Chapter-6

DETERMINATION OF URANIUM BY TXRF IN NON-CONVENTIONAL RESOURCES: SEAWATER AND FERTILIZER

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6.1. Introduction

Uranium is one of the technologically important elements. It has got wide applications in various fields of science and technology. It is the main component in nuclear industry and is used as fuel in nuclear reactors for electricity generation. In addition, it is also used as a catalyst in many organic reactions, in semiconductor industries, etc. [1-3]. Uranium is mined from its ores and with growing demands and limited availability, its exhaustion within 100 years will be apprehensive. The various uranium ores are pitchblende, uraninite, coffinite and carnotite which are present in earth crust. Different scientific groups all over the world are in search of new conventional and non-conventional sources of uranium. In the terrestrial crust, uranium does not occur as a free metal but always exists as compounds of oxide, silicate or potassium. The average concentration of uranium in earth’s crust is about 4 μg/g and is more abundant than other heavy metals such as mercury and silver. Its concentration in seawater is around 3 μg/L and is distributed uniformly in all the world’s oceans. In surface freshwater (rivers and lakes), the average concentration is as low as 0.5 μg/L and depending on the location and contamination of the water, it can reach concentrations as high as 500 μg/L [4]. Another major unconventional source of uranium is the phosphate rocks. Depending on the location, uranium concentration varies and is considered to be present in the range of 1-600 ppm [5] in these phosphate rocks. Digestion of phosphate rocks in fertilizer production process leads to incorporation of uranium in the resulting phosphate fertilizers. The uranium concentration can be as high as a few hundreds of ppm in phosphate fertilizers. Even phosphoric acid, manufactured using phosphate rocks, is a rich non-conventional source of uranium.

Determination of uranium in seawater as well as phosphate fertilizers is important from the point of view of its recovery as well as environmental concerns. Uranium is present in the environment and water bodies due to leaching of ore deposits and release from various industries. Since it is radioactive and toxic, it has considerable effects on biological organism and the human food chain. The provisional guideline value recommended by WHO (World Health Organization) for uranium in drinking water is 15 μg/L [6]. Only a few techniques such as spectrophotometery, alpha/gamma spectrometry and laser fluorometry are available for the determination of low-level concentrations of uranium in various matrices [4, 7-11]. These techniques require tedious separation and preconcentration steps.
In the present work, studies were carried out to determine uranium in unconventional sources like seawater and fertilizers by TXRF. This involved selective extraction of uranium using solvent extraction thereby pre-concentrating and removing the interfering elements from the analyte matrix.

6.2. Uranium Determination in Seawater by TXRF

Seawater is a treasure of many elements — precious and strategic in nature. The possibility of recovering uranium from seawater has gained importance in last few decades. Uranium is present in seawater in very small concentrations of about 3.3 ng/mL [12,13] as uranyl carbonate anions, but considering the huge amount of seawater in the world, the total amount of uranium in seawater works out to be approximately 1000 times to that in earth crust [12]. Different countries of the world, especially those having a sea coastline, are pursuing studies to explore the feasibility of recovering uranium from seawater in an economic way. India is also actively involved in such studies. Determination of uranium in seawater is an important step in these studies. Though TXRF by Mo Kα excitation is a very sensitive method of uranium determination because of better excitation efficiency of Mo Kα for U Lα X-rays, but direct determination of uranium in seawater by this method becomes difficult due to mainly three reasons:

i) Large amount of salt matrix
ii) Very low concentration of uranium in seawater
iii) Interference of Rb Kα (13.40 keV) and Br Kβ (13.29 keV) X-ray lines with U Lα (13.62 keV) line, as rubidium and bromine are also present in seawater in appreciable amounts.

Any TXRF analytical method for uranium determination has to address the above problems before it can be applied for routine uranium determinations in seawater. A few methods of uranium determination in seawater using TXRF are reported in the literature but these methods use complex procedures for pre-concentration [14,15].

In the present study, an attempt was made to determine uranium in seawater by selectively extracting it in diethyl ether (C₂H₅OC₂H₅) and thus removing the interfering elements from the analyte. This study was pursued with an aim of getting an alternative fast method of uranium determination in seawater with its possible application in uranium recovery technology.
from seawater as well as for monitoring of uranium in environment. Also, it will be helpful in establishing TXRF as a routine chemical analysis technique for such determinations.

6.2.1. Experimental

6.2.1a. Sample preparation

The glass wares used in this study e.g. separating funnels, beakers, measuring funnel, etc. were made of high purity quartz. Diethyl ether used was of AR grade, nitric acid was of suprapure grade and water used for cleaning and sample preparation was of Milli-Q grade. The multielement standard used was Merck ICP- standard solution IV. Merck single element standards of uranium and yttrium were used. The glass wares used were cleaned by dipping them in 1.5% solution of suprapure HNO₃ in Milli-Q water for 24 h before use. The cleanliness of the glass wares was ascertained by recording TXRF spectrum of 1.5% suprapure HNO₃ kept in these glass wares for 24 h after cleaning. Four seawater samples, collected in 60 mL cleaned PET wide mouth vials from a site in Arabian Sea near Mumbai City, were processed for the determination of uranium. Diethyl ether was used as an extractant for selective extraction of uranium. Before extracting uranium, diethyl ether was equilibrated thrice with 8M HNO₃. The leftover HNO₃ was free of any traces of uranium and, therefore, was used for the sample preparation purpose. However, in this treatment some amount of uranium present in HNO₃ as impurity may get extracted into diethyl ether. To remove such uranium from the treated diethyl ether, it was again equilibrated with equal amount of Milli-Q water. The diethyl ether received after this treatment was equilibrated with treated 8 M HNO₃ to replenish loss of HNO₃ from it. The organic phase (equilibrated diethyl ether) obtained after this treatment was free from any uranium impurity and was used for extraction of uranium from multielement standards and seawater samples.

In order to study the extraction efficiency of uranium by diethyl ether, a working standard having concentration of 4.9 ng/mL was prepared by diluting the ICP multielement standard solution IV with 1.5% HNO₃. As this standard did not contain any uranium, a single element standard of uranium was added to this solution. The elemental concentration of uranium was similar to all the elements in this standard solution. A 50 mL volume of this standard was evaporated to dryness under an IR lamp. The solid mass obtained was first fumed with a few
drops of 8M HNO₃ two to three times on a hot plate and was finally dissolved in 1 mL of 1.5% HNO₃. A known amount of yttrium standard was mixed to this solution as an internal standard. This solution was analyzed for different elements by TXRF. Another 50 mL volume of the same standard was taken in a beaker and was evaporated to dryness under an IR lamp. The solid material received was redissolved in minimum amount of 8M HNO₃ and then made up to 25mL. This solution was equilibrated three times with the equal amount of treated diethyl ether as described earlier. The organic phases received in each equilibration were removed carefully and mixed together. This organic phase was left for evaporation to dryness on a hot plate. The the residue obtained was fumed with few drops of equilibrated 8M HNO₃ and then was dissolved in 1 mL of 1.5% solution of HNO₃. This solution was analyzed by TXRF after adding the internal standard. The blank corrections in both these TXRF determinations were made by analyzing 50 mL of 1.5% HNO₃ in Milli-Q water processed a in similar way.

To extract uranium from the actual seawater samples, 50 mL of each seawater sample was filtered through Whatmann filter paper-541 and was collected in separate beakers. These filtrates were evaporated to dryness and the solid residues obtained were dissolved in minimum volume of 8 M HNO₃. For uranium extraction, these solutions were processed in similar way as described earlier. In an earlier study, the solid residue obtained was found to contain high concentrations of bromine and chlorine. Because of Br Kβ interference with U Lα line, it had to be removed from the analyte solution. Bromine was removed from this residue by mixing it with few drops of Conc. HNO₃ and evaporating the resultant solution slowly to dryness over a burner. This process was repeated two to three times for removal of bromine and chlorine. Finally, internal standard yttrium was mixed in the residue and the whole mass was dissolved in 1 mL of 1.5% HNO₃. Two aliquots of 10 μL of this solution were taken on two quartz TXRF sample supports and dried under an IR lamp.

6.2.1b. Instrumentation

An ITAL STRUCTURES TXRF spectrometer TX-2000 was used for measurements. Mo Kα radiation produced from a Mo-W dual target X-ray tube operated at 40 kV, 30 mA and monochromatized by a W-C multilayer was used for sample excitation. A Roentec Si(Li) detector with energy resolution of 139 eV at 5.9 keV (Mn Kα) was used for detection of X-rays
produced. For TXRF analysis, 10 μL aliquots of the sample were deposited on clean quartz sample supports and the TXRF spectra were recorded for a live time of 1000 s. Each sample was prepared in duplicate and measured two times. The precision was calculated form the four TXRF determinations.

6.2.2. Results and discussion

6.2.2a. Selective extraction of uranium by diethyl ether

Diethyl ether is known to selectively extract uranium even from very low concentrations [16]. However, it has been now replaced by other extractants for industrial uranium extraction because of its low boiling point and highly inflammable nature. For TXRF analysis of uranium in seawater, its low boiling point was beneficially exploited to remove the organic phase completely, obtained after uranium extraction. The selective extraction of uranium by diethyl ether is maximum from 8 M HNO₃. However, HNO₃ has some solubility in diethyl ether. If diethyl ether is used without any treatment, it will dissolve some HNO₃ from the feed solution and will change its molarity. This will affect its selective extraction behaviour for uranium. In order to overcome this problem, the diethyl ether was saturated with 8 M HNO₃ before its use by equilibrating in a separating funnel for three minutes. The left over acid was free from any uranium impurity because if there was some uranium, it would have gone into the diethyl ether phase during equilibration. This acid was used for further sample preparations.

The concentrations of different elements in synthetic multielement standard solution having concentration of 4.9 ng/mL was determined by TXRF and their expected concentrations are given in Table 6.1. The ratio of TXRF determined and expected elemental concentrations are also given in this Table. The precision, calculated on the basis of four measurements, for most of the elements was within 8% (1σ). The average difference in expected and TXRF determined values of elemental concentrations of elements for which Kα lines were used was 6% after excluding Ca, Fe and Zn data. The large deviation in case of Ca and Fe were because of their presence in environment as aerosol particulate and water contaminants. The precision and accuracy are poor indicating requirement of clean room conditions for the determination of these elements in this concentration range. The accuracy was poorer for the elements for which
La lines were used as the analytical lines of interest. The average percentage deviation was found to be within 13% for such elements except Ba, which had a large deviation.

TXRF analysis of the aqueous phase after solvent extraction of the working standard showed that the recovery of uranium in organic the phase was complete. For Ca and Fe, the recovery was significant whereas for other elements e.g. Ni, Cu, Zn, Ga, Sr, Tl and Bi, it was negligible. The significant recovery of Ca and Fe observed may be due to contamination from the atmospheric aerosol but these elements do not interfere with uranium analysis by TXRF and
will not affect its subsequent determination. A comparison of TXRF determined concentrations of the elements present in the standard and those extracted in organic phase of diethyl ether extraction is shown by means of a bar graph in Figure 6.1.

**Figure 6.1:** A comparison of concentrations of different elements present in standard before and after extraction
6.2.2b. Uranium determination in seawater

Concentration of bromine after treatment with concentrated HNO₃, as observed in the TXRF spectrum given in Figure 6.2, was reduced to negligible amounts. Absence of Rb Kα peak in the spectrum indicates negligible extraction of rubidium by diethyl ether. Hence the two elements, which were interfering with the determination of uranium, were removed successfully.

Figure 6.2: TXRF spectrum of organic phase obtained after selective extraction of uranium in diethyl ether
Four samples of processed seawater were analyzed by TXRF and the results obtained for uranium in these seawater samples are given in Table 6.2. The agreement between TXRF determined values with the reported literature value was found to be satisfactory, showing good extraction recovery for uranium by diethyl ether. Uranium is reported to be present in seawater as a dissolved trace metal at a concentration of 3.3 ng/mL [12] and the average TXRF determined uranium concentration was found to be $2.8 \pm 0.5$ ng/mL. The precision of uranium determinations was better than 17% ($1\sigma$). A comparison of TXRF determined uranium concentration values with the expected values of uranium present in seawater, as reported in the literature, is shown as bar graph in Figure 6.3. The deviation of TXRF values from the expected concentration was about 15%. The detection limit of uranium after the preconcentration step of its extraction in diethyl ether reached 67 pg/mL. These observations clearly indicate that TXRF can be used as a routine technique for uranium determination in seawater samples.

Table 6.2: Results of TXRF determined uranium in seawater samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>TXRF determined uranium concentration (ng/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample-1</td>
<td>$2.6 \pm 0.07$</td>
</tr>
<tr>
<td>Sample-2</td>
<td>$3.4 \pm 0.15$</td>
</tr>
<tr>
<td>Sample-3</td>
<td>$2.1 \pm 0.08$</td>
</tr>
<tr>
<td>Sample-4</td>
<td>$3.1 \pm 0.09$</td>
</tr>
</tbody>
</table>
6.3. Determination of Uranium in Fertilizer Samples by TXRF

Fertilizers employed in agriculture usually contain traces of heavy elements and especially phosphate fertilizers are known to contain uranium in high concentration [17]. The high uranium content in these fertilizers is due to occurrence of this element in phosphate rocks which is usually the raw material for the synthesis of these fertilizers. Because of the concern about the exhaustion of uranium resources in the world, phosphate fertilizers are seen as an alternative source of uranium. The project involving recovery of uranium from such unconventional sources, require a suitable method of uranium determination at trace levels in these fertilizers. Also, there is environmental concern regarding the use of these fertilizers routinely due to the addition of uranium in the soil. Solid State Nuclear Track Detector (SSNTD) is an
excellent tool for the determination of low levels of uranium in environmental samples [18-20]. The only limitation of this technique is the requirement of nuclear reactors for irradiation purpose. TXRF can be used for the determination of uranium in fertilizer samples, provided uranium can be selectively separated from the major matrix of the fertilizers.

Studies are reported in this Section about TXRF determination of uranium in four phosphate fertilizers of Hungarian origin. Uranium was selectively extracted from the phosphate fertilizers using the solvent extraction procedure employing TPB as the extractant.

6.3.1. Experimental

6.3.1a. Sample preparation

All the glasswares such as beakers, separating funnel, measuring cylinder were made of high purity quartz. Solvents like tributyl phosphate (TBP) and dodecane used were of AR grade. Nitric acid used for dissolution and sample preparation was of suprapure grade. Water used for diluting samples / reagents and washing was of Milli-Q grade. Calibration standards of uranium and yttrium internal standard were prepared by diluting and mixing the Merck single element standards of these elements having a concentration of 1000 μg/mL.

Accurately weighed fertilizer samples, about 1 g each, were soaked in a minimum amount of concentrated HNO₃ for 3 h. Any remaining supernatant was evaporated under IR lamp and then 5 mL of 2.5 M HNO₃ was added to the residue thus formed and left overnight. The resultant solution was filtered and the solid material left undissolved was washed with 2.5 M HNO₃. The washings were collected along with filtrate and equilibrated thrice with 30% solution of TBP in dodecane. The organic phase containing extracted uranium was collected carefully after each extraction. Finally, after three equilibrations, the total organic phase collected was equilibrated again with 1.5% HNO₃. The aqueous phase obtained after this extraction was separated from the organic phase and mixed with the internal standard. This solution was evaporated to dryness and then made up to 2 mL with 1.5% HNO₃. The flow chart showing the sample preparation steps in detail is given in Figure 6.4. For the blank determinations, the same sample preparation procedure was followed and instead of sample, HNO₃ was used. Aliquots of 10–30 μL of calibration solution and processed fertilizer samples were deposited on float glass sample supports to measure their TXRF spectra.
Fertilizer samples: Accurately weighed and soaked in minimum amount of concentrated suprapure HNO₃ for three hours.

Heated under IR lamp to dryness, 5 mL of 2.5 M suprapure HNO₃ added to redissolve the residue thus formed and left overnight.

The supernatant was decanted and the undissolved material washed with the 2.5M suprapure HNO₃.

The washings and filtrate mixed and equilibrated with 30% TBP in dodecane (3 contacts).

The organic phase equilibrated with 1.5% suprapure HNO₃ to back extract uranium from organic to aqueous phase.

This aqueous phase mixed with internal standard yttrium and evaporated to dryness and then made up to 2 mL with 1.5% suprapure HNO₃.

**Figure 6.4:** Flow chart showing steps involved in the sample preparation methodology for TXRF analysis of uranium in fertilizer samples.

### 6.3.1b. Instrumentation

The TXRF measurements were carried out using the spectrometer assembled at Raja Ramanna Centre of Advanced Technology (RRCAT) Indore, India [21, 22]. A monochromatized Mo Kα radiation source obtained from the Mo target tube operated at 30 kV and 20 mA using a W-C multilayer was used for sample excitation. The samples were deposited on float glass supports [23]. The live time used varied from 1000 to 3000 s depending on the intensity of U Lα.
peak. The quantity of uranium in the fertilizer samples was determined using the net intensities of U Lα and Y Kα (internal standard) and blank corrections.

6.3.2. Results and discussion

TBP is a well established extractant for selective extraction of uranium from nitric acid medium. 30% TBP in dodecane has maximum extraction efficiency of uranium at 2-4 M HNO₃. Hence all the samples were prepared with 2.5 M HNO₃. Direct determination of uranium in organic phase by TXRF is difficult. This is because in TXRF, the samples deposited on the sample supports need to be dried completely before presenting for measurements. TBP/dodecane have boiling points more than 200°C and hence complete evaporation is difficult and time consuming. The other alternative method is to back extract uranium in the aqueous medium. Therefore, the organic phase was equilibrated with dilute HNO₃ to back extract uranium from organic to aqueous phase. The TXRF spectrum of a typical fertilizer sample after complete processing is shown in Figure 6.5 along with uranium and yttrium peaks. A strong peak of strontium is also seen in the Figure. This is because of its presence as a common trace element in water and environmental samples.

To find out the area of U Lα and Y Kα peaks, profile fitting using the program ORIGIN was used. The sensitivity of the U Lα with respect to Y Kα was determined using TXRF measurements of four specimens taken from the calibration standard solutions of uranium and yttrium. The amounts of uranium in the fertilizer samples were determined using the above sensitivity values and U Lα and Y Kα peak intensities. The uranium amount was found to be in the range of 4– 6 μg/g in two samples, whereas other two fertilizer samples did not show any uranium. The TXRF determined values are given in Table 6.3. The precision of the TXRF determination of uranium was found to be better than 8% (1σ). The TXRF spectra of the leftover solid residues were also measured. These spectra did not show any uranium peak. These observations indicate that uranium present in phosphate fertilizers was in TBP extractable form and such trace amounts of uranium present in fertilizer samples can be leached, extracted and then analysed by TXRF as described above.
Figure 6.5: Profile fitted TXRF spectrum of a processed fertilizer sample (Sample Code : 1845)

Table 6.3: TXRF determined values of uranium in fertilizer samples

<table>
<thead>
<tr>
<th>Fertilizer Sample Code</th>
<th>Description</th>
<th>TXRF Determined uranium (μg/g) ± 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1844</td>
<td>N based mainly NH₄NO₃</td>
<td>Not Detected</td>
</tr>
<tr>
<td>1845</td>
<td>N-P-K, mainly P₂O₅</td>
<td>4.1 ± 0.3</td>
</tr>
<tr>
<td>ANT</td>
<td>P based P₂O₅</td>
<td>6.0 ± 0.1</td>
</tr>
<tr>
<td>LAWN</td>
<td>N-P-K Fertilizers</td>
<td>Not Detected</td>
</tr>
</tbody>
</table>
6.4. Conclusions

This study reveals that uranium can be determined in seawater and fertilizer samples by TXRF, after its selective extraction using a suitable solvent. Solvent extraction serves two purposes: (i) matrix separation and (ii) pre-concentration.

Seawater samples collected from the Arabian Sea were analyzed for uranium after extraction with diethyl ether. The results were found to be in good agreement with the uranium content in seawater reported in literature. The precision of the uranium determination was found to be better than 17%.

The technique applied for the trace determination of uranium in fertilizers involved its selective extraction by TBP. As direct determination of uranium in TBP is difficult, back extraction of uranium in dilute acid was carried out as an additional step.

Both the studies suggest that TXRF is one of the suitable techniques for trace determination of uranium in seawater and fertilizer samples on a routine basis.

6.5. References


