Chapter-3

ANALYTICAL CHARACTERIZATION OF NUCLEAR MATERIALS BY TXRF: TRACE METALLIC DETERMINATIONS

3.1. Introduction

3.2. Trace Element Determination in Thorium Oxide Using TXRF
   3.2.1. Experimental
      3.2.1a. Sample preparation
      3.2.1b. Instrumentation
   3.2.2. Results and discussion

3.3. Determination of Low Atomic Number Elements at Trace Levels in Uranium Matrix Using Vacuum Chamber TXRF
   3.3.1. Experimental
      3.3.1a. Sample preparation
      3.3.1b. Instrumentation
   3.3.2. Results and discussion

3.4. Conclusions

3.5. References
3.1. Introduction

Measurements based on analytical chemistry are important to almost every aspect of life. These applications cover an enormous range of concentrations, starting from percentage level to below parts per trillion. Among these, trace and ultra trace analysis plays a key role in many areas of science. In semiconductor industries, the process materials need to be extremely pure to avoid changes in conductivity [1-2]. Presence of trace elements as impurities can affect the chemical and physical properties, economic value and applications, of chemicals and metals of very high purity [3-4]. Similarly, in environmental samples, trace analysis is required for bio-monitoring the level of pollutants in the atmosphere, water and soil [5]. In nuclear industry, determination of trace and ultra trace elements is an important step with respect to quality control and quality assurance of materials having technological importance [6].

Chemical characterization of nuclear materials for the trace constituents is necessary to ensure that the quality of fuel fabricated is in agreement with the chemical specifications for the fuel. Nuclear reactor design incorporates detailed specifications of the impurities in fuel materials which should be satisfied for the smooth and efficient functioning of the reactors. These specifications differ according to the nature of reactor, material used and their applications (research/power). The Indian program of nuclear energy is designed in such a way that, along with utilization of uranium and plutonium as nuclear fuels, a large emphasis is laid on the use of thorium, as India has the largest thorium reserves of the world. The uranium, thorium and plutonium required for such applications have to undergo stringent quality control. Various forms of fuels used in different nuclear reactors are oxides, metals, alloys and advanced fuels like carbides and nitrides. The amount of trace elements, in particular metallic impurities, which get incorporated in nuclear fuel during various fuel fabrication operations like mining, dissolution, separation, pelletization, etc., can affect the working of the reactors adversely. Hence, the concentrations of these trace impurities in nuclear fuel materials must be below the specification limits and these impurities must be determined by suitable analytical methods.

Another important application of analytical characterization of technologically important materials with respect to their trace constituents, is to develop Certified Reference Standards (CRMs) or Standard Reference Materials (SRMs). These materials are very much essential for the calibration and validation of analytical methods as most of the instrumentation methods are comparative. These standards are also required for quality control and quality assurance of
various technologically important materials. Any discrepancy in the reference standard value can lead to poor accuracy of the analytical results. Generally, CRM/SRM are available commercially for materials like food products, cement, oil, drinking water, alloys and metals used in industries [7-9]. They can be easily procured and used. But unfortunately, CRMs for nuclear materials are not commonly available and their procurement is also very difficult. Hence, it is required to develop indigenous standards for nuclear materials. In order to develop any such standards, Inter- Laboratory Comparison Experiment (ILCE), involving participation of large number of laboratories using different analytical methods having different physico-chemical properties, is conducted [10-11]. The analytical results obtained from various laboratories are compiled and certified values are assigned for different elements.

Different analytical techniques are available for the determination of trace metallic impurities in nuclear fuel materials [6,12-13]. Total reflection X-ray fluorescence (TXRF) is a well established technique for determining impurities present at trace and ultra-trace levels in different materials [14-16]. Applicability of TXRF for trace element analysis depends on two features of total reflection of X-rays: High reflectivity and low penetration depth of the primary radiation. These characteristics allow TXRF to be used for both trace and ultra trace elemental analysis as well as for surface analysis. Though many techniques such as ICP-MS, ICP-AES, AAS, NAA, XRF and a variety of electroanalytical methods are available for trace and ultratrace analysis of elements in various matrices, TXRF has quite a few advantages over the other techniques. It has simple instrumentation (in comparison to ICP and NAA), spectral line interferences are minimum (in comparison to AAS and AES), has got a wide specimen versatility (in comparison to ICP and electroanalytical methods which require sample dissolution, samples in the form of suspensions can also be analysed in TXRF), no matrix effect and memory effects (in comparison to classical XRF and ICP techniques), requires a few microgram or microliter amount of sample, can analyse metals and nonmetals alike and can be used for both trace and bulk analysis. All these features of TXRF are well suited for the determination of trace elements in nuclear samples. But only a few such applications of TXRF for nuclear materials have been reported in literature [17-19]. In the last few years, its applicability for trace element determinations in nuclear materials has been demonstrated in uranium matrix using synchrotron radiation induced and laboratory source TXRF [18, 19]. In TXRF, sample preparation is also very simple compared to other techniques. In aqueous
samples, trace elements can be determined directly or by physically pre-concentrating the sample by evaporation depending on the nature of matrix. But if the matrix is such that it contains heavy elements, then matrix separation is mandatory for the following reasons: Firstly, one of the constraints of TXRF analysis is that the thickness of sample deposited should not be more than a few nanogram and the total matrix amount must be less than 10-50 ng (depending on the nature of matrix) in order to avoid matrix effects. In such low amount of matrix, the analyte transferred on the sample support is sometimes below the detection limits of TXRF. Due to this constrain, the major matrix has to be selectively separated from concentrated solution. Secondly, the separation of major matrix, which normally contains uranium, thorium or plutonium in case of nuclear fuel materials, helps in avoiding the absorption of the characteristic X-ray lines of trace analyte by the heavy elements and thirdly, separation of the major matrix reduces the background caused by scattering of the X-rays by the matrix during TXRF measurements. Various matrix separation techniques such as solvent extraction, pyrohydrolysis, chromatographic adsorption, solid phase extraction, etc., are available. The most common procedures employed for the separation of major matrix of uranium, thorium and plutonium after sample dissolution are solvent extraction and ion exchange separations. Solvent extraction for the separation of uranium and thorium using n-tri-butyl phosphate (TBP) as the extractant is a well established method [12].

In this Chapter, development of TXRF method for trace metallic determinations in nuclear fuel materials (thorium and uranium) is described. The sample preparation involves separation of the major element in the matrix by solvent extraction using TBP as the extractant and determination of the trace elements in the aqueous phase by TXRF.

### 3.2. Trace Element Determination in Thorium Oxide Using TXRF

The Indian Nuclear Energy Program envisages the maximum utilization of thorium because of its limited reserves of uranium and large availability of thorium. Thorium is estimated to be about three to four times more abundant than uranium in the earth crust. Though $^{232}$Th is not a fissile material, it is utilized as a breeder to produce $^{233}$U, which is an excellent fissile material. Thorium is also used for neutron flux flattening in PHWRs and as a blanket material in fast breeder reactors. It is also proposed to be used as a fuel in the third stage of Indian Nuclear Power Program i.e. AHWRs [20]. Another major application of thorium based fuel is in the
Compact High Temperature Reactors (CHTRs) which shall utilise $^{233}$U-Th fuel. Apart from nuclear industry, because of its low work-function and high electron emission, thorium is used to coat tungsten wire used in electronic equipment. Glasses containing thorium oxide have a high refractive index and low dispersion. Consequently, they find applications in high quality lenses for cameras and scientific instruments. Thorium required for such applications as well as for its use in reactor has to undergo stringent quality control. Different analytical techniques such as ICP-AES, GFAAS, MS, etc. are available for trace element determinations in thorium after separation of the major matrix [12, 21-22]. TXRF has good potential for such analysis. But, before TXRF can be used on routine basis for trace element analysis in thorium oxide, the method should be first counter checked for its applicability using certified reference materials.

In the following Section, development of a TXRF method for trace metals analysis in thorium oxide standard after its dissolution in HNO$_3$/HF mixture followed by separation of thorium by solvent extraction is reported. The analytical results obtained by TXRF have been compared with the certified reference values of the elemental concentrations present in thorium oxide standards. The analytical results of different techniques such as ICP-AES, ICP-MS and AAS have been compared with the TXRF determined values.

3.2.1. Experimental

3.2.1a. Sample preparation

The reagents used e.g. tributyl phosphate (TBP), tri-n-octyl phosphine oxide (TOPO), carbon tetrachloride (CCl$_4$) and hydrofluoric acid (HF) were of analytical reagent (AR) grade and HNO$_3$ was of suprapure grade. Merck single element standard of gallium was used as internal standard. All glasswares used for the sample preparation process were made of quartz. High quality PVC vials were used for sample storage. Milli-Q water was used for sample preparation and cleaning purposes. Four ThO$_2$ samples namely ThO$_2$-B, ThO$_2$-D, ThO$_2$-S and (Th,U)O$_2$-MOS prepared by the Department of Atomic Energy, to be developed as certified standard materials, were analyzed for their trace element contents.

Weighed quantities of ThO$_2$ powder equivalent to 2.5 g of thorium were taken in 100 mL capacity high purity platinum dish. Approximately 10 mL of conc. HNO$_3$ was added to the ThO$_2$ taken in the dish and the resultant mixture was boiled gently on a hot plate. In the boiling mixture, 1.5 mL of 0.5% solution of HF was added to get clear solution. This solution was
evaporated to almost dryness. The residue obtained was dissolved in 3 mL of conc. HNO₃ and evaporated to dryness. This process of dissolution and evaporation was repeated four times so that HF was completely removed. After this, the residue was redissolved in 10 mL of 4 M HNO₃. All these dissolution and evaporation operations were carried out inside a hood connected to suction so that corrosive vapours of fluoride are safely collected in an aqueous medium and not left in the atmosphere. The volumes of the solutions obtained after the dissolution of ThO₂ were made up to 15 mL with 4 M HNO₃. For separation of the major matrix thorium, these solutions were equilibrated four times with equal volume of 40% solution of TBP in CCl₄ and later equilibrated two times with 0.2 M TOPO in CCl₄. The major matrix containing thorium was extracted in the organic phase and the aqueous portion containing the trace metallic impurities was carefully separated and made up to 25 mL with Milli-Q water. Aliquots of 1 mL of the above separated solutions were mixed with 100 μL of gallium (19.6 μg/mL) internal standard in pre-cleaned PVC vials. For TXRF measurements, 10 μL aliquot of these solutions were deposited in duplicate on the quartz sample supports and dried under an IR lamp.

3.2.1b. Instrumentation

The TXRF measurements were performed using an ITAL STRUCTURES TXRF spectrometer (TX-2000). Monochromatic Mo Kα radiation having energy of 17.44 keV, obtained from a W-Mo dual target tube and a W/C multilayer monochromator, was used for sample excitation. The applied voltage and current were 40 kV and 30 mA, respectively. A live time of 1000 s was used for recording the TXRF spectra of the samples and standards and a live time of 100 s was set to check the cleanliness of the quartz sample supports. All the measurements were carried out in air atmosphere. The characteristic peaks of the trace elements were recorded using a Si(Li) detector having a resolution of 139 eV FWHM at 5.9 keV.
3.2.2. Results and discussion

The TXRF measurements of processed thorium oxide showed that the major matrix thorium was removed almost completely after solvent extraction. A typical TXRF spectrum of the aqueous portion of ThO$_2$-MOS is shown in Figure 3.1. The thorium oxide samples used in the present study were having different trace elements with varying concentrations, were latter certified by Department of Atomic Energy (DAE) after conducting an ILCE involving a number

![Figure 3.1: A typical TXRF spectrum of a processed thorium oxide (ThO$_2$-MOS) with gallium internal standard](image-url)
of laboratories using different techniques. The trace elements certified in these standards were Al, B, Be, Ca, Cd, Ce, Cr, Cu, Dy, Er, Eu, Fe, Gd, Mg, Mn, Mo, Ni, Sb, Sm and V. The certified values were arrived at by considering all the results obtained by different analytical laboratories lying within an uncertainty of 30% (for the elemental concentrations $> 10 \mu g/g$) and 50% (for the elemental concentrations in the range of 0.1–10 $\mu g/g$) from the mean of the mean values. Out of the above stated elements, Be and B could not be determined by TXRF because of its limitation for low Z elements. The present TXRF instrumental conditions did not allow the determination of Al and Mg, since W L$_\alpha$ excitation source and measurements in vacuum or helium atmosphere would be needed. Although L$_\alpha$ lines of Cd, Ce, Dy, Er, Eu, Gd, Mo, Sb and Sm can be detected by TXRF using the present excitation conditions, these elements could not be determined in the present study mainly due to very low concentrations of these elements present in these oxides and relatively lower fluorescence yield of L lines. The rest of the elements Ca, Cr, Cu, Fe, Mn, Ni, and V in ThO$_2$ were determined by considering the dilution of the matrix and blank corrections. Tables 3.1 and 3.2 give the TXRF determined results of all the four standards and their certified values. The analytical results of the trace elements determined by TXRF differed from the corresponding certified values by $< 20\%$ for most elements where the certified concentration is $> 10 \mu g/g$ of Th. The average precision of the analytical results were found to be 23%. The TXRF spectrum of the processed samples showed characteristic X-ray lines of some additional elements whose certified concentrations were not available. These additional elements e.g. K, Co, Zn, Sr, Y, Ba and Pb were also determined by TXRF and their analytical results are included in Tables 3.1 and 3.2.

The TXRF determined concentrations of calcium are higher than the certified values in three samples namely ThO$_2$-D, ThO$_2$-S and ThO$_2$-MOS (Tables 3.1 and 3.2). This may be due to the presence of calcium in atmospheric aerosol as contaminants. Even a very small contamination of the sample can change the analysis results significantly. In Figure 3.2, a comparison of the TXRF analytical results of calcium in ThO$_2$-S with other laboratories involved is shown. It can be seen that though TXRF determined calcium concentration is higher than the certified calcium concentration, it is within a deviation of 30% from the certified concentration and the average precision is 7% for all the four standards.
Table 3.1: Comparison of TXRF determined elemental concentrations of different elements with the corresponding certified values in thorium oxides ThO$_2$-B and ThO$_2$-D

<table>
<thead>
<tr>
<th>Element</th>
<th>ThO$_2$- B</th>
<th></th>
<th></th>
<th>ThO$_2$- D</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TX (σ)</td>
<td>Cer</td>
<td>TX/Cer</td>
<td>TX (σ)</td>
<td>Cer</td>
<td>TX/Cer</td>
</tr>
<tr>
<td>Ba</td>
<td>ND</td>
<td>-</td>
<td>NR</td>
<td>-</td>
<td>0.70</td>
<td>1.21</td>
</tr>
<tr>
<td>Ca</td>
<td>67</td>
<td>7</td>
<td>73</td>
<td>0.92</td>
<td>874</td>
<td>116</td>
</tr>
<tr>
<td>Co</td>
<td>0.3</td>
<td>0.4</td>
<td>NR</td>
<td>-</td>
<td>0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
<td>0.6</td>
<td>8.5</td>
<td>0.53</td>
<td>14.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Cu</td>
<td>1.9</td>
<td>0.4</td>
<td>3.1</td>
<td>0.61</td>
<td>93</td>
<td>4</td>
</tr>
<tr>
<td>Fe</td>
<td>46</td>
<td>8</td>
<td>56</td>
<td>0.82</td>
<td>122</td>
<td>2</td>
</tr>
<tr>
<td>K</td>
<td>7.3</td>
<td>0.9</td>
<td>NR</td>
<td>-</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Mn</td>
<td>2.4</td>
<td>0.2</td>
<td>3.0</td>
<td>0.80</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>Ni</td>
<td>7.7</td>
<td>0.6</td>
<td>11</td>
<td>0.70</td>
<td>47</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>0.5</td>
<td>0.2</td>
<td>NR</td>
<td>-</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Sr</td>
<td>0.28</td>
<td>0.08</td>
<td>NR</td>
<td>-</td>
<td>1.63</td>
<td>0.08</td>
</tr>
<tr>
<td>V</td>
<td>ND</td>
<td>-</td>
<td>0.2</td>
<td>-</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>Y</td>
<td>ND</td>
<td>-</td>
<td>NR</td>
<td>-</td>
<td>ND</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7</td>
<td>0.2</td>
<td>NR</td>
<td>-</td>
<td>0.30</td>
<td>0.04</td>
</tr>
</tbody>
</table>

σ: Standard deviation (1 s) of TXRF determinations for four measurements.
TX: TXRF determined elemental concentration in μg/g of thorium.
Cer: Certified values of elemental concentration in μg/g of thorium.
ND: Not detected by TXRF.
NR: Not reported in certification.
Table 3.2: Comparison of TXRF determined elemental concentrations of different elements with the corresponding certified values in thorium oxides ThO$_2$-S and ThO$_2$-MOS

| Element | ThO$_2$- S | | | ThO$_2$- MOS | | | |
|---------|-----------|---|---|-------------|---|---|
|         | TX  | (σ)  | Cer | TX/ Cer | TX  | (σ)  | Cer | TX/ Cer |
| Ba      | ND   | -    | NR  | -        | 2.60 | 4.50 | NR  | -        |
| Ca      | 454  | 8    | 351 | 1.29     | 641  | 19   | 479 | 1.34     |
| Co      | 1.0  | 0.4  | NR  | -        | 0.3  | 0.3  | NR  | -        |
| Cr      | 6    | 1    | 7.3 | 0.82     | 14.1 | 0.8  | 19.0| 0.74     |
| Cu      | 50   | 3    | 63  | 0.79     | 50   | 2    | 71.0| 0.70     |
| Fe      | 65   | 6    | 78  | 0.83     | 112.9| 1.1  | 137 | 0.82     |
| K       | ND   | -    | NR  | -        | 7    | 3    | NR  | -        |
| Mn      | 4.0  | 0.5  | 4.3 | 0.93     | 4.9  | 0.2  | 5.5 | 0.89     |
| Ni      | 29   | 2    | 32  | 0.91     | 25.5 | 0.9  | 38  | 0.67     |
| Pb      | ND   | -    | NR  | -        | 0.3  | 0.3  | NR  | -        |
| Sr      | 0.65 | 0.05 | NR  | -        | 1.4  | 0.3  | NR  | -        |
| V       | 3.1  | 1.2  | 3.0 | 1.03     | 4.8  | 0.8  | 3.3 | 1.45     |
| Y       | ND   | -    | NR  | -        | 0.3  | 0.3  | NR  | -        |
| Zn      | 1.4  | 0.1  | NR  | -        | ND   | -    | NR  | -        |

σ: Standard deviation (1 s) of TXRF determinations for four measurements.
TX: TXRF determined elemental concentration in μg/g of thorium.
Cer: Certified values of elemental concentration in μg/g of thorium.
ND: Not detected by TXRF.
NR: Not reported in certification.
The certified concentration of manganese in these samples lies between 3 and 7.3 μg/g. As the concentrations are between 0.1 and 10 μg/g, the requirement for certification of manganese in these samples was that the relative standard deviation (RSD) of different laboratories should be less than 50%. Normally manganese is not present in atmospheric aerosol and hence chances of TXRF samples getting contaminated from the ambient air for manganese are less. A comparison of TXRF determined concentration of manganese in ThO$_2$-B and that reported by other laboratories is given in Figure 3.3. In this comparison, laboratories 1–16 used Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), 17–18 used Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and 19–21 used Atomic Absorption Spectroscopy (AAS) for trace element determinations. The comparison of TXRF and certified
analytical results for other elements can be seen from Tables 3.1 and 3.2. It can be seen that deviations of TXRF determination results for manganese, in these samples, from the corresponding certified values is 20%. The precision obtained in TXRF determination of manganese is within 15% (1σ). These comparisons show the suitability of TXRF for trace elements determinations in thorium oxide. The TXRF method has the prime benefit of requirement of very small amount of sample and mutielemental analytical capability. This can be exploited beneficially for the safe and faster analysis of radioactive materials producing smaller waste amounts thereby lesser environmental pollution.

**Figure 3.3:** A comparison of analytical results of different laboratories with certified and TXRF determined manganese concentration in ThO$_2$-B

(Error bars represent standard deviation i.e. 1σ obtained in TXRF determinations for four measurements)
3.3. Determination of Low Atomic Number Elements at Trace Levels in Uranium Matrix Using Vacuum Chamber TXRF

The amounts of low atomic number (Z) trace impurities in nuclear fuel should be within specified limits for neutron economy, better fuel density and quality assurance [6, 23-24]. Low Z element boron is a neutron absorber and should not be present in the nuclear fuel as this will absorb neutrons and make the nuclear fission process inefficient [23]. Determination of carbon and nitrogen is important for characterization of advanced carbide and nitride fuels, respectively. Presence of carbon in excess as a trace impurity may cause carburization of cladding materials thereby making them fragile. Oxygen amounts other than the specified values may change the oxygen to metal ratio (O/M) of the oxide fuel leading to changes in thermal conductivity, melting point, diffusion coefficients and vapor pressure [25]. Na, Mg and Al, if present, in uranium oxide fuel in amounts higher than the specified levels, may reduce the relative amount of fissile materials and form appreciable amounts of uranates of these elements having uranium in lower and higher oxidation states in reactor operating and transient conditions. If formation of these uranates is appreciable, it may cause expansion of fuel volume leading to rupture of fuel cladding. Also in accidents involving crack of cladding, uranates with higher valency of uranium may be formed which may lead to fuel expansion, due to their low density, and may propagate further cracking of the clad. Thus determination of low Z elements present at trace and major concentration levels in nuclear fuel is important. A variety of analytical techniques can be employed for the determination of medium and high Z elements but only a few techniques are applicable for the low Z elements (Z ≤ 13). Trace determination of low Z elements by XRF is challenging because of following reasons [26, 27]:

i) Low fluorescence yield (ω) and photoelectric mass absorption coefficient (τ/ρ), therefore the emitted intensity from these elements is very low.

ii) Higher background in the characteristic X-ray energy region and higher absorption of the characteristic X-rays by the spectrometer components and matrix leads to low signal to noise ratio.

iii) The detector efficiency for detecting low energy X-rays is less. Figure 3.4 shows the plot of efficiency of Si(Li) detector for energies 1-6 keV. The efficiency is low for elements up to Cl ( ≤ 0.8 ) and it is almost equal to 1 for Mn [28].
If efficient excitation sources for low Z elements and the TXRF spectrometer attached with vacuum chamber to minimize the absorption losses, are used then low Z elements at trace levels can be determined by TXRF [29]. The first publication of low Z determination by vacuum chamber TXRF reported the analysis upto oxygen (Z=8) [30]. Synchrotron radiation induced TXRF can efficiently excite the low Z characteristic K-line X-rays of elements upto boron and can be used for determination of these elements [31, 32]. However, synchrotron sources are not easily available for routine analysis. The limitations of TXRF spectrometry for low Z elements can be taken care in a special TXRF spectrometer having vacuum chamber and low energy excitation source, though with comparatively higher detection limits than those achievable with synchrotron radiation sources. Since, the specifications of Na, Mg and Al in nuclear fuel materials e.g. UO$_2$, ThO$_2$, PuO$_2$, etc. are comparatively higher than those of other elements and are in μg/g levels, these elements can be determined in such nuclear materials using vacuum chamber TXRF spectrometer. Studies were, therefore, carried out to determine trace levels of Na, Mg and Al in uranium matrix using WOBISTRAX TXRF spectrometer [33, 34] with a Cr target X-ray tube. The major matrix uranium was separated by solvent extraction using TBP prior to the analysis of the trace elements by TXRF.
3.3.1. Experimental

3.3.1a. Sample preparation

The stock solutions of sodium and magnesium were prepared by dissolving high purity NaNO$_3$ and MgSO$_4$·7H$_2$O salts of AR grade in 1.5% suprapure HNO$_3$ in Milli-Q water to get sodium and magnesium concentrations of 375 and 99 μg/mL, respectively. Merck single element standard solutions of aluminum and scandium (internal standard) having a concentration of 1000 μg/mL were used after required dilution with 1.5% HNO$_3$. These solutions were mixed in different volumes to prepare a calibration solution with Na, Mg, Al and Sc having concentrations of 57, 15, 30 and 13 μg/mL, respectively. Ten microliter of this solution was pipetted at the center of three Plexiglas sample supports of 30 mm diameter and 2 mm thickness and left overnight for drying in a class 100 clean bench. After drying, the TXRF spectra of these plexiglas supports were recorded and the relative sensitivities of Na, Mg and Al with respect to Sc were determined using the respective peak areas of Kα lines of these elements. Three sample solutions of Na, Mg and Al in uranium matrix were prepared by mixing different volumes of the above stock solutions in nuclear grade uranyl nitrate solution with uranium concentration of 85 mg/mL in such a way that the concentrations of low Z elements Na, Mg and Al were in the range of 100–300 μg/g with respect to uranium and 10–20 μg/mL in the solution as given in Table 3.3. Uranium present in these solutions in major concentration level was separated by solvent extraction using 30% TBP solution in dodecane. The samples were equilibrated thrice with this TBP solution. The organic phase containing uranium obtained after each equilibration was discarded. The aqueous phase containing trace elements obtained after final separation was equilibrated once more with dodecane solution to remove the dissolved TBP and mixed with scandium internal standard as shown in flow chart given in Figure 3.5. Five microliter of each of these solutions obtained from samples-1, 2 and 3 (Table 3.3) was deposited on siliconised Plexiglas sample supports, dried in similar way as the calibration solutions and the TXRF spectra were recorded.

The blanks for different samples were prepared by taking 1.5 % HNO$_3$ in Milli-Q water instead of Na, Mg and Al solutions in uranyl nitrate solution in the same proportions as used for the preparation of respective sample solutions, processing them in similar manner as the samples, adding scandium internal standard solutions to the aqueous phase obtained after solvent extraction and recording their TXRF spectra.
Table 3.3: Details of preparation of sample solutions for low Z elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample-1</th>
<th>Sample-2</th>
<th>Sample-3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volume taken (µL)</td>
<td>Elemental concentration</td>
<td>Volume taken (µL)</td>
</tr>
<tr>
<td></td>
<td>µg/mL</td>
<td>µg / g of uranium</td>
<td>µg/mL</td>
</tr>
<tr>
<td>Na</td>
<td>80</td>
<td>10.3</td>
<td>141</td>
</tr>
<tr>
<td>Mg</td>
<td>300</td>
<td>10.2</td>
<td>140</td>
</tr>
<tr>
<td>Al</td>
<td>30</td>
<td>10.3</td>
<td>141</td>
</tr>
<tr>
<td>U</td>
<td>2500</td>
<td>73024</td>
<td>-</td>
</tr>
</tbody>
</table>

Concentration of stock solutions used for preparing the samples Na = 375.3 µg/mL, Mg = 99 µg/mL, Al=1000 µg/mL, U=85 mg/mL.

3.3.1b. Instrumentation

For TXRF measurements, an Atominstitut Vienna, Austria, vacuum chamber low Z TXRF spectrometer (WOBISTRAX) was used. The spectrometer utilizes Cr Kα X-rays for sample excitation. The monochromatic Cr Kα X-rays are obtained using a W–C multilayer. A Peltier Cooled, KETEK SDD detector of 10 mm² active area, with ultra thin kapton window and electron trap around the window was used for detection and measurement of the X-ray intensities. The TXRF spectra of solution used for calibration of the instrument were recorded for a live time of 1000s whereas those of samples were recorded for a live time of 500s. All the measurements were made under a vacuum of \(10^{-2}\) mbar. The TXRF spectra were processed using the AXIL program from IAEA, Vienna [35].

109
3.3.2. Results and discussion

The relative sensitivities of Na, Mg and Al determined with respect to Sc were found to be in increasing order with atomic number showing a trend as shown in Figure 3.6. This increasing trend shows that the TXRF condition is satisfied.
The separation of uranium was accomplished using solvent extraction method optimized for TXRF measurements. In order to avoid any loss of intensity due to thicker and non-uniform samples on plexiglas sample support by heating under IR lamp, especially when the aqueous phase contains a slight amount of organic matter i.e. TBP, because of its partial solubility in nitric acid, the samples were left overnight for self drying on these sample supports in a class 100 clean bench. To keep the background low, only 5 μL aliquots of the processed samples were deposited on Plexiglas supports. Scandium was used as internal standard as it is not present in samples and can be excited very efficiently (Sc K\textsubscript{abs}=4.493 keV) with Cr K\textalpha\ (5.414 keV) X-ray source used for sample excitation in the present spectrometer. A representative TXRF spectrum of the aqueous phase of sample-3 mixed with internal standard is shown in Figure 3.7. From this

![Relative sensitivities of sodium, magnesium, aluminum with respect to gallium](image)

**Figure 3.6:** Relative sensitivities of sodium, magnesium, aluminum with respect to gallium
spectrum, it can be seen that Na, Mg and Al Kα peaks are very clear, though less intense, indicating that the method is promising for TXRF determination of these low Z elements. The intense peaks of Kα lines of C (282 eV) and O (523 eV) seen in the spectrum are from TBP and sample supports. A part of the C Kα line may be from the detector window also. The peaks of Si Kα originating from siliconised plexiglas supports and P Kα from TBP are also seen in the spectrum. In addition, the less intense U M lines observed in the spectrum are due to trace amounts of uranium left in the aqueous phase after solvent extraction. Some elements e.g. S from MgSO4, K, etc. are also visible. The Kα lines of Na, Mg and Al are visible better in expanded spectrum of the same sample shown in Figure 3.8. For the processing of the spectra, the IAEA

![TXRF spectrum after selective extraction of uranium and addition of scandium internal standard (Sample-3)](image)

**Figure 3.7:** TXRF spectrum after selective extraction of uranium and addition of scandium internal standard (Sample-3)
program AXIL was used. In order to assess the area under the analytes peak accurately by profile fitting, the data were processed in two parts. First Na, Mg and Al Kα lines were processed together and then Sc Kα line was processed separately. The concentrations of Na, Mg and Al were determined by using the net intensities of characteristic Kα X-ray peaks of the analytes, internal standard and their relative sensitivity values. The blank values of Na, Mg and Al of each sample were determined and subtracted from the respective values obtained from the TXRF spectra of the samples. The blank corrected TXRF determined concentrations of Na, Mg and Al are given in Table 3.4. It can be seen that the average deviations of the TXRF determined concentrations of Na, Mg and Al from the respective calculated concentrations are within 15, 17 and 9%, respectively. The deviation of TXRF determined Mg values from calculated Mg concentration are quite high in sample-2 and was not included in calculation of the average deviations. The average RSD (1s) of TXRF determined concentrations for the three samples for Na, Mg and Al were found to be 39, 31 and 21%, respectively. The comparison of the calculated
Table 3.4: Results of TXRF determinations of low Z elements in sample solutions

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample-1</th>
<th>Sample-2</th>
<th>Sample - 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Elemental concentrations (µg/mL)</td>
<td>Cal</td>
<td>TXRF #</td>
</tr>
<tr>
<td>Na</td>
<td>10.3</td>
<td>9 ± 2</td>
<td>14.5</td>
</tr>
<tr>
<td>Mg</td>
<td>10.2</td>
<td>10 ± 2</td>
<td>14.3</td>
</tr>
<tr>
<td>Al</td>
<td>10.3</td>
<td>10 ± 2</td>
<td>14.4</td>
</tr>
</tbody>
</table>

Cal = Calculated concentrations of the elements on the basis of the preparation of samples
TXRF = TXRF determined concentration of elements ± 1s (n=4)

and TXRF determined concentrations in three samples is shown in Figure 3.9. It can be seen that the TXRF determined concentrations of all the analytes are in agreement with the calculated concentrations after consideration of the standard error involved. However, the TXRF determined concentration of Mg is very low compared to the calculated Mg concentrations in samples-2 and 3 even after consideration of standard deviation (1s) value.

It can also be seen from Table 3.3 that the minimum amount of low Z elements determined in the present work was 10 µg/mL, which is comparatively higher than the amount of trace elements generally determined by TXRF and this amount can be decreased further by dissolving actual uranium fuel samples in smaller amounts of HNO₃ and preconcentrating the aqueous phase obtained after matrix separation. This will lead to lower detection limits required for real uranium sample analysis. These determinations were possible due to use of vacuum chamber, special geometry of the spectrometer and separation of high Z matrix.
3.4. Conclusions

The applicability of TXRF for the determination of trace metallic elements in thorium and uranium was demonstrated.

The TXRF determined analytical results of trace metallic impurities in ThO₂ were in good agreement with the analytical results of different laboratories using different techniques e.g. ICP-AES, ICP-MS, AAS, etc. The precision (1σ) and accuracy observed in such TXRF determinations are better than 20%. This method was successfully applied for the development of Certified Reference Materials for trace metallic impurities in ThO₂ standards.

Figure 3.9: Comparison of calculated and TXRF determined concentrations of low Z elements Na, Mg and Al in sample -1, sample-2 and sample-3

(Cal: Calculated concentrations on the basis of the preparation of the solution, TX: TXRF determined concentrations of low Z elements ± 1 σ (n = 4), Samp: Sample)
Application of TXRF for determination of low Z elements Na, Mg and Al in nuclear samples was demonstrated for the first time. These elements can be determined by TXRF after dissolving the solid samples and separating the major matrix. The average precision of the TXRF determinations for low Z elements was 31% (RSD 1σ) and the average deviation of the TXRF determined concentrations of low Z elements from the calculated concentrations was 14%. Though the RSD and deviation of the TXRF determined concentration values from the expected concentrations are slightly higher than the ideal values and will require improvements, these are satisfactory for such nonconventional application of TXRF.

The studies conclude that TXRF is a competitive and complementary technique for the trace element determinations in nuclear materials. In case of analysis of radioactive samples, TXRF has additional benefit of producing less waste and consequently lower radiation hazard risk to the analyst. This technique may be well suited for routine sample analysis of radioactive samples.

3.5. References

5. Maurizio Bettinelli, Maurizio Perotti, Sandro Spezia, Claudio Baffì, Gian Maria Beone, Federico Alberici, Sara Bergonzi, Claudio Bettinelli, Paola Cantarini, Laura Mascetti, The


