Determination of uranium and thorium in zircon by energy dispersive X-ray fluorescence technique

V Natarajan*, N K Porwal & S V Godbole
Radiochemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085 India

Received 19 September 2011 ; accepted 29 March 2012

An energy dispersive X-ray fluorescence method has been developed for the determination of uranium and thorium in zircon, using synthetic powder standards containing uranium and thorium in the range 50 - 1000 ppm. After optimization of instrumental parameters, calibration is carried out using six synthetically prepared standards in pellet form. The experimental limits of detection for uranium and thorium analytes are found to be 200 and 100 ppm respectively. The accuracy of the method has been evaluated by measuring the concentration of uranium and thorium in two synthetic samples and is found to be about ± 5%. Three ore samples have been analyzed by the proposed method and by gamma spectrometry and/or neutron activation analytical techniques for uranium and thorium. The standardized method can be used for fast determination of uranium and thorium in zircon samples non-destructively with a precision of ± 5 - 20%.

Keywords: Energy dispersive x-ray fluorescence technique, Thorium, Uranium, Zircon

Zircon is a naturally occurring silicate mineral, majority of which is ZrSiO₄ and is available in many locations all over the world. Many zircon varieties contain traces of thorium (Th) and uranium (U) at about 100-1000 parts per million (ppm) level¹,² and may exhibit natural low level radioactivity. Siyanbola et al.³ used energy dispersive X-ray fluorescence spectrometry (EDXRFS) to determine qualitatively the elemental composition of natural zircons obtained from Jos plateau, Nigeria. Meor Yusoff⁴ utilized EDXRFS to determine the selective leaching of uranium and thorium from zircon. Further, it has been demonstrated ⁵,⁷ that zircon exhibits characteristics that are location specific. In terms of applications, the mineral has also been identified as a potentially useful material for the production of TL dosimeters⁸. Besides, zircon finds use as refractory material in the glass and iron industry, in abrasives and in the manufacture of zirconia and zirconium chemicals as well as in ceramics⁹. Recent interest in zircon is centered on its potential use as a host phase for the disposal of radioactive actinides such as weapon grade plutonium¹⁰-¹² arising because of its high chemical durability. In nuclear power, zirconium is used in the alloy form as a cladding tube to contain reactor fuel, etc. It is also used in chemical equipment and electronic industries.

Several techniques have been developed for the determination of trace elements in nuclear materials. Trace concentrations are usually determined by neutron activation analysis¹², inductively coupled plasma optical emission spectrometry (ICP-OES)¹³ and spectrography¹⁴. Roy et al.¹⁵ reported the estimation of Ti, Zr, Nb, Hf, Ta, Th and U in beach placers and ferrodiorites by inductively coupled plasma-mass spectroscopy using fusion digestion technique. These techniques are very sensitive but have some disadvantages, such as the use of sophisticated equipment, time-consuming chemical pretreatment of samples and interferences. Time to produce results from these methods vary from a few hours to several days. The production chemist is expected to conduct between 5 and 10 analyses per hour for process control purposes. A suitable technique that fits this requirement is x-ray fluorescence. Louw¹⁶ reviewed the work related to U and Th analysis in zircon. Bazzarri et al¹⁷. determined U in zircon by fluorimetry and alpha spectrometry and Th in zircon by colorimetry and alpha spectrometry. Asakura et al.¹⁸ determined Si, Al, Fe, Ti, Cu, Mg, Na, K, P, Cr, Zr and Hf in series of reference materials by x-ray fluorescence spectrometry.

The Kβ x-rays for Th and U extend from 93.35 keV to 97.75 keV. Although such high energies cannot be obtained with the existing x-ray machine, Lα and Lβ x-rays of Th and U can be utilized with ease gainfully.

*Corresponding author.
E-mail: vnatra@yahoo.co.in
In comparison with the conventional methods, EDXRF has additional advantages, such as rapid analysis and minimum handling of the sample without any need of sample dissolution, simultaneous determination of many analytes including minor and major elements and non destructive in the sense that rare or precious samples as well as calibration standards can be tested an unlimited number of times. The present study is aimed at demonstrating the feasibility of EDXRFS method for the determination of U and Th quantitatively in zircon ores without sample dissolution.

Experimental Procedure

Instrumental conditions
A Jordan Valley EX-3600 M EDXRF spectrometer, equipped with a Rh source, an assembly of 6 filters (Cu, Fe, Mo, Rh, Sn and Ti) and a Si(Li) detector with a 12.5 µ thick beryllium window was used for the determination of U and Th in zircon matrix. The instrument is equipped with a 10-position sample chamber for measuring samples sequentially. Samples can be handled in solid, powder or liquid form. For the present work, only air medium in the sample chamber was used. The system software (nEXT) for spectra acquisition and analysis runs under Windows NT 4.0 or higher operating system. Si(Li) detector has a resolution of 139 eV at Mn-Kα (5.9 keV) and is capable of acquiring a spectrum in the 1-40 keV region. The data acquired was processed with the help of the attached computer. The resulting intensity is expressed in counts per second (cps). In the sample chamber, the samples are placed in teflon cup assemblies, whose bases are fitted with mylar film of thickness 6.3 µm for supporting purpose.

Preparation of standards and samples
A series of synthetic standards containing U and Th was prepared by blending pre-analyzed pure ThO₂ and U₃O₈ powders with specpure zirconium oxide and silica (99.999%) in an appropriate ratio and grinding thoroughly for fixed time intervals. Thus, five standards were prepared with U and Th concentrations at 100, 200, 500, 600 and 1000 ppm level in the required matrix in addition to a blank standard without U/Th. Further, two synthetic samples with U and Th concentrations at 300 ppm and 750 ppm were also prepared in a similar manner in order to check the precision and accuracy of the developed technique. Three zircon ore-samples, obtained from different locations in India, were analyzed by the developed method and the same samples were analyzed by gamma spectrometry and neutron activation (NAA) technique. 100 mg each of the standard as well as the samples were mixed with 100 mg of cellulose (binder) and made into pellets of 1 cm diameter. The cross-sectional area for the central aperture of the x-ray beam at the sampling location is of circular dimension with 8 mm diameter. The pellets were always centrally and uniformly placed in the sample holder with the help of a polyvinyl chloride tubular guide of 12 mm diameter.

Optimization
Optimization of the experimental parameters was carried out with synthetic standard having U and Th concentration of 1000 ppm. X-ray tube voltage for Rh source and current were varied, without any filter and with Mo, Rh and Sn filters, in order to arrive at optimum parameters for obtaining maximum counts and sensitivity. Mo filter was found to provide best results for U and Th in zircon matrix. Final instrumental parameters chosen for calibration are as follows: Rh source, Mo filter, tube voltage 30 keV, tube current 100 µA, counting time 200 s, medium air and U Lα peak 13.6 keV/Th Lα peak 12.9 keV. Counts for each standard was obtained under these conditions in air and the data was stored. While fitting the data utilizing an equation, we have used linear regression method available in the software nEXt. By matching standard and sample composition, inter-element interference effects have been minimized. Calibration plots were prepared using these data for U-Lα x-ray at 13.6 keV and Th-Lα x-ray at 12.9 keV. Two synthetic samples were analyzed by the present method for U and Th. In addition, three ore samples were analyzed by the present method and also by gamma spectrometry and neutron activation analytical techniques for uranium. In the case of Th, the ore samples were analyzed by the present method as well as by gamma spectrometry.

Results and Discussion
While optimizing the different instrumental parameters, calibration was done in gross mode as well as in digital-filter mode, wherein the background correction is automatically taken into account by the computer. The digital-filter mode is found to be more precise. The intensity in terms of counts per second (cps) and calculated concentration values for the different synthetic standards obtained, using the calibration program, are listed in Table 1. It may be
noted that the intensity value for synthetic standard with 100 ppm of U is marginally higher than the blank standard. Further, in the case of synthetic standards, all the calculated values from the calibration plots for respective concentrations are found closer to the added values of uranium and thorium. The calibration plots for U and Th Lα peaks in the synthetic standards were obtained using the following relationship:

\[
\text{Concentration} = A_0 + A_1 \times (\text{Signal Intensity})
\]

where \(A_0\) is the constant; and \(A_1\), the slope parameter obtained. These plots are shown in Fig. 1.

The reproducibility of the uranium and thorium determination was evaluated by conducting eight measurements on two synthetic samples. The determined concentrations are shown in Table 2 for synthetic sample-1 (added amount at 300 ppm level) and synthetic sample-2 (added amount at 750 ppm level). Here, the agreement between the determined values and the added concentrations is found to be quite good. The precision of the determination is found to be within ±3-12%, depending upon the region of concentration (high/low) for the analyte. Comparison of the mean determined values for U and Th with their added concentration values suggests that the accuracy of the method is within ±5%. However, no standard reference material was available for further ascertaining this value. Considering the intensity values for blank and 100 ppm standards and their reproducibility, the experimental limits of detection for U and Th analytes are determined to be 200 and 100 ppm respectively.

Three zircon ore samples, previously analyzed using gamma spectrometry by utilizing \(^{235}\)U gamma ray of 1001 keV, \(^{235}\)U gamma ray of 185 keV and neutron activation analysis, were analyzed using this procedure for U concentration and the results are given in Table 3. It can be seen from this table that the agreement between the values obtained for uranium from three different techniques for the three different ore samples is good. The same ore samples were analyzed for Th concentration by the present method and also by gamma spectrometry using gamma ray of 911 keV for thorium determination (911 keV corresponds to \(^{228}\)Ac, which is in secular equilibrium with \(^{232}\)Th) and the results for the same are given in Table 3. The values obtained by the present method are found to be comparable with the values reported by gamma spectrometry. Compared to gamma spectrometry and neutron activation analysis techniques, EDXRF analysis is very fast, involving negligible sample preparation and less analysis time.

### Table 1—Intensities of U and Th peaks and calculated concentrations of U and Th in zircon standards

<table>
<thead>
<tr>
<th>U/Th conc. (in standards) ppm</th>
<th>Intensity* (Lα), cps</th>
<th>Calculated conc., ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
<td>Th</td>
</tr>
<tr>
<td>0</td>
<td>13.655</td>
<td>7.890</td>
</tr>
<tr>
<td>100</td>
<td>14.220</td>
<td>9.090</td>
</tr>
<tr>
<td>200</td>
<td>15.310</td>
<td>10.135</td>
</tr>
<tr>
<td>500</td>
<td>17.145</td>
<td>11.215</td>
</tr>
<tr>
<td>600</td>
<td>17.671</td>
<td>12.931</td>
</tr>
<tr>
<td>1000</td>
<td>19.830</td>
<td>14.900</td>
</tr>
</tbody>
</table>

*Values are the average of quadruplicate measurements on each standard pellet. The relative standard deviation of individual measurement is within ±5%, except for blank and 100 ppm standards, for which it is ±10-20%.

### Table 2—U and Th concentrations in synthetic sample-1 and sample-2

<table>
<thead>
<tr>
<th>Sample-1</th>
<th>Sample-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>U conc., ppm</td>
<td>Th conc., ppm</td>
</tr>
<tr>
<td>330</td>
<td>292</td>
</tr>
<tr>
<td>350</td>
<td>252</td>
</tr>
<tr>
<td>370</td>
<td>290</td>
</tr>
<tr>
<td>310</td>
<td>340</td>
</tr>
<tr>
<td>280</td>
<td>275</td>
</tr>
<tr>
<td>348</td>
<td>300</td>
</tr>
<tr>
<td>260</td>
<td>285</td>
</tr>
<tr>
<td>290</td>
<td>320</td>
</tr>
<tr>
<td>317±39*</td>
<td>293±26*</td>
</tr>
</tbody>
</table>

* Average values are given for \(n = 8\)

![Fig. 1—Calibration plots of standards using U and Th Lα X-rays](image-url)
Hence, the developed EDXRF method can be used for fast routine analysis of U and Th in zircon samples.

**Conclusion**

The EDXRFS method developed for the determination of U and Th contents in zircon is useful for fast routine measurements of samples avoiding the cumbersome dissolution route as required in chemical and mass-spectrometric techniques. The reproducibility of the determination is found to be within ±5-20%.

**Acknowledgement**

Authors are thankful to Dr A Goswami, Radiochemistry Division, BARC, Mumbai for providing the gamma-spectrometric results of sample ores for comparison purpose. Thanks are also due to Dr R N Acharya, Radiochemistry Division, BARC, Mumbai for providing the results of neutron activation analysis of the zircon ores for uranium.

**References**