Standardless EDXRF technique using bremsstrahlung radiation from a transmission type x-ray generator

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Abstract:
We demonstrate the use of bremsstrahlung radiation in energy dispersive x-ray fluorescence technique as a tool to perform elemental analysis of solid samples employed in inter-disciplinary science research. The bremsstrahlung radiation can be taken from a small, portable, transmission type x-ray generator. Theoretically generated bremsstrahlung spectra are found to be in good agreement with the experimentally observed spectra obtained with various operating anode voltages of the x-ray generator. A computer program is written by using few atomic parameters to obtain the elemental concentrations in the sample by a single run. In this case knowledge of incoming x-ray flux, geometry of experimental arrangement are not required. To validate the technique, we have taken an Indian one-rupee coin of year 2000 as a sample, whose composition is well known, to expose to the bremsstrahlung radiation produced by the
operating voltages 20, 25, and 30 kV. The relative concentrations of different elements are determined, which is in good agreement with the earlier results.

1 Introduction:

In various scientific fields like geological, biological, environmental, atomic, and nuclear sciences, elemental analysis of the samples used in the experiments holds an important role for users. For this purpose, Energy-Dispersive x-ray Fluorescence (EDXRF) \[1\] technique makes an remarkable footstep. In comparison with other techniques like Particle Induced x-ray Emission (PIXE), Neutron Activation Analysis (NAA), it is cheaper as well as also easy to handle. EDXRF system may consist either a radioactive x-ray source or an x-ray generator, an x-ray detection device and a data acquisition system. Composition analysis using EDXRF technique can be done by two methods namely alpha co-efficient method\[2\] and Fundamental Parameter Method(FPM)\[3\]. Before the availability of the computer facility people made some calibration curves\[4\] manually with standard references in order to find elemental concentration of different elements existing in the sample. With the advancement of computer facility people started using alpha-coefficient method where exhaustive regression analysis is required. In this procedure there was a need of only ratio ($R_i$) of intensity of particular element coming from the sample to that from a standard. There was no need of knowing the values of the incident flux, experimental geometry, detector efficiency as well as photo-electric cross-sections. But for each and every element in the sample there was a need of making separate standards, which was very time consuming as well as costlier also. In comparison to the above technique, elemental analysis by Fundamental Parameter
Method (FPM) is quite simple. In this method either one can use monochromatic primary radiation coming directly from radioactive nuclei (e.g. $^{109}Cd$ and $^{241}Am$), or by using nearly monochromatic fluorescence radiation coming from secondary target due to the incidence of polychromatic primary radiation produced by an x-ray generator. In the later case weighted average energy of emitted $K\alpha$ and $K\beta$ radiation of secondary target can be treated as monoenergetic radiation which will be considered as the exciting radiation for the sample. Characteristic x-rays coming from different elements present in the sample can be detected. By using the intensities of the characteristic lines one can calculate the elemental concentrations with the help of detector efficiency and few atomic parameters such as photo-ionization cross-section, fluorescence yields, Coster-Kronig transitions etc. No standard sample is required in this method. In case of low power, small sized x-ray generator, emitting x-ray flux is very small. The intensity of the near monochromatic secondary radiation is even smaller which in turn will take longer time for accumulating appreciable statistics under different characteristic x-ray lines in the spectrum. So, one can take the whole bremsstrahlung coming from the x-ray generator for exciting the sample instead of taking the fluorescence radiation coming from the secondary target to solve the time consuming problem. But due to the presence of large band energy range in bremsstrahlung it is not an easy task.

In this paper we would like to demonstrate how one can use the whole bremsstrahlung radiation, coming from low power, transmission type portable [5, 6] x-ray generator (Amptek), to find the elemental concentrations of the samples using the principles of FPM. As per our knowledge goes, no attempt has ever been made for EDXRF technique by using ‘white spectrum’[7] of bremsstrahlung radiation directly coming from a transmission type x-ray generator.
2 Experiment:

Now a days in market very small sized x-ray generator is easily available to perform EDXRF analysis for elemental detection. If there is a stable power source like car battery, elemental analysis operation is possible for geological, archaeological, mineralogical, industrialsamples including in-situ analysis of any damaged samples. Here we have used an EDXRF system with a small transmission type portable x-ray generator of Amptek (Mini-X), having maximum operating power of 4 W with maximum attainable high voltage of 50 kV. This x-ray generator is made with metal-ceramic type anode consists of silver(Ag) backed with $\text{Al}_2\text{O}_3$. While performing our experiment we first record bremsstrahlung spectra directly for three different anode voltages of 20 kV, 25 kV and 30 kV coming from tube by placing x-ray detector in front of it at a distance of 12 cm air gap. To clean our required energy region, which is comparatively at the low energy side, we placed two absorbers of tungsten(W) and aluminium (Al) having thicknesses of 1 mil and 10 mil respectively in front of the x-ray generator. The efficiency of the detector is supplied by the manufacturer. The sample was placed in front of the x-ray generator to irradiate with bremsstrahlung in such a way that the entrance and exit angles of x-rays were fixed at 45° with respect to target plane.

3 Analysis:

For convenience we split our work in to two parts. Firstly, we have fitted the experimental bremsstrahlung spectrum with appropriate theoretical model for transmission type x-ray tube. Secondly, by using this bremsstrahlung x-ray as an exciter of the sample we find the concentrations of different elements present in the sample.
3.1 Bremsstrahlung Spectrum fitting:

To the best of our knowledge no attempt has been made to theoretically generate bremsstrahlung x-ray from a reflection type x-ray generator [8, 9]. We have used the semi-empirical[10] formula of Storm[11, 12] which is in good agreement with modified Kramer-Kulenkampff-Dyson (KKD) expression [13, 14] to reproduce x-ray bremsstrahlung theoretically. The modified KKD expression is given by

\[ I_{E_0,k} = \frac{11Z(E_0 - k)(1 - exp^{-3k/E_k})}{4\pi(k/E_0)^{\frac{1}{3}}(1 - exp^{-E_0/E_k})}f_{E_0,k} \times [\text{erg/s/mA/keV/sr}] \] (1)

where \( I_{E_0,k} \), \( Z \), \( E_0 \) are for bremsstrahlung emission intensity, target atomic number, incident electron energy in keV respectively. \( k \) and \( E_k \) denote emitted photon energy and K-shell ionization potential in keV of anode element respectively. Photon attenuation correction factor in silver anode of metal ceramic transmission type tube \( f_{E_0,k} \) is given by

\[ f_{E_0,k} = exp[-\mu_kx] \] (2)

where \( \mu_k \) is the total attenuation coefficient of a photon at energy \( k \) in silver. Effective thickness of silver anode can be calculated by using the following expression

\[ x = \frac{E_0^2 - k^2}{\rho C} \] (3)
where density of silver is denoted by $\rho$. The above mentioned equations (2) and (3) are the modified expressions for transmission type x-ray tube. $C$ is the Thompson-Whiddington constant which can be extracted by fitting the data given in the paper of Birch-Marshwall[15] for all the anode voltages.

To compare the bremsstrahlung emission intensity as given by equation (1) with the experimental spectrum, we converted it to the photon number in energy gap $\Delta k$ at photon energy $k$. This energy gap is exactly the same as we used during the calibration of our x-ray detector in present experiment. We maintain the same calibration through out our experiment for all the operating anode voltages. For conversion of bremsstrahlung emission intensity to photon number[11] we use the relation as follows

$$I_{E_0,k} = \frac{N_k \times 1.602 \times 10^3[\text{erg}]}{N_E \Delta k (\Omega/4\pi) \epsilon [\text{smAKeVsr}]}$$

where $N_k$ denotes the total photon number in the energy gap $\Delta k$. $N_E$, $\Omega$, $\epsilon$ are the total charge (nC) at the target, solid angle subtended by the x-ray detector at target and the detector efficiency at photon energy $k$ which is supplied by the manufacturer of the detector respectively.

Now this photon has to cross the ceramic ($Al_2O_3$) part of metal ceramic anode. As the thickness of $Al_2O_3$ is not supplied by the manufacturer, we normalised the theoretical spectra with different thicknesses through several trials in order to match the experimental one and used the same thickness of $Al_2O_3$ for all the operating anode voltages[17]. Two absorbers of aluminium and tungsten of thicknesses 1 mil and 10 mil respectively are placed to suppress the low energy side of the spectrum. Bremsstrahlung emission intensity that emerges out by passing through ceramic part of anode as well
as two absorbers is given by

\[ N_k^{\text{final}} = N_k e^{\sum (-\mu_k)_i(x)_i} \]  \hspace{1cm} (5)

i=1, 2 and 3 for \( Al_2O_3 \), aluminium and tungsten.

Figure 1 shows the bremsstrahlung spectrum with and without considering the efficiency of the detector as well as the experimental one. We also generated the characteristic lines of silver k x-rays due to the silver anode with the help of reference [18, 19]. However, contributions due to the characteristic lines, used as an exciter, is negligible in comparison to the continuous bremsstrahlung spectra. We have done this experiment for various operating anode voltages of 20 kV, 25 kV, 30 kV and for each case the experimental spectrum is perfectly matched with theoretical one.

\section*{3.2 Concentration Calculation:}

Now while considering the elemental analysis by monochromatic x-rays, fluorescent x-ray line intensity of an element \( (I_i) \) [20] can be written as

\[
I_i = \frac{I_0\Omega}{4\pi \sin \theta_1} [\sigma_i \omega_i f_i] A_i \epsilon_i C_i (1 + H_i)
\]

\[
= S[\sigma_i \omega_i f_i] A_i \epsilon_i C_i (1 + H_i)
\]

\[
= SV_i C_i \]  \hspace{1cm} (6)

where \( I_0, \Omega, \theta_1 \) are for incident flux, solid angle subtended by the detector with respect to the target and entrance angle, respectively. \( \sigma_i \) and \( \omega_i \) denote photo-ionization cross
section of the $i^{th}$ element for primary radiation and fluorescence yield. $f_i$ is the fraction of radiation of considered x-ray line and $A_i$ is the absorption correction not only for the primary x-rays but also for the fluorescent x-rays inside the target. $\epsilon_i$ is the detector efficiency for fluorescent radiation, $H_i$ is the inter-element enhancement factor and $C_i$ is for relative concentration for $i^{th}$ element of the sample. We calculate $I_i$ by the area under the K-alpha line of each sample. The other terms can be explained as

$$S = \frac{I_0 \Omega}{4\pi \sin \theta_1}$$

(7)

$$A_i = 1 - \exp(-[\mu_i^0 / \sin \theta_1 + \mu_i^i / \sin \theta_2]t)$$

(8)

$$\mu_s^0 = \sum C_i \mu_i^0;$$

(9)

$$\mu_s^i = \sum C_i \mu_i^i;$$

(10)

$$V_i = [\sigma_i \omega_i f_i] A_i \epsilon_i (1 + H_i)$$

(11)

where $\theta_2$ is for exit angle, $t$ denotes the thickness of sample, $\mu_s^0$ and $\mu_s^i$ denote the mass absorption coefficients of the sample for primary and fluorescent radiation, respectively. Inter-element enhancement factor $H_i$ for infinitely thick sample can be easily calculated by analytically developed expression of Spark[21] as given by

$$H_i = \frac{C_j [\sigma_0]_j [\omega_k f_k]_j [\sigma_j]_i}{2[\sigma_0]_i} \times \left\{ [\sin \theta_1 / \mu_s^0] \ln \left( \frac{\mu_s^0}{\mu_s^j} \sin \theta_1 \right) + 1 \right\}$$

$$+ [\sin \theta_2 / \mu_s^0] \ln \left( \frac{\mu_s^0}{\mu_s^j} \sin \theta_2 \right) + 1 \right\}$$

(12)

This enhancement factor denotes the effect of excitation of the $i^{th}$ element due to the $j^{th}$ element. $[\sigma_j]_i$ is for photo-ionization cross-section of the $i^{th}$ element due to the $j^{th}$ element where as $[\sigma_0]_i$ and $[\sigma_0]_j$ are the same for $i^{th}$ and $j^{th}$ element due to the primary
radiation. Now from equation (6) we can write

\[ C_i = \frac{I_i}{SV_i} \quad (13) \]

We have assumed that all the detectable elements will add up to 100%. To fulfill this condition we must use

\[ \sum C_i = 1 \quad (14) \]

So, by using the set of equations (6) to (13), assuming an initial arbitrary concentration of each element we can find the corresponding modified concentrations, which is used as assumed concentration for the next iteration. After each iteration, concentration of each elements \( C_i' \)s is normalized by

\[ C_i = \frac{C_i'}{\sum C_i'} \quad (15) \]

The above mentioned procedure is applicable only when monoenergetic x-rays are used as an exciter. But here we used bremsstrahlung coming from transmission type x-ray tube to irradiate the sample. In order to use the above procedure we divided the whole bremsstrahlung spectrum into a large number of energy slices so that each energy slice can be treated as a source of monoenergetic x-ray beam. We have calculated the concentrations \( C_i' \)s of each element for all the energy slices separately and add them up and normalize to get the modified one for the next iteration if needed.
4 Results and discussions:

Figure 2 shows the typical spectrum which we got due to the irradiation of our sample [Indian one rupee coin (2000)] by the bremsstrahlung radiation coming directly from transmission type x-ray tube operated at 25 kV anode voltage. By using the above procedure the concentrations of each element in the sample has been calculated and the result is shown in table 1 along with the previously published result [22] in which they used monochromatic x-rays as incident beam. Both the results agree well within the error bar.

The error in the concentration comes from only the terms $I_i$ and $V_i$. The term $S$ cancels out while normalizing the concentrations. Errors are almost negligible for the elements with higher concentrations. The error in $V_i$ is propagated through the errors in (i) photo-ionization cross section of k-shell($\sim2\%$) and (ii) atomic parameters ($\omega_f$) of k-shell ($\sim3\%$), (iii) mass attenuation coefficients ($\sim2\%$). Neglecting the error in $H_i$ due to its small contribution, the error in $C_i$ turns out to be within 3-8%.

Thus it can be seen that one can easily find the concentrations of each elements of the sample by irradiating them with bremsstrahlung radiation directly coming from a portable transmission type x-ray tube without using any secondary source as well as any standard references. The main advantages of this type of setup are (i) a very low powered portable x-ray tube can be used, (ii) which can be operated by using a stable power source like car battery, and (iii) with a laptop.
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### Results of Indian One Rupee Coin (2000) made of Cr and Fe

| Anode Voltage | Our Results          | Average Value | Earlier Results [22] |
|---------------|----------------------|---------------|----------------------|
| 20 KV         | Cr 17.1 ± 1.5        | 17.1 ± 1.4    | Cr 16.8 ± 1.2        |
|               | Fe 82.9 ± 4.2        | 82.9 ± 4.2    | Fe 83.2 ± 5.8        |
| 25 KV         | Cr 17.2 ± 1.4        |               |                      |
|               | Fe 82.8 ± 4.1        |               |                      |
| 30 KV         | Cr 16.9 ± 1.4        |               |                      |
|               | Fe 83.1 ± 4.3        |               |                      |
Figure 1

- Theoretically generated Bremsstrahlung
- Theoretically generated Bremsstrahlung including detector efficiency
- Experimental Bremsstrahlung

Operating anode voltage 30kV

Operating anode voltage 25kV

Operating anode voltage 20kV

Counts vs. Energy (KV)
Table 1: Concentration of Indian one rupee coin (2000)

Figure 1: Experimental (dotted), simulated (dashed line), simulated with inclusion of the efficiency of x-ray detector (red line) bremsstrahlung spectra for various operating anode voltages of the transmission type x-ray generator.

Figure 2 caption: A typical spectrum obtained due to bremsstrahlung x-ray irradiation, from a transmission type x-ray generator operating at 25 kV anode voltage, of an Indian one rupee coin [2000].