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Analytical note

Bulk determination of uranium and thorium in presence of each other by Total Reflection X-ray Fluorescence spectrometry

Sangita Dhara, Nand Lal Misra *, Khush Dev Singh Mudher, Suresh Kumar Aggarwal

Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Abstract

A study to assess the applicability of Total Reflection X-ray Fluorescence (TXRF) spectrometry as a microanalytical technique for the determination of uranium and thorium as major elements in presence of each other has been made. Effect of dilution of the sample on the analytical results has been investigated. It has been found that dilution of the sample does not affect the analytical results significantly. Also the analytical results of uranium and thorium are similar with different internal standards e.g. cobalt, gallium and yttrium. With a sample size of 10 µL and the concentrations of the analytes in the range of 1–50 µg/mL and total matrix concentration less than 200 µg/mL, the precision and accuracy of the method were found to be better than 3% (1 s) and 4%, respectively. For higher concentration ranges of the analyte (up to about 700 µg/mL), the precision and accuracy values were better than 6% (1 s) and 5%, respectively. The TXRF method has an advantage of using small sample volume of about 10 µL, produces very small radioactive waste and is nondestructive but requires dissolution of the sample.
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1. Introduction

Uranium, thorium and plutonium have special importance among actinides as these are used as fuel for electricity production in nuclear reactors. India has moderate amount of uranium and plenty of thorium resources. The three stage Indian nuclear power production program utilizes uranium and thorium resources in a systematic way. Mixed oxides of ^{233}U, ^{232}Th and ^{239}Pu are the fuels proposed for the third stage of power production utilizing Advance Heavy Water Reactors (AHWRs) [1,2]. The composition of uranium–thorium oxide fuel is specific and requires strict quality control by means of determination of trace as well as major elements present in these oxides. As these samples are radioactive, it is imperative that sample amount used for such determinations should be as low as possible so that there is minimum risk of radiation hazards and less radioactive waste generation. Different

methods are used for the determination of uranium and thorium in different concentration ranges for characterization of nuclear fuel materials [3,4]. Though Wavelength Dispersive and Energy Dispersive X-ray Fluorescence (WDXRF and EDXRF) methods have the capability of nondestructive analysis of different elements, these methods require different calibration plots for different matrices and are more suited to find out elemental ratios rather than absolute elemental concentrations [5]. Total Reflection X-ray Fluorescence (TXRF) spectrometry is being progressively applied in different areas of analytical chemistry for trace element determinations [6–11]. This technique can also be used as a microanalytical technique to determine major elements after some modifications [12]. Due to the requirement of very small amount of sample, it poses less problem of waste management as compared to other techniques and is thus more suited for radioactive samples [13]. Recently, we have studied its applicability for trace elements determinations in uranium and thorium oxides [10,11]. Few years back Haarich et al. have explored the capability of TXRF for analyzing real life solutions of nuclear reprocessing plants [13]. In this paper, we

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report a study for a new type of application of TXRF for the bulk determination of uranium and thorium in their mixed matrices.

2. Experimental

2.1. Sample preparation

Merck uranium standard solution having uranium concentration of 1000 μg/mL and thorium standard solution with thorium concentration of 891 μg/mL (prepared by dissolving $Th(NO_3)_4 \cdot 5H_2O$ in HNO_3 and concentration determination done by complexometric titration using EDTA) were used for the preparation of synthetic mixtures of uranium and thorium. These solutions were mixed after dilution, in different ratios, to give synthetic U–Th mixtures with uranium and thorium contents in range of 16 to 84% as shown in Table 1. These solutions were used for standardization of TXRF method for uranium and thorium determinations in this work. The sensitivities of uranium and thorium were determined with respect to yttrium using a Merck yttrium single element standard solution mixed in another synthetic U–Th mixture and by recording its TXRF spectrum. The composition of the synthetic mixture used for determining the relative sensitivities of uranium and thorium is given in Table 2. In order to see the effect of using different internal standards, Merck single element standard solutions of cobalt and gallium were also used as internal standards in some of the synthetic samples prepared in similar way.

2.2. Instrumental conditions

An ITAL STRUCTURES Total Reflection X-ray Fluorescence spectrometer TX-2000 was used for TXRF spectrum measurement of the samples. The samples were excited with Mo K_α radiation produced at 40 kV and 30 mA in a dual target X-ray tube having W and Mo targets. The Mo K_α radiation was monochromatized by a W–C multilayer. For each measurement, 10 μL aliquot of the sample was deposited on quartz sample support and dried under an IR lamp to make a thin film of the sample suitable for TXRF measurements. The sample supports were put in twelve position sample chamber of the TXRF spectrometer for sequential measurement using a live time of

Table 1
Composition of synthetic U–Th mixtures prepared by mixing diluted standard solutions

Synthetic mixtures	Uranium concentration (μg/mL) (A)	Thorium concentration (μg/mL) (B)	% U (100*A/ (A+B))	% Th (100*B/ (A+B))
U–Th-1	0.56	2.79	16.7	83.3
U–Th-2	1.42	2.54	35.9	64.1
U–Th-3	500	742.48	40.2	59.8
U–Th-4	3.32	1.97	62.8	37.2
U–Th-5	300	133.65	69.2	30.8
U–Th-6	714.24	254.57	73.7	26.3
U–Th-7	142.86	50.91	73.7	26.3
U–Th-8	28.96	9.75	74.8	25.2

Table 2
Composition of synthetic mixture used for relative sensitivity determinations of uranium and thorium w.r.t. Y

S. No.	Element	Conc. (μg/mL)	X-ray line used	Average X-ray peak area	Relative sensitivity
1	Uranium	28.57	U L_α	625,440	0.345±0.006
2	Thorium	10.18	Th L_α	198,691	0.306±0.009
3	Yttrium	0.99	Y K_α	62,959	1

1000 s. The X-rays were detected with a Si (Li) detector having a resolution of 139 eV (FWHM) at 5.9 keV (Mn K_α). The X-ray data were acquired and processed by computer programs TXRFACQ-32 and EDXRF-32 provided with the instrument.

3. Results and discussion

3.1. Analytical strategy

In order to validate the TXRF method of analysis, the instrument was calibrated using Merck ICP multielement standard solution IV as described in our earlier publication [10]. The detection limits were found to vary in the range of 145 ng/mL for Al to 3 ng/mL for Sr for a diluted Merck multielement standard solution-IV having elemental concentrations in the range of about 900 ng/mL. On the basis of this calibration, another synthetic sample having elemental concentrations of about 50 μg/mL, prepared by diluting the Merck multielement standard solution-IV, was analyzed. The results of the TXRF elemental determinations were found within 5% of the expected concentrations. These results certified the TXRF geometry of the spectrometer and validated the analytical strategy.

The synthetic mixtures prepared were analyzed for uranium and thorium by TXRF using yttrium as an internal standard. Yttrium was chosen as internal standard because Y K_α (14.956 keV) energy is near to U L_α (13.612 keV) and Th L_α (12.967 keV) energies and it can be excited by Mo K_α radiation in an efficient way. Aliquots of 400 μL each of the synthetic
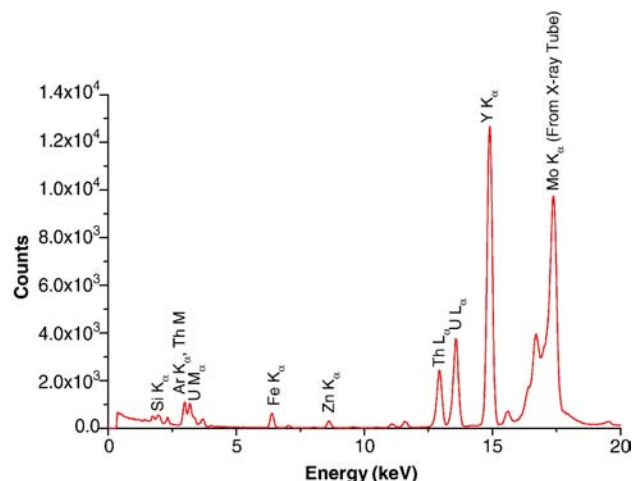

Fig. 1. TXRF spectrum of a uranium–thorium synthetic sample (U–Th-4) mixed with internal standard.

Table 3
Comparison of TXRF analytical results of uranium and thorium with expected concentrations of uranium and thorium in synthetic U–Th mixtures

Synthetic mixtures	Uranium concentration (µg/mL)		Expected/ TXRF [c]	Thorium concentration (µg/mL)		Expected/ TXRF [c]
	Expected [a]	TXRF [b]		Expected [a]	TXRF [b]	
U–Th-1	0.56	0.53±0.01	1.06	2.79	2.88±0.02	0.97
U–Th-2	1.42	1.36±0.01	1.05	2.54	2.55±0.09	1.00
U–Th-3	500	523±18	0.96	742.48	721±1	1.03
U–Th-4	3.32	3.29±0.07	1.01	1.97	1.89±0.06	1.04
U–Th-5	300	297±5	1.01	133.65	152±8	0.88
U–Th-6	714.24	727±8	0.98	254.57	242±40	1.05
U–Th-7	142.86	143±2	1.00	50.91	53.8±0.2	0.95
U–Th-8	28.96	29.0±0.2	1.00	9.75	9.8±0.2	0.99

[a] Expected concentration on the basis of dilution of the standard solution.
[b] Average of TXRF determined concentrations of four measurements±1 s.
[c] Ratio of expected and TXRF determined concentrations.

mixtures were mixed with different volumes of yttrium internal standards in precleaned PVC bottles with the help of a shaker. 10 µL aliquots of each of these solutions were deposited on two quartz sample supports followed by drying under an IR lamp. TXRF spectrum of one such synthetic sample is shown in Fig. 1. Some impurities e.g. Fe, Ca and Zn can be seen in the TXRF spectrum. Argon K_α peak is due to presence of argon in the atmosphere whereas Si K_α peak is from the sample support material. The analytical results obtained by TXRF analysis were compared with the expected concentrations of uranium and thorium in these synthetic mixtures and are given in Table 3. It can be seen that the precision of the method for uranium determination is better than 3.5% (1 s) whereas for thorium determinations it is better than 5.5% (1 s) in the uranium concentration range of 0.5–714 µg/mL, thorium in the concentration range of 2.8 to 743 µg/mL and the total matrix in the concentration range of 3 to 1245 µg/mL. The analytical results for uranium and thorium determinations agreed within 3.5% and 5.6% (except U–Th-5) respectively with the expected values. The precision of the uranium and thorium determinations were better than 2.1% and 3.2%, respectively, for uranium,

thorium and total matrix concentrations varying approximately in the range of 3–143, 2–51 and 5–192 µg/mL, respectively. The deviations of the uranium and thorium determinations from the expected concentrations in these situations were less than 0.9 and 3.15% respectively. It will be advisable to dilute the samples of uranium and thorium approximately in this concentration range for better precision and accuracy. For higher range of concentrations, the absorption and enhancement effects contribute to comparatively poor precision and accuracy of the method. The plot of expected vs. TXRF determined concentrations of uranium in the samples gave a regression coefficient 0.9995 for a linear fit. Similarly the plot of expected uranium % in (U+Th) matrix vs. TXRF determined uranium % gave a regression coefficient of 0.9977. A good and comparable agreement between the expected and TXRF determined concentrations in both these cases indicates the presence of negligible matrix effects.

3.2. Effect of dilution

In order to satisfy the TXRF conditions, the amount of sample deposited on sample supports should be as small as possible so that after drying, a thin layer of the sample forms keeping the matrix effects minimum. This requires the dilution of the
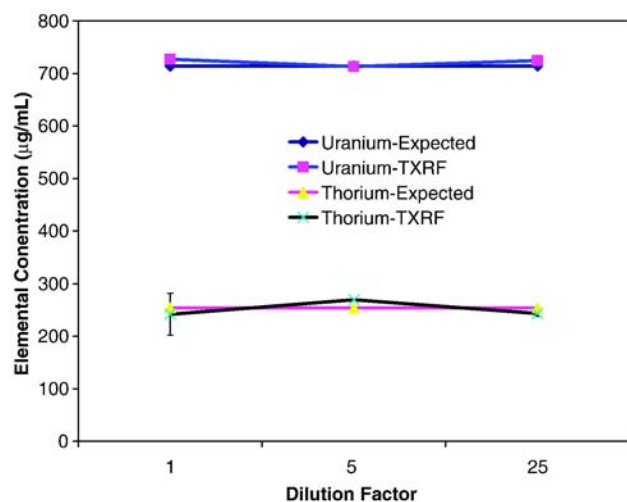

Fig. 2. Variation of TXRF analytical results for uranium and thorium with respect to dilution of the sample.

Table 4
TXRF determination of uranium and thorium using Co, Ga and Y as internal standards

Sample	Internal standard	Uranium determination			Thorium determination		
		Exp. (µg/mL)	TXRF [a]	TXRF/ Exp. [b]	Exp. (µg/mL)	TXRF [a]	TXRF/ Exp. [b]
U–Th–IS-1	Co	2.22	2.31±0.06	1.04	1.32	1.38±0.05	1.05
	Ga	2.22	2.21±0.04	1.00	1.32	1.32±0.03	1.00
	Y	2.22	2.20±0.02	0.99	1.32	1.31±0.01	1.00
U–Th–IS-2	Co	1.81	1.81±0.07	1.00	1.62	1.59±0.05	0.99
	Ga	1.81	1.78±0.05	0.98	1.62	1.57±0.04	0.97
	Y	1.81	1.77±0.04	0.98	1.62	1.56±0.02	0.97

Exp.: expected concentration on the basis of dilution of the standard solution.
[a] Average of TXRF determined concentration of four measurements± standard deviation (1 s).
[b] Ratio of TXRF determined and expected concentrations.

concentrated samples for measurement of uranium and thorium concentrations. It was therefore considered worthwhile to study the effect of dilution on the analytical results by TXRF. For this study, one sample was diluted to different concentrations using 1.5% suprapure HNO_3 prepared in Milli-Q water. The amounts of uranium and thorium in this sample were calculated from the TXRF determined uranium and thorium amounts in the diluted samples. The TXRF determined and expected concentrations of uranium and thorium have been plotted against dilution factor in Fig. 2. It was found that as long as total matrix is less than 1000 μg/mL, the TXRF determined concentrations for both uranium and thorium are close to the expected concentrations. However, for thorium analysis by TXRF when the total matrix concentration is 968.9 μg/mL, the precision is comparatively poor. Keeping this point in view along with the effect of total matrix amount on uranium and thorium determinations described earlier, it can be concluded that for better precision and accuracy, the analyte concentration should be in the range of 1–50 μg/mL.

3.3. Effect of using other internal standards

One of the advantages of TXRF technique over Energy Dispersive X-ray Fluorescence (EDXRF) and Wavelength Dispersive X-ray Fluorescence (WDXRF) is that same calibration is valid for different matrices and different internal standards can be used for elemental determinations. In order to experimentally investigate the effect of using other internal standards on the TXRF analytical results of uranium and thorium determinations, cobalt, gallium and yttrium Merck single element standards were mixed in two synthetic samples of uranium and thorium prepared in similar way. Uranium and thorium in these samples were determined by TXRF using cobalt, gallium and yttrium as internal standards. The results of these determinations are given in Table 4. It can be seen that these results are comparable with one another as well as with the expected uranium and thorium concentrations with respect to precision and accuracy. From these observations, it can be concluded that any internal standard can be used for uranium and thorium determinations by TXRF. Thus the TXRF method gives a flexibility of using different internal standards.

4. Conclusion

From the above observations, it is concluded that TXRF can be used for the bulk determination of uranium and thorium in presence of each other. The advantage of the method is that it is applicable to different types of matrices and requires a small amount of sample solution. This feature of TXRF will be helpful in containing the radioactive waste generated during analysis to a minimum amount. For accuracy better than 4% and precision better than 3% (1 s), analyte concentrations should be approximately in the range of 1–50 μg/mL for a 10 μL sample size. The method has flexibility of using more than one internal standard. The only limitation is that it requires dissolution of the sample. The study will initiate a new kind of application of TXRF as a microanalytical technique for the bulk determination of radioactive samples.

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