Total reflection X-ray fluorescence and energy-dispersive X-ray fluorescence characterizations of nuclear materials

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Abstract. Nuclear energy is one of the clean options of electricity generation for the betterment of human life. India has an ambitious program for such electricity generation using different types of nuclear reactors. The safe and efficient generation of electricity from these reactors requires quality control of different nuclear materials, e.g. nuclear fuel, structural materials, coolant, moderators etc. These nuclear materials have to undergo strict quality control and should have different specified parameters for their use in nuclear reactors. The concentration of major and trace elements present in these materials should be within specified limits. For such chemical quality control of these materials, major and trace elemental analytical techniques are required. Since some of these materials are radioactive, the ideal chemical characterization techniques should have multielement analytical capability, should require very less sample (micrograms level) for analysis so that the radioactive waste generated, and radiation exposure to the detector and operator are minimum. Total reflection X-ray fluorescence (TXRF) and energy dispersive X-ray fluorescence (EDXRF) with improved features, e.g. application of filters, secondary target and instrumental geometry require very small amount of sample and thus can be suitably used for the characterization of nuclear materials mainly for the determination of elements at trace and major concentration levels. In Fuel Chemistry Division, TXRF analytical methods have been developed for trace element determinations in uranium and thorium oxides, chlorine determination in nuclear fuel and cladding materials, sulphur in uranium, uranium in sea water etc. Similarly, EDXRF analytical methods with radiation filters (to reduce background) and improved sample preapartion techniques, e.g. fusion bead and taking samples in the form of solution on filter papers have been used for developing analytical methods for the determination of U and Th in their mixed matrices, Cd in uranium etc. Some of these studies have been reported in this paper.

Keywords. Total reflection X-ray fluorescence; energy-dispersive X-ray fluorescence; nucler fuel; trace elements.

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1. Introduction

India has an ambitious program for the generation of electricity using nuclear reactors [1]. In these reactors U, Th and Pu in different forms and combination are used as

nuclear fuel and different materials are used as cladding and structural materials. These materials have to undergo stringent quality control before they can be used in the reactor. The impurities, metallic and nonmetallic, which get incorporated with the fuel during various fuel fabrication procedures have to be under specified limits for safe and efficient operation of the reactors [2,3]. Different techniques, e.g. inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS) and spark source mass spectrometry (SSMS) [2,3], are used for such trace element determination in uranium and thorium oxides. Though X-ray fluorescence has been used for major element determinations in actinide oxides, for trace element determinations normal XRF cannot compete with the above well-established instrumental techniques. As these materials are radioactive, the ideal chemical characterization techniques should have multielement analytical capability, should require minimum sample for analysis so that the radioactive waste generated and radiation exposure to the detector and operator are minimum. Total reflection X-ray fluorescence (TXRF) is a comparatively new multielement analytical technique for trace element determinations [4,5]. It is a special variant of EDXRF where the X-ray beam falls at a flat polished sample support at an angle less than the critical angle and thus gets totally reflected. A few-nanometer thin layer of the sample deposited on this support is excited by incident as well as totally reflected beam. For the deposition of the sample, 2–10 μl volume of the sample solution mixed with internal standard and containing $<1000\,\mu$g/ml of matrix is put on the sample support and heated under an IR lamp or a hot plate. The concentrations of different elements are measured after evalutaing the X-ray intensities of their characteristic lines and comparing these intensities with that of internal standard characteristic X-ray line with proper corrections for the sensitivities [5,6].

The instrumental set-up of TXRF is given in figure 1. The TXRF analysis is almost free from matrix effect, requires very less amount of sample ($\approx$10 μl), can analyse metals and nonmetals alike, can be used for major element determination as a trace and ultratrace analytical technique as well as a microanalytical technique for major element determinations etc. Unlike normal XRF, only one internal standard is sufficient for TXRF analysis. However, it requires dissolution of the sample. Some of the major advantages and disadvantages of TXRF are summarized in table 1. The advantage of TXRF for the characterization of nuclear materials is that it requires only a few ng of sample, thereby analytical waste generated is very less. Such a small amount of sample does not give
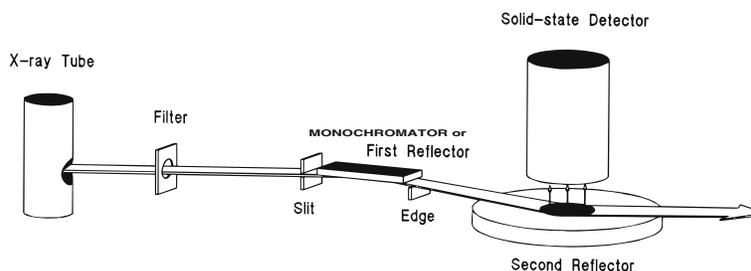

**Figure 1.** Instrumental set-up for TXRF.

Table 1. Major advantages and disadvantages of TXRF.

Advantages	Disadvantages
Lower detection limit in pg level	Dissolution of the sample is required
Lower sample size (2–50 μl)	In nonuniform sample the analysis does not give complete picture
Multielement analysis	The d spacing of multilayer may change with temperature. May require alignment from time to time
Universal calibration, single internal standard can be used for most elements	Difficult alignment

high radiation dose to the operator and the instrument. This feature of TXRF makes it attractive for characterizing nuclear materials. But, so far the application of TXRF for such applications are very limited [6–8]. In the last few years different TXRF methods for the characterization of nuclear materials, e.g. development of TXRF method for the determination of trace metals in uranium/thorium oxides, nonmetals, e.g. Cl, S in uranium, thorium, uranium–plutonium oxides and carbides, cladding materials, a touchstone technique of TXRF compositional characterization of mixed uranium–thorium oxides in the form of sintered as well as green pellets, powders and microspheres etc. have been developed in the Fuel Chemistry Division. Low-Z element determinations by XRF has been always difficult. We have developed vacuum chamber TXRF method for determining ppm levels of Na, Mg and Al in uranium matrix. Though energy-dispersive X-ray fluorescence (EDXRF) [4,9] has relatively higher detection limits compared to TXRF,
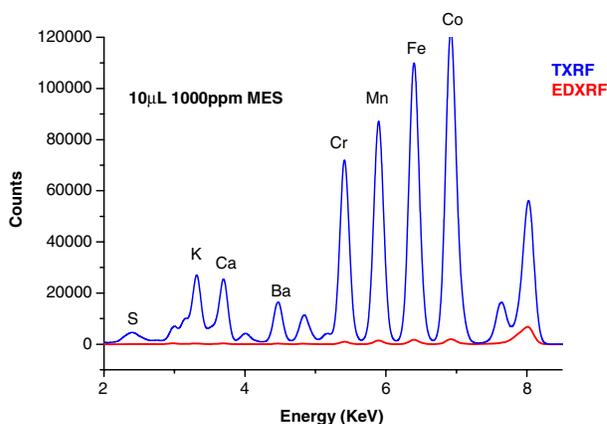
Figure 2. Difference in EDXRF and TXRF spectra (The EDXRF spectrum was recorded by depositing 10 μl of sample on an absorbent sheet, whereas the TXRF spectrum was recorded on quartz sample support.) W L$_\alpha$ was the exciting radiation.
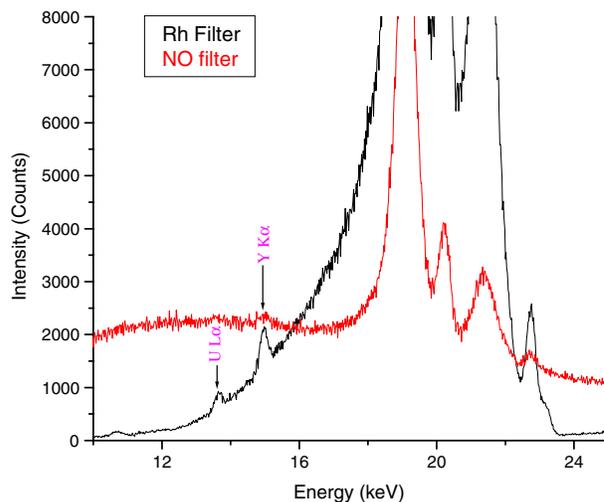
Figure 3. Difference in EDXRF spectrum of a mixed Y and U solution containing 19 μg/ml of each element. The reduction in background and increase in intensity of both U L$_\alpha$ and Y K$_\alpha$ lines are clearly visible.

because of the comparatively simple instrumentation and continuous improvements in different instrumental features, e.g. proximity of the sample with the source/detector, use of filters and secondary targets to increase the peak to background ratio, it can also be a good technique for major and minor element determination in nuclear materials. However, as far as trace element determination is concerned, TXRF has several orders of lower detection limit than that of EDXRF. The difference in TXRF and EDXRF spectra and the advantage of using filter in EDXRF are shown in figures 2 and 3, respectively. We have developed EDXRF method for major element determination in mixed uranium–thorium oxides of AHWR fuel composition with and without dissolution of the sample using different sample preparation techniques. Also we have developed EDXRF method for determining ppm level of Cd in uranium matrix and semiquantitative determination of indium in heavy water samples. Based on these studies, TXRF and EDXRF have been established as ideal analytical techniques for nuclear materials. In the present paper a brief review of the above activities is presented.

2. Experimental methods

In most of the studies in Ital Structures, Italy, TXRF spectrometer TX-2000 with a Mo–W dual target and twelve position sample chamber was used for TXRF measurements. The TXRF spectra were recorded by depositing the samples on quartz sample supports. W L$_\alpha$ or Mo K$_\alpha$ lines selected from a W–C multilayer were used for the excitation of X-ray spectra according to the requirement. The computer programs TXRFACQ32 and EDXRF32 were used for TXRF measurements and data processing. The computer program EDXRF32 is capable of profile fitting and removing the interfering X-ray lines from

the analyte line. However, for low-Z element determination, an Atominstitut Vienna, Austria, vacuum chamber low-Z TXRF spectrometer (WOBISTRAX) located at Eotvos University Vienna was used [10]. The spectrometer utilizes Cr K_α X-rays for sample excitation. The monochromatic Cr K_α X-rays are obtained using a W–C multilayer. For EDXRF measurements a Jordan Valley EX-3600TEC EDXRF spectrometer having rhodium target was used. The instrument is equipped with a low power 50 W tube, radiation filters and secondary targets. The computer program nEXT provided along with the instrument was used for EDXRF measurements and data processing.

3. Results and discussion

3.1 *Applications of TXRF for the characterization of nuclear materials*

3.1.1 *Trace element determinations in uranium and thorium oxides.* In Fuel Chemistry Division, TXRF methods have been developed for determining trace elements in uranium and thorium oxides. For this, these oxides were dissolved in nitric acid. To satisfy the TXRF conditions by making thin films of the samples, uranium and thorium were selectively extracted from the solutions using the well-established procedure of tri-n-butyl phosphate (TBP) extraction; the aqueous phases containing the trace elements were then mixed with Y internal standard and 10 μl of the mixtures were deposited on quartz sample supports for TXRF measurements. After processing these TXRF spectra, the amounts of trace elements were determined for each sample. The TXRF-determined concentrations are in good agreement with the certified and ICP-AES determined values. These studies have indicated that TXRF is not only comparable but also, in certain cases, better than the well-established trace element determination techniques mentioned above, i.e., it can analyse metals as well as nonmetals, the interference of different elements is comparatively less and can be taken care of by profile fitting. The elements K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Y, Ba and Pb present in ppm and sub-ppm levels were determined in these oxides. The detection limits were in ng/ml level [11,12]. A typical TXRF spectrum of an aqueous phase obtained after the extraction of thorium using TBP as extractant is shown in figure 4. A comparison of values determined by TXRF and ICP-AES is given in table 2.

3.1.2 *Trace element determination of low-Z elements in uranium.* Determination of low atomic number (Z) elements in the matrix of heavy elements like uranium is always a difficult task. Normal TXRF cannot be used for the determination of low-Z elements, like B, C, N, O, Na, Mg, Al etc., mainly because of the low fluorescence yield of these elements. A TXRF spectrometer attached with a vacuum sample chamber may be helpful. TXRF method using vacuum sample chamber [10] was used for the determination of low-Z elements in a synthetic mixture of Na, Mg, Al and uranium. The synthetic mixtures of the samples were prepared by mixing standard solutions of Na, Mg, Al in uranyl nitrate solution in such a way that the concentration of these low-Z elements in solution was in the range of 10–20 μg/ml, whereas with respect to U this value was in the range of 150–300 μg/g. Uranium from these solutions was separated using TBP and the aqueous phase containing Na, Mg and Al was mixed with Sc internal standard. 10 μl aliquots
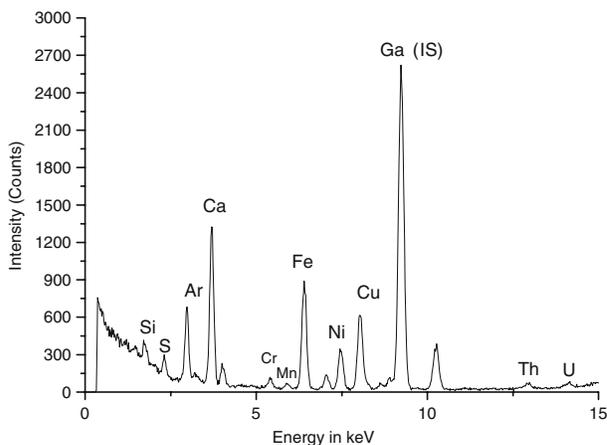
Figure 4. A typical TXRF spectrum of an aqueous phase obtained after extraction of Th using TBP as the extractant (Ga was added as an internal standard).

of this mixed solution were taken on four plexiglass sample supports and left for drying overnight. The TXRF spectrum of these specimens for each sample was measured. Presence of Na, Mg and Al were clearly seen in the spectrum. In addition, the characteristic X-ray lines of some other low-Z elements, e.g. C, O, P etc., were also clearly visible. Na, Mg and Al in the samples were determined using the relative sensitivity values and by averaging the values obtained in four measurements. On the basis of this study [13], it was concluded that the low-Z elements Na, Mg and Al can be determined by vacuum chamber TXRF on routine basis after preconcentration of the samples. The precision observed in the present study for the determination of Na, Mg and Al was 31% (1σ) and

Table 2. Comparison of TXRF and ICP-AES analytical results of trace elements in two uranium oxide samples.

Elements	Concentration (μg/g) in U			
	Sample 1		Sample 2	
	TXRF[a]	ICP-AES[b]	TXRF[a]	ICP-AES[b]
Ca	24.0 ± 0.9	29.1 ± 0.9	4.0 ± 0.9	4.4 ± 0.1
Cr	1.3 ± 0.3	1.50 ± 0.03	1.080 ± 0.004	0.30 ± 0.01
Cu	4.0 ± 0.4	4.30 ± 0.04	1.870 ± 0.003	0.30 ± 0.02
Mn	0.89 ± 0.07	0.90 ± 0.02	0.730 ± 0.005	0.10 ± 0.01
Ni	1.59 ± 0.06	1.8 ± 0.1	0.5 ± 0.4	0.40 ± 0.07
Fe	19.27 ± 0.05	19.8 ± 0.5	7.09 ± 0.85	40 ± 0.09
Zn	10.6 ± 0.1	7.5 ± 0.2	2.13 ± 0.06	1.40 ± 0.02

[a]TXRF-determined value $\pm 1\sigma$.

[b]ICP-AES-determined value $\pm 1\sigma$.

the results deviated from the calculated concentrations by 14%. The TXRF spectrum of a sample is shown in figure 5 and the comparison of TXRF and expected concentrations are given in table 3.

3.1.3 *Trace element determination of nonmetals (S and Cl) in nuclear materials.* TXRF can determine metals and nonmetals alike. A method for TXRF determination of Cl and S in nuclear materials has been developed. The method for determining chlorine at ppm levels in U_3O_8, $(U,Pu)C$, PuO_2 and Pu alloys involves the separation of chlorine from these matrices by pyrohydrolysis followed by collecting the evolved chlorine in a 5 mM NaOH solution. This solution was analysed for chlorine by TXRF spectrometry using cobalt as an internal standard. Chlorine was collected in NaOH solution instead of acidic solutions to prevent its loss as HCl while preparing TXRF samples by heating on quartz sample supports. For better results helium purging was used. The precision obtained by this approach was 15% (1σ, $n = 4$). The results obtained from TXRF method were also compared with the ion chromatography results [14] and are given in table 4. This study is still under progress.

Similarly, S in uranium oxide was determined using TXRF. Uranium, the main matrix, was separated from the samples obtained after dissolution in nitric acid. The TXRF spectrum of aqueous phase was measured after mixing Sc as an internal standard. The TXRF-determined concentrations were found to be in good agreement with the expected concentrations [15] as shown in table 5.

3.1.4 *Determination of uranium in sea water.* Uranium concentration in sea water is about 3.3 ng/ml. It is very difficult to determine such a small amount of uranium in a high salt matrix. TXRF has been used for determining uranium in sea water. Uranium was
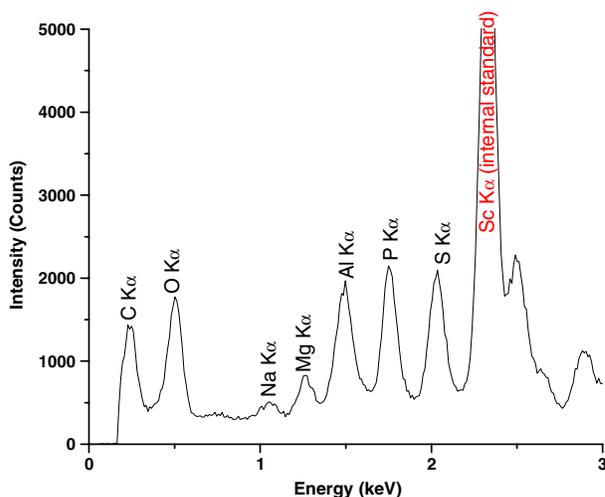
Figure 5. A typical TXRF spectrum of an aqueous phase obtained after extraction of uranium from the U and low-*Z* mixed sample.

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Table 3. Comparison of TXRF-determined concentrations of low atomic number elements with the expected concentrations.

Elements	Elemental concentrations (μg/ml)					
	Sample 1		Sample 2		Sample 3	
	Exp.	TXRF	Exp.	TXRF	Exp.	TXRF
Na	10.3	9 ± 2	14.5	11 ± 5	19.9	18 ± 9
Mg	10.2	10 ± 2	14.3	6 ± 4	19	13 ± 1
Al	10.3	10 ± 2	14.4	15 ± 4	19.1	23 ± 4

Exp. = Expected concentrations of the elements on the basis of the preparation of samples.

TXRF = TXRF-determined concentration of elements $\pm 1\sigma$ ($n = 4$).

Table 4. Comparison of TXRF and IC determinations of chlorine.

Sample	Sample mass taken for pyrohydrolysis[a] (g)	TXRF[b]	IC[c]
U_3O_8	0.9969	890 ± 232	1232
(U,Pu)C-1	0.5173	323 ± 69	278
(U,Pu)C-2	0.5299	208 ± 52	257
(U,Pu)C-3	0.5233	411 ± 148	333

[a]The evolved chlorine was collected in 5 mM NaoH which was later made up to 25 ml.
[b]TXRF-determined conc. of chlorine in solution (ng/ml).
[c]IC-determined conc. of chlorine in solution (ng/ml).

Table 5. A comparison of TXRF-determined and expected sulphur concentrations of some mixed standard solutions of sulphur and uranium.

Solution No.	Expected sulphur (μg/ml)	TXRF-determined sulphur $\pm 1\sigma$ ($n = 4$) (μg/ml)	Deviation of TXRF-determined values from expected values (%)
1	50	46 ± 4	–8
2	1.1	0.97 ± 0.07	–11.8
3	12.9	9.3 ± 0.7	–27.9
4	1.3	1.1 ± 0.1	–15.4
5	1.0	0.82 ± 0.04	–18

selectively extracted from sea water using diethyl ether and was analysed by TXRF after its preconcentration by evaporation and subsequent dissolution in 1.5% suprapure HNO_3. For this TXRF determination, yttrium was used as an internal standard. The uranium

concentrations determined by TXRF were in good agreement with the values reported in the literature. The precision obtained was $<5\%$ (1σ) and by such preconcentration the detection limit of uranium in sea water was in the range of pg/ml [16].

3.1.5 *Major element determinations in uranium–thorium oxides.* The compositional characterization of reactor fuel is an important step in its quality control. Since TXRF requires only ng amount of analytes it can be a good technique for major element determination also. Mixed actinide oxides are important as nuclear fuel for electricity generation in a nuclear reactor. We have developed a fast TXRF method for major element determination in nuclear fuel. Normally, the nuclear fuel is dissolved in acids for trace determination by various instrumental techniques. In TXRF method a small amount (a few microlitres) of this solution is mixed with Y internal standard. After recording the TXRF spectra of this solution, the amount of U and Th can be determined with an accuracy of $\sim$3%. The method was tested with solutions prepared by mixing single element standard of U and Th and had shown promising potential for routine determinations of U and Th in their mixed matrices after dissolution [17].

As the dissolution of the actinide oxides, specially ThO_2, is a difficult task, it was desirable to develop a TXRF method for their compositional analysis without dissolution. In the Fuel Chemistry Division, work is under progress to develop a touchstone method of compositional analysis of $(U,Th)O_2$ in the form of sintered and green pellets and microspheres. In this method samples will be rubbed at the centre of the quartz sample support very gently and their TXRF spectra will be taken. This rubbing transfers only a very small amount of sample on the support but this amount is sufficient for TXRF determination. After recording TXRF spectra the amount of one component (either U or Th) is determined with respect to the other using sensitivity values and TXRF spectrum [18]. The method is giving encouraging results.

3.2 *Applications of EDXRF for the characterization of nuclear fuel*

3.2.1 *Compositional characterization of AHWR fuel after dissolution.* India has an ambitious program of power production using its abundant thorium resources. It is proposed to use (^{233}U, ^{232}Th)O_2 and (^{239}Pu, ^{232}Th)O_2 having U and Pu respectively in the range of 3–4% as fuels for these reactors. For compositional characterization of these fuels a fast analytical method is required. Moreover, as these samples are radioactive, the sample required for the compositional characterization should be as small as possible. One such EDXRF method requiring only micrograms of analytes, i.e. uranium (U) and thorium (Th), in their mixtures in solution form has been developed. Calibration and sample solutions covering the fuel composition range (0–5% of U in U + Th) of advanced heavy water reactor (AHWR) were prepared by mixing uranium and thorium solutions. In a fixed volume of these solutions fixed amount of Y internal standard was added. EDXRF spectra were recorded by absorbing 20 μl aliquots of these solutions on 30 mm diameter filter papers, after drying. A typical EDXRF spectrum is shown in figure 6. Calibration plots were made by plotting U/Y and Th/Y ratios against the respective intensity ratios of Th L_α, U L_α and Y K_α. The results of U and Th determinations showed a precision

of about 3% (1σ) and the results deviated from the expected values by <3% in most of the cases [19]. This method requires only microgram amount of samples. Radioactive analytical waste generated in the process is quite small and the method can analyse other elements also. Though it requires sample in solution form, it is not a problem as fuel is dissolved for impurity analysis by other analytical techniques.

3.2.2 *Compositional characterization of AHWR fuel without dissolution.* Though EDXRF determination of elements in solutions gives a more accurate and precise data, the dissolution of nuclear fuel, especially thorium oxide, is a very difficult task. A method of compositional characterization of nuclear fuel is desirable. The general sample preparation methodology of making pellets for the analysis of the samples has the disadvantages that the problems associated with particle size and different oxidation states affect the results adversely. These problems are solved if the samples are fused in an oxidizing fusion mixture, e.g. lithium tetraborate. Studies are in progress in Fuel Chemistry Division, BARC for developing an EDXRF method for uranium and thorium determination using fusion bead method. This process avoids the cumbersome method of dissolution of uranium and thorium oxides and gives accurate and precise values comparable with that obtained with samples in the form of solutions.

3.2.3 *EDXRF determination of trace levels of cadmium in uranium matrix using Cd K_α line excited by continuum.* Presence of even ultratrace levels of Cd in nuclear fuel is undesirable as it is a strong neutron absorber. A suitable analytical method for its determination is desirable. The determination of Cd by EDXRF using Cd L_α line has
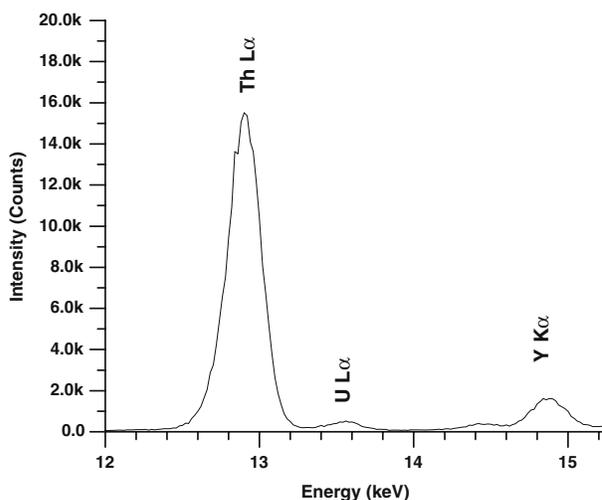
Figure 6. An EDXRF spectrum of a sample of mixed uranium and thorium (having 1% U in U + Th) in solution form. The spectrum was recorded by absorbing the sample on an absorbent sheet.

certain disadvantages, e.g. low fluorescence yield and energy, lying in low energy region having high background, etc. EDXRF determination of Cd using Cd K_α (23.172 keV) as analytical line will be free from these disadvantages. However, sufficient sources are not available to excite Cd K_α line. Though continuum X-ray sources can excite Cd K_α, these are of lesser intensity compared to characteristic X-rays. The continuum sources can be tuned for experimental requirements by proper choice of instrumental parameters and thus will be suitable for routine sample analysis. An energy-dispersive X-ray fluorescence (EDXRF) method for determining cadmium (Cd) in uranium (U) matrix using continuum source of excitation was developed. The method consists of separating uranium from calibration and sample solutions. 1.5 ml of aqueous phases thus obtained were taken directly in specially designed leak-proof Perspex sample cells, fabricated in-house, for the EDXRF measurements. For reduction of background in Cd K_α region, an Mo filter was used. The calibration plots were made by plotting Cd K_α intensity against the respective Cd concentration. The results obtained showed a precision of 2% (1σ) and the results deviated from the expected values by 4% on an average [20].

4. Conclusions

From the above discussion it is clear that TXRF, because of its attractive trace elemental analytical features, has a very promising potential for trace and major element determinations in nuclear materials. The small amount of sample avoids high radiation dose to the instrument, and the operator, and at the same time generates much less analytical waste. It has been used for trace metal and nonmetallic elemental determinations in uranium oxide, thorium oxide and also for major element determination in mixed U–Th solutions, U and Th determination by a simple touchstone technique, determination of uranium in sea water etc. The major disadvantage is that it requires dissolution of the sample. By using various features, e.g. filters, secondary targets etc., the peak to background ratio in EDXRF determination can be increased. It results in better detection limits and requires small sample volumes. This technique is useful mainly for major element determination though it can also be used for trace element determination at ppm levels.

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