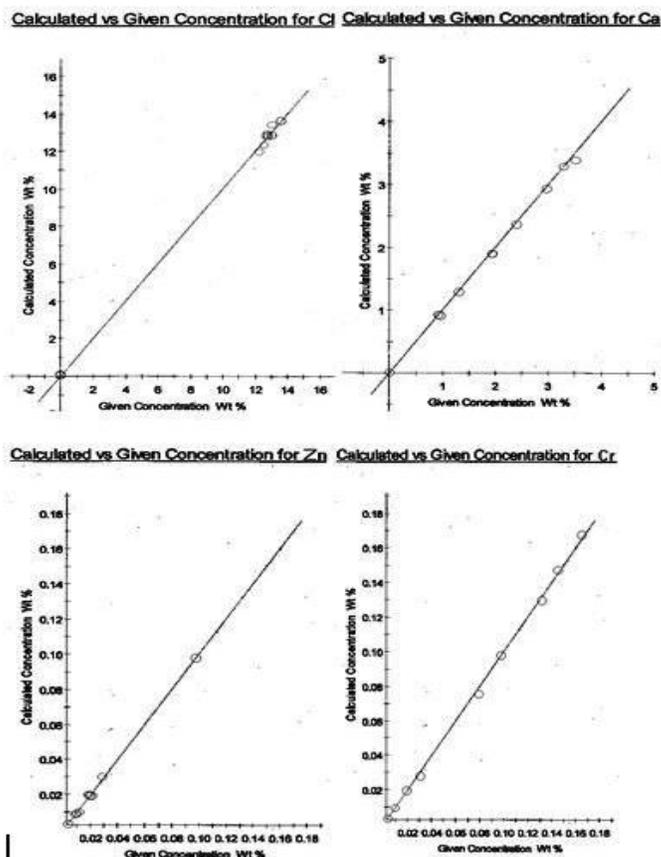


Fig. 9: Plot of known vs calculated concentrations for analytes Cl, Ca, Cr and Zn after regression.

Direct proportional relationship and strong positive correlation from Pearson's correlation coefficient coupled with low standard error values confirms accuracy of the calibration.

## 5. ROUTINE ANALYSIS

Routine analysis is only possible when a method has been calibrated. Such methods (referred to as 'Calibration or Empirical' methods) can be provided as part of a dedicated application package which gives those users who do not have extensive knowledge of XRF theory the opportunity to achieve excellent analytical results. Typically, it involves measuring a number of calibration standards using a dedicated application method. This establishes, for each element, a relationship between X-ray intensities and analyte concentrations. This was practically executed to confirm precision of the empirical (calibrated) method. The result (Fig. 10) shows a high precision and accuracy of the empirical method.

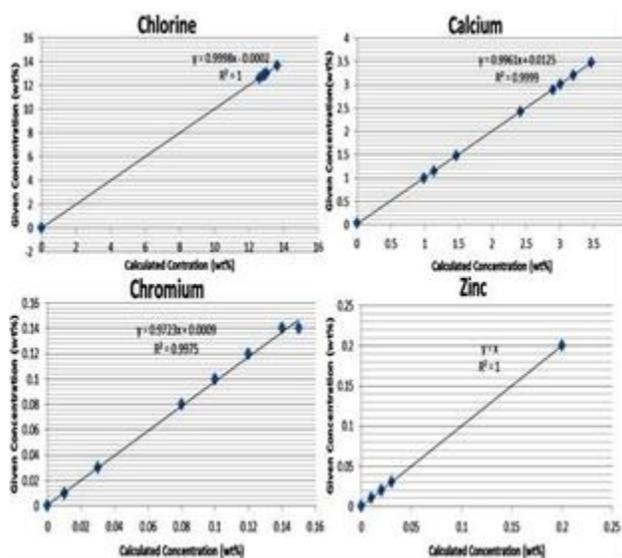


Fig. 10: Plots of Known vs Calculated Concentration for analytes in routine analysis

## 6. CONCLUSION AND RECOMMENDATION

After calibration methods were researched, and a better calibration program was created and implemented, the XRF measurements increased in accuracy. Because of this calibration, users are now enabled to collect reproducible data with a standard error range of  $\pm 0.001$ - $0.013$ wt%. Therefore, XRF analyses of varieties of materials (solids and liquids) are possible if standard reference materials (standards) are available. From the foregoing, it has been shown that:

- Tube current, voltage and measurement time setting is critical for qualitative spectrum scan.
- Precision and accuracy is dependent on appropriate method set up and suitable analyte conditions.

Also, routine practical calibrations with geological and biological standard reference materials are recommended to explore versatility of X-Supreme 8000.

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