

XRF Study on Some Indian Mackerel Samples

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Abstract—X-ray fluorescence analysis is a powerful analytical tool for the determination of almost all the elements present in a sample. The aim of this paper was to study the X-ray fluorescence emissions from some fish tissue samples. The excitation source used was an annular radioactive source of Am-241 and the X-ray fluorescence from the sample were counted using a high purity Germanium (HPGe) detector. The spectra obtained were analyzed using a Multi-Channel Analyzer-3 analyzer and Microsoft Excel. Seven fish samples of Indian Mackerel were bombarded with Am-241 photons without any sample preparation. Each data were collected for four hours. The X-ray fluorescence spectra from these samples were complex due to the presence of natural tissues of the fish. From the spectra obtained, there were some trace elements suggested to be present in the samples. The possible trace elements present in the sample were Manganese (Mn), Iron (Fe), Rubidium (Rb), Niobium (Nb), and Molybdenum (Mo). The presence of these trace elements might due to the essential nutrition of the fish

Keywords: x-ray fluorescence, XRF analysis, trace elements, biological sample

I. INTRODUCTION

X-RAY fluorescence (XRF) is the emission of characteristic "secondary" X-rays from a material that has been excited by bombarding with high-energy photons. Each element has electronic orbitals of characteristic energies. Therefore, x-ray fluorescence is a well-established technique of elemental analysis. The process of detecting and analyzing the emitted x-rays is called "X-ray Fluorescence Analysis." In most cases the innermost K and L shells are involved in X-ray Fluorescence detection. The phenomenon is also widely used for chemical analysis, particularly in the investigation of metals, glass, ceramics and building materials, and for research in geochemistry, forensic science and archaeology. This method is a non-destructive analytical technique.

In the following years after the discovery of characteristic x-rays, many researches and studies had been done employing the application of x-ray fluorescence. Radioisotopes excited x-ray fluorescence has been applied in the determination of copper impurity in gold ornaments [1], in elemental analysis of rubber samples [2] and elemental analysis in rock, ore and particulate matter [3]. Magalhaes., et al, (1995) has demonstrated the use of Am-241 to study the scattering of 60keV photon by biological materials [4].

The main purpose of this study was to analyze the XRF emitted from Indian Mackerel tissue sample. The XRF spectrum from the sample was analyzed based on the peaks present. Fish have been found to be a good indicator of heavy metal contamination in aquatic system. Usually, there will be some trace elements in fish due to the essential nutrition of fish. If the level of the materials exceeds the standard value, the fish could be hazardous for consumption.

II. MATERIALS AND METHODS

A. Experimental Design

XRF from the samples were measured with the experimental arrangement shown in Fig. 1. A 100 mCi, annular source of Am-241 was used as the excitation source of the fluorescence. The Am-241 was mounted in the source shield made of lead, parallel with the detector window. High-purity, germanium (HPGe) semiconductor detector was used for the detection fluorescence in the target. Germanium detectors have the best gamma-ray energy resolution available, giving them the greatest ability to identify and differentiate various gamma-ray emitting isotopes. The HPGe detector supplied by DSG Detector System GmbH; Semiplanar Detector Type: 1000-13. The detector coupled with a 0.25 mm Beryllium window thickness. The pre-amplifier type was REB-51 while the main amplifier was TC 244.

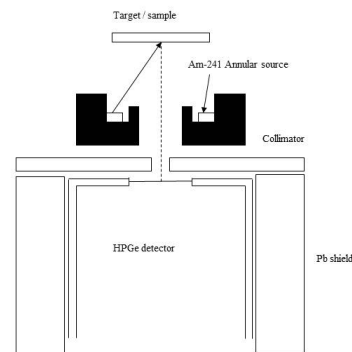


Fig 1: Experimental set-up

Amplified pulses from detector were analyzed in an 8000 channel analog to digital converter and recorder in a personal computer. MCA-3 Series / P7882 (supplied by FAST COMTEC) were used in order to analyze the amplified pulses from the detector. This MCA-3 Series / P7882 is a versatile family of advanced multichannel analyzers. This high-performance hardware is matched by sophisticated software delivered with each MCA-3; MCDWIN, the MS-WINDOWS, based operating software. The MCDWIN WINDOWS provide a powerful graphical user interface setup, data transfer and spectral data display. Once conversion has been accomplished, the extensive technology available for the storage and display of digital information can be utilized. The near-detector scattering was strongly reduced by a collimator made of a 3mm thick lead plate with a 4mm diameter hole, which was placed on the collimator holder 5cm in front of detector window. The detector was covered by lead shield in order to reduce the background resulting from cosmic rays and from natural radioactive traces in building materials. The shielding for the detector is absolute necessity for low-level measurement [5].

B. Energy Calibration

In gamma-ray spectroscopy with germanium detectors, the pulse height scale must be calibrated in terms of absolute gamma-ray energy if various peaks in the spectrum are to be properly identified. Accurate calibration should involve a standard source with gamma-ray energies that are not widely different from those to be measured in unknown spectrum. An Am-241 point source was used for the energy calibration. This radioactive source was used due to the two relative intense gamma-rays emitted with energy 26.35 keV and 59.94 keV and a number of several characteristic *L X-rays* lines [5] (Table 1). The source was placed at a distance of about 45 mm in front of the HPGe detector. The fine gain was set at 7 while the coarse gain set was 500. The spectrum was obtained for 1800 seconds.

C. XRF from Fish Samples

XRF spectra were obtained from natural fish tissues without any sample preparation. Seven samples of Indian Mackerel were bought daily from Pasar Taman Tun Sardon, Penang. The lengths of those samples were about 22 cm to 24 cm. The samples were placed on the sample holder in the set-up describe earlier (Fig. 1). Each sample was bombarded with Am-241 at the body part; from dorsal surface to the ventral surface, along the lateral line to the caudal peduncle of the fish [6]. The measurement was counted for about 4 hours. The fine gain was set at 7 while the coarse gain used was 500. Since there were no sample preparations done, the part of the fish studied was considered at the skin and slight contribution from the muscle. Before the measurement done, the background spectrum was obtained without sample. In order to get the real spectrum from the sample, the background spectrum was subtracted from the sample spectra.

III. RESULTS AND DISCUSSION

A. Energy Calibration

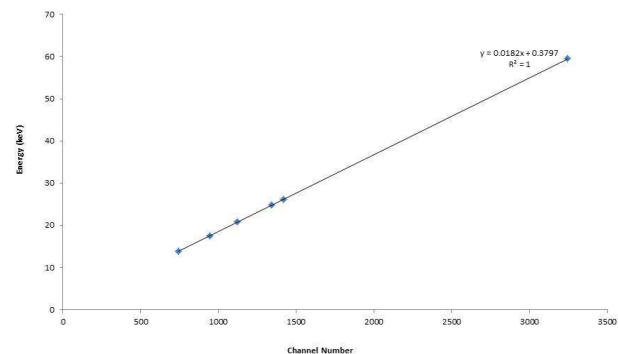


Fig. 2: Energy calibration curve of Am-241

The five main energies emitted from Am-241 were plotted against channel number to form a calibration curve (Fig. 2). Each peak corresponds to the standard energy emitted from Am-241 (Table I).

TABLE 1:
THE PHOTON ENERGIES EMITTED FROM Am-241

Types of radiation	Energy
L- α	13.9 keV
L- $\eta\beta$	17.6 keV
L- γ	20.8 keV
gamma-rays, γ	26.2 keV
gamma-rays, γ	59.5 keV

The linear regression coefficient, R^2 is 1. The curve is described by $E = 0.0182C + 0.03797$, where E is energy and C is channel number. The conversion factor is 0.0182 keV/channel.

B. XRF from Fish Samples

Fig. 3 shows a typical measured characteristic x-rays emitted from the Indian mackerel samples. The background spectrum was subtracted from the spectra from samples. Since all samples emitted similar XRF spectrum, only three of them were shown in Fig 3. Biological tissues or environmental samples consist of many elements; therefore they usually have very complex spectra due to backscatter effects and Compton interaction.

From the spectrum obtained, five peaks are prominent. The energy of each peak was calculated based on the calibration curve in Fig. 2. The energies were presented in Table 2. XRF energies emitted from the samples, there were some trace elements suggested to be present in the samples (Table II).

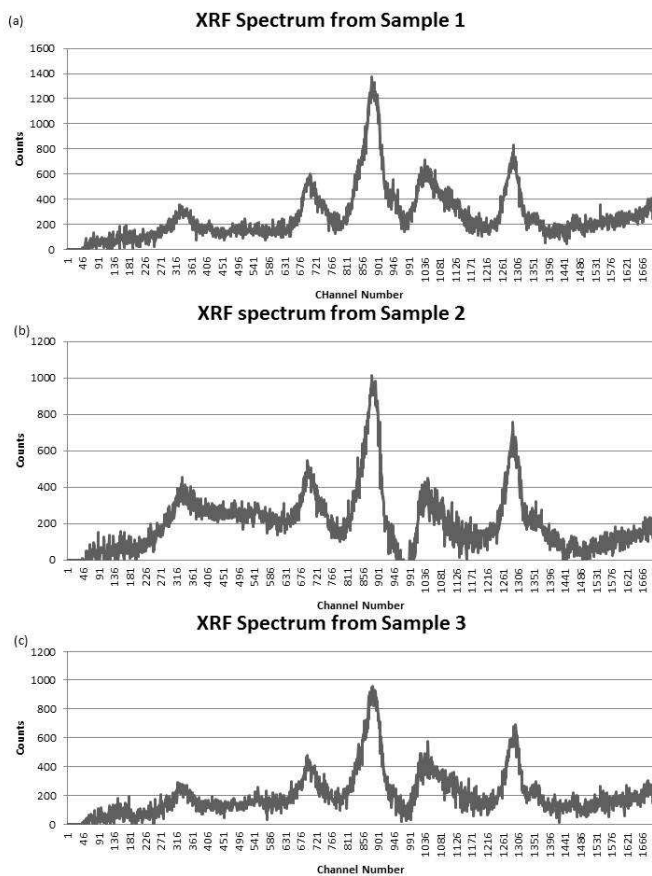


Fig. 3: XRF spectrum emitted from Indian Mackerel samples.

The trace elements present might be due to the essential nutrient in fish. Iron, Manganese and Rubidium has been reported found in some Indian Mackerel samples [7] and different amount of Mn present in different type of fish [8]. Manganese is an essential nutrient for both animals and plants. Iron is an essential macronutrient in the formation of hemoglobin and nutrients in numerous enzyme systems. Manganese and Iron are essential macronutrient for fish and the concentrations of these should be evaluated recognizing their roles as essential nutrients [9]. Rb also has been reported higher in muscle compared to liver and gill [7].

TABLE II
POSSIBLE ELEMENTS PRESENT IN THE SAMPLES DUE TO THE PEAKS IN THE SPECTRUM

Peak	Energy	Possible elements due to the XRF energy
Peak 1	6.39 – 6.51 keV	Manganese (Mn) K β ; 6.490 keV Iron (Fe) K α ; 6.403 keV.
Peak 2	13.08 – 13.31 keV	Rubidium (Rb) K α ; 13.3 keV
Peak 3	16.5 – 16.70 keV	Niobium (Nb) K α ; 16.5 keV.
Peak 4	19.27 – 19.81 keV	Molybdenum (Mo) K β ; 19.608 keV
Peak 5	23.92 – 24.02 keV	Am-241 photons

This study was carried out without any special preparation therefore only the body region were evaluated, which more

prominent at the skin of the fish. Concentration of trace element in fish varies at different part of the fish. Heavy metals are taken up through different organs of the fish because of the affinity between them. In Malaysia, Tetsuro et al. (2005) did the first study on multielemental accumulation in marine fish from the Malaysian coast and they found that levels of V, Cr, Mn, Co, Cu, Zn, Ga, Sr, Mo, Ag, Cd, Sn, Ba and Pb in liver were higher than those in muscle, whereas Rb and Cs concentrations showed the opposite trend[7].

The concentration of the trace elements present should be related to the intensities of characteristic x-ray line of each peak, but the relation is not simple. The measured intensity of single emission line depends on the energy spectrum and of exciting x-rays, on the efficiency of the detector and the geometry of source and sample. It also depends on the other elements in the sample.

IV. CONCLUSION

The result from this study suggested there were several trace elements suspected to be present in the Indian Mackerel sample. However, levels or concentration of the trace elements present cannot be identified; further study should be done in consideration of sample preparation and the part of evaluation. As recommendation, study of XRF from different parts of fish tissue such as gills and liver should be suggested. Furthermore, different types of fish can be used as the sample or fish from different market should be compared. For more deep study, the sample also suggested to prepare in the powder form or in palette form.

V. LIMITATION

Basically, this study was done based on X-ray fluorescence analysis method to examine the elements presents in fish tissue; Indian Mackerel samples. Since there are some constraints, sample preparation cannot be done properly. So, this study covers only XRF from natural fresh samples tissue.

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