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Particle Induced X-ray Emission (PIXE): A Tool of Qualitative Elemental Analysis for Biological Sample

M. Hasnat Kabir
Dept. of Information and Communication Engineering
University of Rajshahi, Rajshahi 6205, Bangladesh.

Abstract

The facility of ion beam laboratory at Kochi University of Technology (KUT) has been extended by installing the Particle Induced X-ray Emission (PIXE) technique, in order to provide qualitative and quantitative elemental analysis and in-air micro-PIXE analysis. This paper is a description of PIXE setup and its application in biological sample for qualitative elemental analysis. The energy calibration of the system shows linearity. The minimum detection limit indicates that the system has good detection limit. The homogeneity shows uniformity of the sample itself and the internal standard within the sample. A 4 MeV He^{++} ion beam was used to analyze shellfish samples. Analyzing samples, it was found that the lower Z elements as well as some trace elements were detected.

Keywords: PIXE, LOD, Qualitative analysis.

1. Introduction

PIXE is a very powerful analytical technique among others for qualitative as well as quantitative analysis [1-2]. The multi-elemental, non-destructive and high sensitivity of PIXE technique makes it popular. This technique can detect several elements in a single analysis within a very short time. PIXE uses protons or heavier particles of a few MeV to generate characteristic X-rays. The elements in the target can identify from the energies of the characteristic peaks in the X-ray emission spectrum. In recent years, high-energy PIXE is widely used in different aspect for elemental analysis [3-6]. The experimental setup of Particle Induced X-ray Emission (PIXE) has been established in the ion beam laboratory at Kochi University of Technology, Japan. Its main mission is delivering the facility to perform quality research both in vacuum and in-air on different application fields such as environmental, geological, archeological and biological. The accuracy of elemental detection depends on experimental setup as well as homogeneity of the samples. In the case of measurement, it is quite important to know the essential parameters those are related to the experimental setup. Therefore, it is significant to standardize the precious energy calibration and minimum detection limit of the

system as well as the homogeneity of the samples those are presented in this paper.

2. Experimental

2.1 Instruments setup

A Nissin high voltage accelerator (NT1700S) with a 1.7 MV (Maximum voltage) has been setup at the beginning of ion beam laboratory at KUT. Target chamber is made by steeliness steel. The inner diameter of the target chamber was 50 cm. A computer control sample holder made by aluminium was placed inside the chamber which can tilt 45^o in y-axis whereas 180^o in x-axis. Sample holder was monitored by PC through a stepping motor. The diameter of beam spot on the target was about 1 mm with a roughly circular shape, defined by a graphite collimator. A camera was placed around 10 cm before to the beam entry in the analysis chamber to control the beam alignment and its focusing. The vacuum pressure could reach 10^{-6} torr inside the target chamber using a turbo-molecular pump [7]. In order to accurate measurement, secondary electron was suppressed by ring shape suppressor electrode shown in figure 1 which was placed in front of target with a biased voltage of -250 V . The distance between target and Si(Li) detector may vary from 15 to 50 mm. The collected charge was measured by current integration from the sample holder which was served as a Faraday cup, electrically isolated from the analysis chamber.

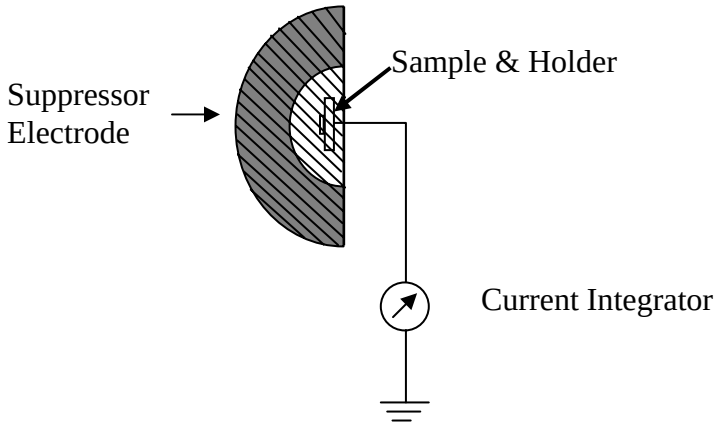

Figure 1: Sketch of suppressor electrode position.

RÖNTEC XFlash 2001, a Silicon Drift Detector (SDD) type detector was fixed at 135^{o} referring to the beam direction in the target chamber for detecting X-ray emission from targets. The active area and the silicon thickness of the detector are 10 mm^2 and 0.3 mm, respectively. A polymer coated beryllium window of 8 μm thickness is equipped with the detector. A zirconium ring with an aperture of 3.4 mm serves as a collimator in the detector. The detector was connected to a high resolution pulse processing unit with a single cable. The ORTEC 572 amplifier was coupled to the pulse processing unit to amplify the signal from the detector. This amplifier was used for its low noise, wide-gain range and selectable shaping networks. Finally, the output of the ORTEC 572 amplifier was then connected to a computer via an analog to digital converter (ADC) and a multi-channel analyzer (MCA).

2.2 Acquisition system setup

The data acquisition system should have the facility to improve multiple-parameter data-acquisition, on-line data visualization and monitoring which enable a wide range of ion-beam experiments. To achieve this goal, system was configured into two ways for data acquisition system: a front-end computer with MCAWIN software system for monitor and real-time data-acquisition, and a back-end system for data collection from the detector via processing unit, pre-amplifier and multi-channel analyzer (MCA). The transportation of data from the back-end to the front-end system is controlled by the front-end system. Block diagram of data acquisition system is shown in figure 2.

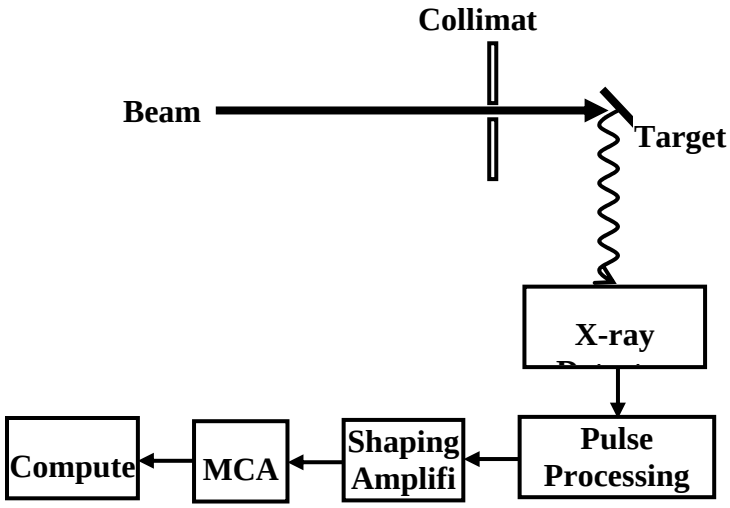

Figure 2: Block diagram of data acquisition system.

3. Energy Calibration

If it is considered a pulse-height spectrum containing *i*th peaks for the ions of energies E_i, then the centroids (Y_i) of the peak can be expressed as

$$Y_i = X_a + X_b E_i \qquad (1)$$

where X_a and X_b are constants. The centroid of a specific peak may be shifted due to high X-rays count rates, the linearity should be maintained by adjusting the value of parameters. In the pulse processor systems, the amount of peak shifting is very small, near about 1 eV at a rate of 100000 counts per second. Using equation (1), the energy calibration was done for the system shown in figure 3. It clearly shows the linearity of energy calibration as a function of channel of the desired system.

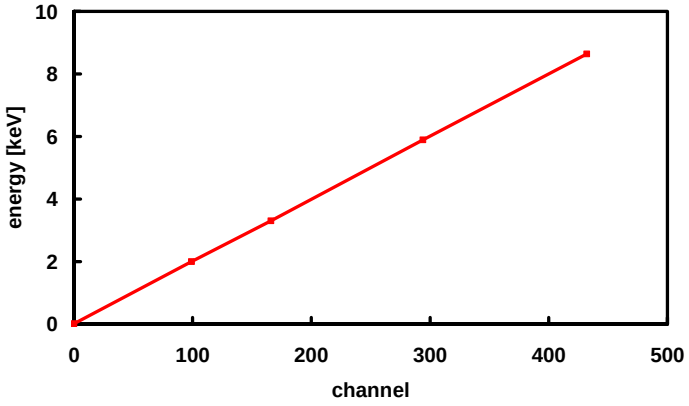

Figure 3: Energy calibration curve for PIXE analysis with XFlash 2001 detector.

The energy resolution of any detector is usually denoted as the full width at half-maximum (FWHM) of the Gaussian. The energy resolution of XFlash 2001 detector is 139 eV @ manganese K_α line, this is a general practice for energy calibration which is easily acquired from standard thin radionuclide sources [8]. The choice of manganese $K_{\alpha 1}$ line due to the small separation of 11 eV between the $K_{\alpha 1}$ and $K_{\beta 1}$ line, which is negligible for the system rather than the large separation of 173 eV for choice of silver. The K X-ray line of manganese is shown in figure 4 with indication of background level. This PIXE spectrum was routinely used to calibrate the spectroscopy system. It can be seen from this

figure that the system was calibrated as 20 eV per channel, i.e. Mn $K_{\alpha 1}$ at 295 channels.

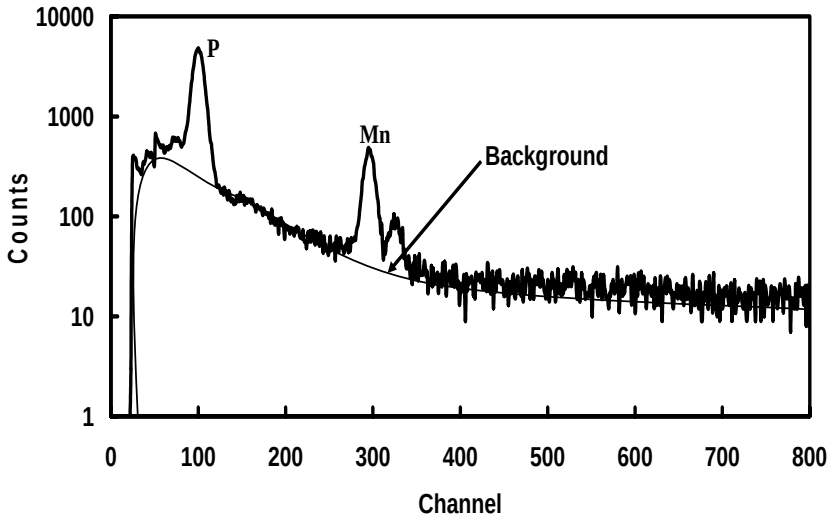

Figure 4: K X-ray spectra of Manganese for energy calibration.

4. Results and Discussion

4.1 Limit of Detection:

Since very low amount of materials are available in the biological sample, high sensitivity of the system is required for analysis. The detection limit of biological sample in PIXE analysis is below 1 μg/g which indicates the ability of trace-element analysis. The limit of detection (LOD) indicates the sensitivity of a measurement system. The LOD is correlated with the signal peak and the background for the measurement of fluorescence spectrum. Several calculation methods of the limit of detection in X-ray spectroscopy have been reported in literatures [9-11]. The beam current, counting time and accelerating voltage play the key role for calculating the detection limits. In PIXE analysis, the detection limit is calculated by assuming the minimum intensity of the peak is three times the square root of the background at full width half maximum intensity as indicated by equation,

$$LOD = \frac{3\sqrt{BG}}{S} * C \qquad (2)$$

where, *S* and *BG* are the total number of counts in the peak and background areas, respectively. *C* is the known concentration of the standard element. Figure 5 shows that the detection limits of PIXE system used in this study that is calculated using experimentally measured data of various standard samples. It is clearly seen from this figure that the detection limit is decreased despite the higher ionization cross-section for lighter elements. This is because of decreasing fluorescence yield, increasing bremsstrahlung background for lighter elements and increasing absorption in detector window [1]. For heavier elements the detection limit does not increase sharply even though the bremsstrahlung background is smaller. Because ionization cross-section is steeply decreased for heavier elements and detector efficiency is fall-off due to the high X-ray energies enough to penetrate the detector crystal without interacting. The detection limit of Ca was found less than one (0.14 ppm), clearly shown in this figure. This indicates that the system has a very good sensitivity to do experiment with biological sample.

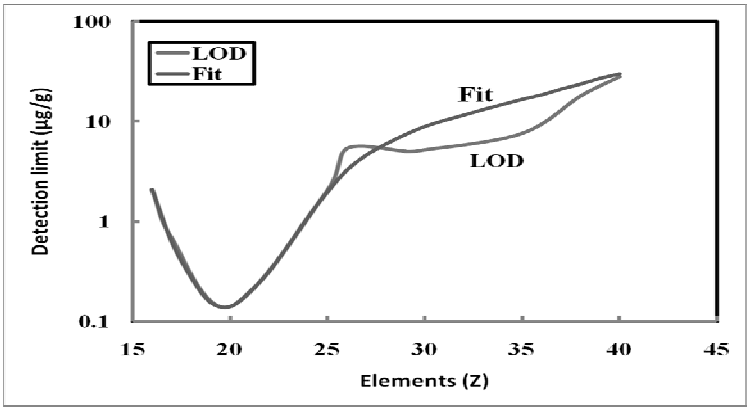

Figure 5: Limit of detection obtained with a 30 µC of 4 MeV He^{++} beam.

4.2 Homogeneity

The homogeneity of various elements in a sample is essential for a reliable analysis especially for applications of analytical techniques. In order to examine the homogeneity of different elements within a sample, it is necessary to take into account the variations of the measurements in a sample. The description of sampling and the preparation of sample can be found from our previous study [12]. The homogeneity of the sample was inspected by comparing three spectra taken from different places within a sample which was covered the three-forth area of the sample as shown in figure 6. The same beam conditions were applied for obtaining these spectra, therefore the ratio of internal standard and other

elements are nearly identical depending on the irradiation positions. This result represents the uniformity of both the sample itself and the internal standard within a sample.

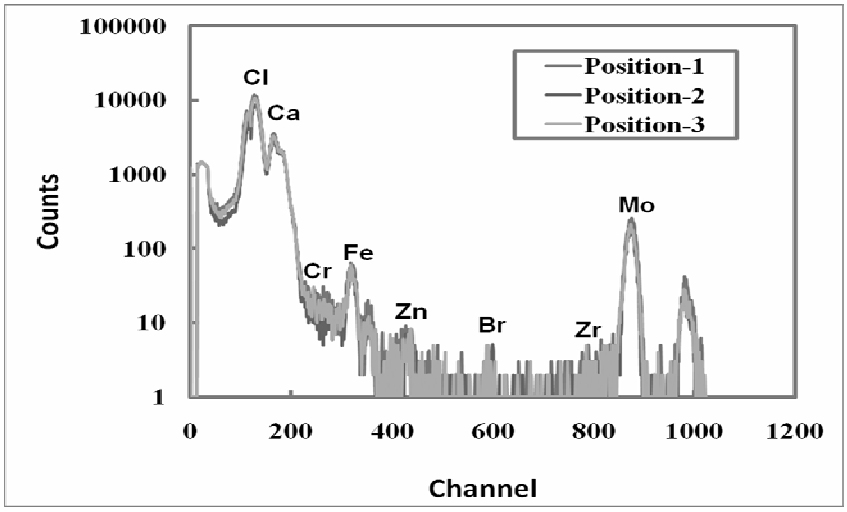

Figure 6: Homogeneity of the market shellfish obtained with 4MeV He^{++} beam.

4.3 Qualitative Analysis

It has performed the qualitative analysis of shellfish called Japanese littleneck clam (*Ruditapes philippinarum*) collected from Uranouchi bay, Kochi, Japan using Particle Induced X-ray Emission (PIXE). A brief description of Uranouchi bay can be found in elsewhere [13]. A 4 MeV He^{++} beam from 1.7 MV tanden accelerator with a 1mm circular size was used to analysis which was covered the quarter area of the samples.

A graphite collimator was used to collimate the beam size. The total distance between the target and Si(Li) detector was around 40 mm. The detector effective solid angle was 0.0063 sr. The sample was placed 300 mm apart from the beam collimator. The beam dose of about 30 μC was used for sample irradiation. Characteristic X-rays excited from targets were measured by an RÖNTEC XFlash 2001 detector positioned at 135° angle to the beam line. A 125 μm thick Mylar film was placed in front of X-rays detector, which was performed as a filter. Mylar was used to attenuate lower energy X-rays and to reduce X-rays interference. The experimental setup of the target chamber is shown in figure 7.

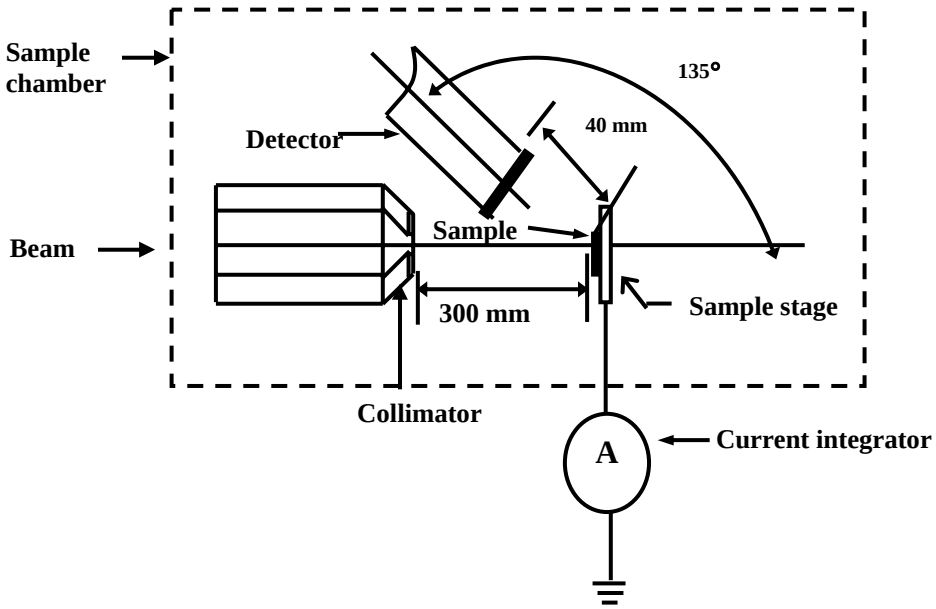

Figure 7: Experiment setup in the target chamber.

Figure 8 shows the typical PIXE spectrum of Uranouchi shellfish obtained with 4 MeV He^{++} beam. The detected elements are assigned as shown in this figure. The system was calibrated as 20 eV per channel. The $K_{\alpha 1}$ X-ray energy of Cl is 2.34 KeV. Therefore, $K_{\alpha 1}$ line of Cl should be appeared at channel 185 which is clearly shown in this figure. Similarly we can find other elements in the spectrum easily. The Mo signals come from 0.2 wt% internal Mo standard. In the present study, 4 MeV He^{++} ion beam was used which is equivalent to 1 MeV proton beam according to the scaling law of PWBA theory. Although 2-3 MeV proton beams are generally used for PIXE analysis but in this study He (Helium) ion beam was used because of some limitations in the laboratory.

Concerning the qualitative elemental analysis, Cl, Ca, Mn and Fe were detected as major low Z elements. The most attractive feature of this figure is Ca, which shows the higher concentration among other major elements. Naturally, Ca is rich in shellfish than other elements. The high concentration of Cl comes due to high NaCl content in marine environment. On the other hand, the element Cu, Zn, Br, Sr and Zr were detected as trace elements. The K line of these elements is prominently shown in this figure. It can be noted that it might be detected more

heavy elements with proton beam. However, this result point out that PIXE is a suitable technique for detecting lower Z elements as well as trace elements in a single analysis within a very short time.

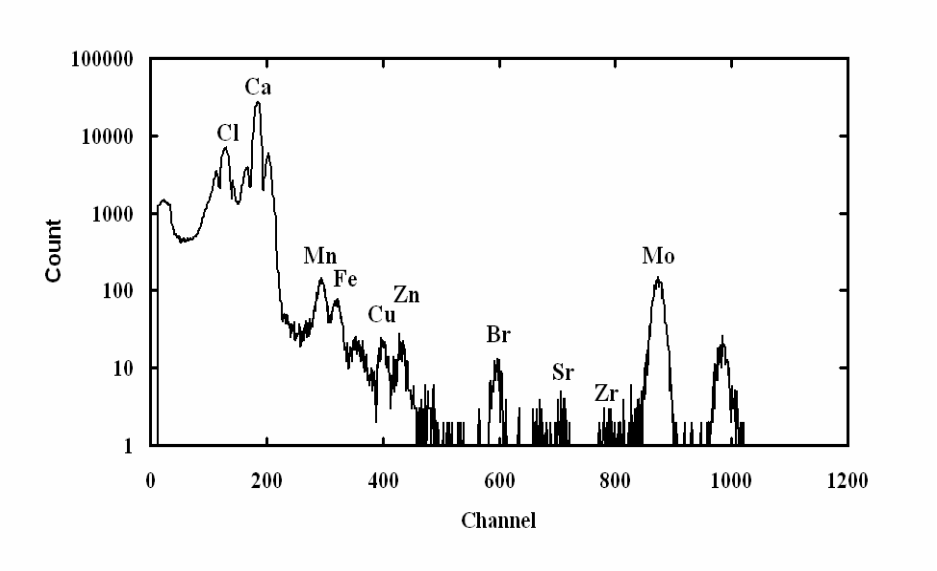

Figure 8: Typical PIXE spectrum of Uranouchi Shellfish obtained with a 4MeV He^{++} beam.

5. Conclusion

The uniformity between sample itself and internal standard for target preparation was confirmed by homogeneity check. The minimum detection limit of Ca is 0.14 ppm which represents very good sensitivity of the system. Analyzing shellfish, Cl, Ca, Mn and Fe were found as major elements whereas Cu, Zn, Br, Sr and Zr were detected as trace elements. Hence, it can be concluded from the present study that PIXE is a well-suited method for trace element analysis in biological sample.

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