Proton Induced X-ray Emission Analysis of Trace Elements in Thick Bread Samples

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Proton induced X-ray emission (PIXE) technique has been used for identification and quantitative analysis of the elemental concentration in thick bread samples. Bread samples were air-oven dried at 60 °C and milled in a clean agate mortar to homogenize the sample and pressed into a pellet. PIXE technique relies on the analysis of the energy spectra of the characteristic X-ray emitted from the thick bread sample and the orchard leaf standard (NIST- SRM -1571) bombarded with 2.0 MeV protons. The concentration of the elements (Cl, K, Ca, Mn, Fe, Cu, and Zn) in the bread samples was determined by comparison with NIST orchard leaf standard. The accuracy of the measurements ranged between ±2% and ±10% for the most elements detected in this method. The aim of this study is to establish the reference concentration of trace elements in the Iraqi bread using PIXE technique.

Keywords: Thick bread samples; PIXE technique; elemental concentration; quantitative analysis.

1. Introduction

PIXE,\(^{1-12}\) thick target particle induced X-ray emission (TTPIXE),\(^{13-15}\) and particle induced gamma emission (PIGE)\(^{13,15}\) have recently emerged as powerful analytical tool for the elemental analysis of materials. The detection limits of PIXE technique are in the parts per million (ppm) ranges which can be routinely achieved.

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However, in certain cases the detection limits of PIXE was extended in the parts per billion (ppb) range\textsuperscript{3,8,9} depending on the elemental concentrations, energy and total charge of incident particles, and the quality of the detector being used for the analysis.

So far PIXE, PIGE, X-ray fluorescence (XRF)\textsuperscript{16} and radioisotope induced X-ray fluorescence (RIXRF)\textsuperscript{17} have been demonstrated as adequate and nondestructive techniques for the study of multi-elemental concentrations in vegetables,\textsuperscript{4} water,\textsuperscript{5,9} honey,\textsuperscript{7} raw cow milk,\textsuperscript{8} rice flour,\textsuperscript{10} water residues\textsuperscript{14} and in organic objects,\textsuperscript{11} archaeological bronze,\textsuperscript{12} biological samples\textsuperscript{16,17} and human stones.\textsuperscript{18} Recently energy-dispersive X-ray fluorescence (EDXRF) technique has been used for elemental analysis of vegetable,\textsuperscript{19} human milk\textsuperscript{20} and copper coins.\textsuperscript{21}

Trace element analysis can be carried out by either, XRF, EDXRF and neutron activation analysis (NAA)\textsuperscript{22} or X-ray emission spectroscopy. The selection of an appropriate analytical technique is decided by many factors. Methods differ widely in their sensitivity, quantitative analysis, precision, accuracy, detection limits, ease of operation and cost. The analytical tool of X-ray emission spectroscopy is more convenient, non-destructive multi-elemental analysis, adequate, faster and cheaper than other techniques.\textsuperscript{11–13,17}

Charged particles induced X-ray emission (PIXE) has the advantage of large cross section for X-ray production, and the background contribution from bremsstrahlung radiation is low,\textsuperscript{4} which results in enhanced sensitivity in the peaks. These features of PIXE greatly improve the signal-to-background ratio of trace elements\textsuperscript{2–4} in the spectra, and enable to detect much lower levels of concentration in the parts per billion range.\textsuperscript{2,3,8,9}

There is growing interest in quantitative determination of toxic elements in the environment. The determination of trace elements composition of bread samples has made a valuable contribution to environmental sciences and toxicology. These elements are often present in very small concentrations in bread, water and food, and for long time has an effect on the human health.

Bread is widely eaten three times in a day by most Iraqi people and is considered the most important daily dietary. Bread samples were collected during 2007/2008 from 10 different bakeries in Baghdad.

This paper describes the PIXE technique for identification and quantitative measurement of multi-elements in thick dry bread samples by bombarding the samples and the NIST (National Institute of Standards and Technology) standard reference materials with 2.0 MeV protons which then induced X-ray emission characteristic energies from elements present in the bread samples. NIST- orchard leaf (NIST- SRM-1571) was used as a standard material for the analysis of all elements present in the bread samples. So far, no data available for bread in Iraq or in other countries to compare our experimental results with.
2. Experimental Procedure

2.1. Sample preparation for PIXE analysis

White bread samples (grains were produced from Australia) were collected during 2007/2008 from ten different bakeries in Baghdad. The samples were air dried in oven at 60°C under atmospheric pressure and subsequently homogenized and grounded with a clean agate mortar to fine powder. The targets of ground bread were prepared as pellets of 4 mm thick and 15 mm diameter, using a stainless steel hand-press pellet maker and irradiated with 2.0 MeV protons.

2.2. PIXE experimental setup

The proton beam has been obtained from 2.0 MeV Van de Graaff accelerator at the King Saud University. The proton beam was incident on the target in the scattering chamber, and the X-rays were detected by a Si(Li) X-ray detector. The advantage of using Li-drifted silicon was the ability to measure the entire spectrum simultaneously with the help of computers. A simple scattering chamber is shown in Fig. 1 which has been designed for the present PIXE experiment. It is made of brass and consists of two parts. The first part A is a tube with a diameter of 60 mm with one end cut at an angle of 45° with respect to the incident proton beam, while the other end has a similar flange. Part B can be introduced into the tube A closing its open end. The two parts fitted together with screws and an O-ring was used between the flanges to ensure a vacuum tight connection. The chamber was isolated from the beam tube so that the ion beam current can be measured in the chamber directly. The nominal beam current was 12 nA. Before the beam enters the chamber, it passes through a tantalum collimator which has a 2 mm diameter aperture. The collimator has been electrically isolated from the rest of the beam tube and the target chamber. The target is fixed at 45° inclined surface using two clamps (see Fig. 1). X-rays emitted by the target through a thin window covered with Kapton foil of a 50 μm thick in the scattering chamber and detected by Si(Li) X-ray detector. Kapton foil is allowed an increase in the signal-to-noise ratio of trace elements. The cooling fluid has been introduced into part B through a narrow tube to cool the target.

The PIXE spectrometer in the present study consisted of a 30 mm² Si(Li) detector with a resolution of 175 eV (FWHM) at 5.9 keV (Mn Kα, X-rays), charge sensitive preamplifier, an analogue-to-digital converter (ADC) and a computerized multichannel analyzer. The X-ray spectra from the detector were accumulated in a multichannel analyzer that was interfaced to the on-line computer using GUPIX software. The area under each peak of the spectrum was calculated individually and was subtracted from the background. The concentrations of the elements in the bread samples were estimated by comparison with the characteristic X-rays signals to those obtained from charged leaf, standard reference materials (NIST-SRM-1571). In this study, the standard reference elements used are actually very similar in composition to the bread samples analyzed.
3. Methods of Analysis of Thick Targets

The analysis is performed by first measuring the X-ray yield $A_i(E)$ at X-ray energy detected in the peaks of the spectrum by Campbell et al.,\textsuperscript{25} according to the following equation:

$$A_i(E) = N_iN_pC_i(\Omega/4\pi)\mu_i \int_0^E \sigma_i(E)[S(E)]^{-1} \exp(-\mu_i x) dE$$  \hfill (1)

where $A_i(E) =$ X-ray yield at X-ray energy corresponding to the ith element in the sample

- $N_i =$ number of target atoms per unit volume of the element $i$
- $N_p =$ number of incident protons at the same energy $E$
- $C_i =$ detector efficiency at X-ray energy corresponding to the element $i$
- $\Omega =$ detector solid angle
- $\mu_i =$ absorption coefficient for X-rays of element $i$th in emerging a path length $x$ in thick sample
- $\sigma_i(E) =$ X-ray production cross section for the element $i$th
- $S(E) =$ stopping power of proton at energy $E$ in thick bread sample
- $dE =$ energy loss of protons in thick bread sample.

If a sample contains more than one atomic component contributing to the stopping power, the total stopping power can be calculated using Bragg–Kleeman rule as given by:

$$S(E) = \sum_{i=1}^{n} C_i S_i(E)$$  \hfill (2)
where

\[ S(E) = \text{the stopping power of the matrix for proton energy } E \]

\[ N = \text{number of the atomic component} \]

\[ S_i(E) = \text{the stopping power of the } i\text{th element in bread sample} \]

\[ C_i = \text{the fraction of the } i\text{th element in the matrix} \quad (= 1 \text{ for pure element}). \]

In our case Eq. (1) becomes:

\[ A_i(E) = N_i N_p E (\Omega / 4 \pi) \mu_i C_i \int_0^\infty \sigma_i(E) |S_{\alpha}(E)|^{-1} \exp(-\mu_\alpha x) dE \quad (3) \]

where \( \mu_\alpha \) refers to the absorption coefficient for the X-rays in the bread sample and \( S_{\alpha} \) refers to the absorption stopping power of the bread sample.

The method used in the present work to determine the concentration \( C_i \) of the \( i\text{th element in the matrix} \) was based on the comparison of X-ray yield \( A_{ib}(E) \) from a thick bread sample to that from a standard pure sample \( A_{is}(E) \) of the element \( i\text{th when bombarded under the same experimental conditions and with the same number of protons } N_p \) at the same energy \( E \) and the same geometry. It was felt unnecessary to correct them for geometry, detector efficiency or X-ray absorption after leaving the target. Thus, we have:

\[ \frac{A_{ib}}{A_{is}} = C \frac{I_b}{I_s} \quad (4) \]

where \( I_b \) and \( I_s \) are the integral intensity values in Eq. (3) for thick bread sample and standard element respectively. In the above equation \( C \) refers to the concentration ratio of the trace elements in bread \( (C_b) \) sample to that in the standard reference \( (C_s) \) sample.

Since the bread sample has the element \( i\text{th as its main constituent} \), one can assume that the values of the two integrals \( I_b \) and \( I_s \) will contribute the same i.e. \( I_b \approx I_s \).\textsuperscript{26,27} In this case Eq. (4) will have the form of:

\[ C = \frac{C_b}{C_s} = \frac{A_{ib}}{A_{is}}. \quad (5) \]

Equation (5) was used to obtain the concentration of some elements present in each thick bread sample.

4. Results and Discussion

It is clear that the detector resolution (175 eV FWHM) was quite adequate to resolve X-ray lines for all elements studies. Figure 2 shows a typical PIXE spectrum obtained from dry thick bread sample. It consists of a number of peaks corresponding to \( K_\alpha \) and \( K_\beta \) X-rays of the elements indicated in the bread sample. For determining the elemental concentration Eq. (5) has been employed which assumes that for thick targets the correction factor is the same for both the dry bread samples and the standard reference elements.
Fig. 2. Typical PIXE spectrum of thick bread sample using 2.0 MeV protons.

Table 1. The concentration of the elements in orchard leaf (NIST-SRM-1571) standard reference materials used for PIXE procedure.

<table>
<thead>
<tr>
<th>Element</th>
<th>This work Mean ± S.D. (ppm)</th>
<th>Certified value ± S.D. (ppm)</th>
<th>Accuracy (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>13965 ± 556</td>
<td>14700 ± 300</td>
<td>-5.0</td>
</tr>
<tr>
<td>Ca</td>
<td>21700 ± 510</td>
<td>20900 ± 300</td>
<td>-8.83</td>
</tr>
<tr>
<td>Mn</td>
<td>93.2 ± 4.5</td>
<td>91 ± 4</td>
<td>2.42</td>
</tr>
<tr>
<td>Fe</td>
<td>290 ± 18</td>
<td>300 ± 20</td>
<td>-3.33</td>
</tr>
<tr>
<td>Cu</td>
<td>13.15 ± 1.0</td>
<td>12 ± 1</td>
<td>9.58</td>
</tr>
<tr>
<td>Zn</td>
<td>26.5 ± 2.5</td>
<td>25 ± 3</td>
<td>6.0</td>
</tr>
<tr>
<td>As</td>
<td>9.5 ± 1.3</td>
<td>10 ± 2</td>
<td>-5.0</td>
</tr>
<tr>
<td>Br</td>
<td>10.3 ± 0.5</td>
<td>(10)</td>
<td>3.0</td>
</tr>
<tr>
<td>Rb</td>
<td>12.5 ± 1.2</td>
<td>12 ± 1</td>
<td>14.16</td>
</tr>
<tr>
<td>Sr</td>
<td>30 ± 1.0</td>
<td>37 ± 1</td>
<td>-2.7</td>
</tr>
</tbody>
</table>

S.D. = Standard deviation.

In this study, the accuracy of the measurements was checked using NIST or charged leaf standard. Table 1 gives the mean values of the elemental concentrations detected in NIST-SRM-1571 compared with certified values. The accuracy of the measurements is within ±2% to ±10%.
Table 2. Mean values and standard deviation for elemental concentration in thick bread samples using PIXE technique.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean concentration ± S.D. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>0.485 ± 0.162*</td>
</tr>
<tr>
<td>K</td>
<td>3778 ± 529</td>
</tr>
<tr>
<td>Ca</td>
<td>2257.2 ± 502</td>
</tr>
<tr>
<td>Mn</td>
<td>0.125 ± 0.033</td>
</tr>
<tr>
<td>Fe</td>
<td>0.1148 ± 0.029</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0966 ± 0.014</td>
</tr>
<tr>
<td>Zn</td>
<td>0.2214 ± 0.033</td>
</tr>
</tbody>
</table>

* = Concentration in percent (%)

The mean concentration values and the standard deviation in ppm for elements (Cl, K, Ca, Mn, Fe, Cu, and Zn) in bread samples from 10 different bakeries in Baghdad are summarized in Table 2. No experimental data available for bread sample in Iraq or in other countries to compare our experimental results with.

The overall errors presented in the mean values represent the counting statistical error in the range of (±1 to ±10%) and the proton beam current measurements (±2%). However, the total uncertainty in these results is probably in the range of ±1 to ±10%.2,3 This is in agreement with the data published by Vodopivec et al.11 and Cohen et al.13 which show that the precision of the results ranged from ±5% to ±10% for thick target PIXE analysis and Yamazaki et al.6 which shows that the experimental error less than ±14% depending on the elemental concentrations and may be affected by particle size in-homogeneities. This limit of uncertainty is typical for PIXE analysis of thick samples13,15,17 because of the errors introduced in calculating the correction factor.

Despite of all the mentioned source of errors, the present results clearly demonstrate the ability of the PIXE technique for determination of elemental composition down to trace levels.2–4,16,17

5. Conclusions

The main goal of this study was to establish the reference concentrations of trace elements of Cl, K, Ca, Mn, Fe, Cu, and Zn in Iraqi bread samples using PIXE technique. The determination of trace elements composition of bread samples has made a valuable contribution to environmental science and toxicology.
References


