

Trace determination of uranium in fertilizer samples by total reflection X-ray fluorescence

N L MISRA^{1,*}, SANGITA DHARA¹, ARIJEET DAS², G S LODHA²,
S K AGGARWAL¹ and I VARGA^{3,*}

¹Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

²X-ray Optics Section, Raja Ramanna Centre of Advanced Technology, Indore, 452 013, India

³Eötvös Loránd University, Institute of Chemistry, H-1518 Budapest, Hungary

*Corresponding authors

E-mail: nlmisra@barc.gov.in (N L Misra); vargaip@chem.elte.hu (I Varga)

Abstract. Uranium is reported to be present in phosphate fertilizers. The recovery of uranium from the fertilizers is important because it can be used as fuel in nuclear reactors and also because of environmental concerns. For both these activities suitable method of uranium determinations at trace levels in these fertilizers are required. Studies have been initiated for such TXRF determination of uranium and the results are reported in the present paper. For TXRF determinations the fertilizer samples were processed with nitric acid and the uranium present in it was removed by solvent extraction using tri-n-butyl phosphate as the extractant. The organic phase containing uranium was equilibrated with 1.5% suprapure nitric acid to bring out uranium in aqueous phase. This aqueous phase was mixed with internal standard Y and the TXRF spectra were measured by depositing samples on float glass supports. The amounts of uranium in four fertilizer samples of Hungarian origin were determined by processing these TXRF spectra. Uranium concentrations in two fertilizer samples were found to be in the range of 4–6 $\mu\text{g/g}$, whereas two fertilizer samples did not show the presence of uranium. The precision of the TXRF determination of uranium was found to be better than 8% (1σ).

Keywords. Phosphate fertilizers; trace elements; total reflection X-ray fluorescence; solvent extraction.

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1. Introduction

Uranium being used as nuclear fuel in nuclear reactors is a material of immense technological importance. The conventional uranium sources used for uranium production are uranium ores which are limited in supply. Continuous efforts are being made all over the world to explore conventional and nonconventional uranium sources. Trace amounts of uranium have been reported in sea water, phosphoric acid, phosphate fertilizers etc. [1–3]. The recovery of uranium from phosphate fertilizers is important from the point of

view of its recovery as well as environmental concerns. So, suitable methods of uranium determination at trace levels in these fertilizers are required [4,5]. TXRF is a trace and ultra-trace elemental analytical technique used for quantitative determination in different matrices. It can be used for the determination of uranium in fertilizer samples, provided uranium is selectively separated from the fertilizers. Some studies were initiated for such TXRF determination of uranium from phosphate fertilizers of Hungarian origin and the preliminary results are reported in the present paper.

2. Experimental procedure

2.1 Instrumentation

For TXRF measurements a self-assembled TXRF spectrometer at Raja Ramanna Centre of Advanced Technology (RRCAT) Indore, India was used [1,2]. A monochromatized Mo K_{α} source obtained from the Mo target tube operated at 30 kV and 20 mA using a W-C multilayer was used. The samples were deposited on float glass supports [2]. The live time used varied from 1000 to 3000 s depending on the intensity of U L_{α} peak. The quantity of uranium in the fertilizer samples was determined using the net intensities of U L_{α} and Y K_{α} (internal standard) and blank corrections.

2.2 Sample preparation

Accurately weighed, about 1 g each of the four fertilizer samples were soaked in a minimum amount of concentrated nitric acid for about 3 h. Any remaining supernatant was

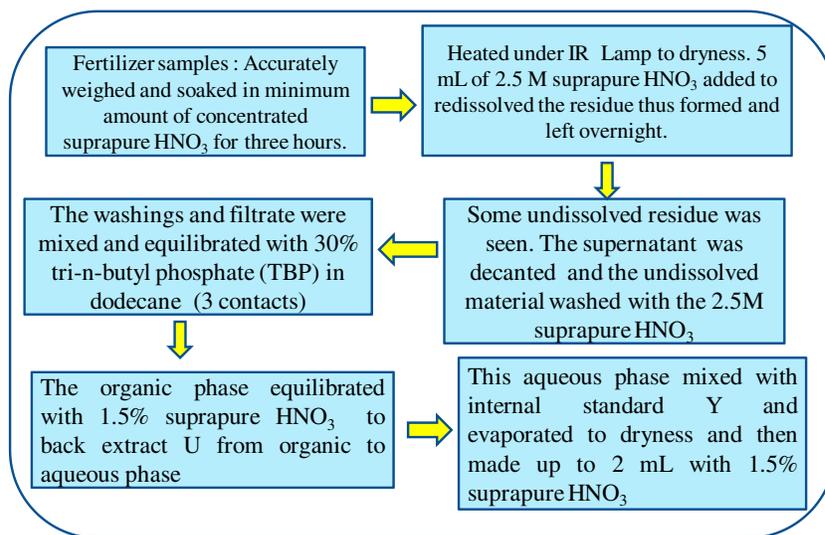


Figure 1. A flow chart showing sample preparation methodology for TXRF analysis of uranium in fertilizer samples.

Trace determination of uranium in fertilizer samples by TXRF

evaporated under IR lamp and then 5 ml of 2.5 M suprapure HNO_3 was added to the residue thus formed and left overnight. The supernatant was filtered and the solid material left undissolved was washed with the 2.5 M suprapure nitric acid. The washings were collected along with filtrate and equilibrated three times with 30% solution of TBP in dodecane [7]. Finally the organic phase was equilibrated with 1.5% suprapure nitric acid to bring out uranium in aqueous phase. This aqueous phase was mixed with internal standard Y, evaporated to dryness and then made up to 2 ml with 1.5% suprapure HNO_3 . Aliquots of 10–30 μl of this solution were deposited on float glass sample supports to measure the TXRF spectra. The flow chart of the sample preparation methodology is given in figure 1.

3. Results and discussion

The TXRF spectrum of a typical fertilizer sample is shown in figure 2. To find out the area of U L_α and Y K_α peaks, profile fitting using the program ORIGIN was used. The sensitivity of the U L_α vs. Y K_α was determined using similar TXRF measurements of four specimens taken from a mixture of U and Y standard solution. The amounts of uranium in the two fertilizer samples were determined using the above sensitivity values and U L_α and Y K_α intensities. The uranium amount was found to be in the range of 4–6 $\mu\text{g/g}$ in two samples, whereas other two fertilizer samples did not show the presence of uranium as shown in table 1. The TXRF spectra of the leftover solid residues did not show any U L_α peak. These observations indicate that uranium present in phosphate fertilizers is 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. As the method requires a very small amount of sample, the analytical waste generated will be minimum. The precision of the TXRF determination of uranium was found to be better than 8% (1σ). The results are being compared with ICP-MS.

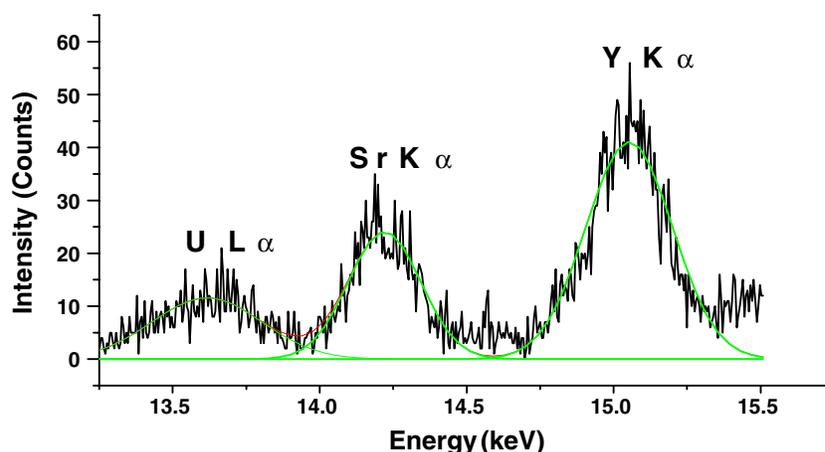


Figure 2. A profile-fitted TXRF spectrum of processed fertilizer sample (1845).

Table 1. The TXRF-determined values of uranium in fertilizer samples.

| Fertilizer sample codes | Description | TXRF-determined U ($\mu\text{g/g}$) \pm 1 s |
|-------------------------|------------------------------------------|-------------------------------------------------|
| 1844 | N-based, mainly NH_4NO_3 | Not detected |
| 1845 | N-P-K, mainly P_2O_5 | 4.1 ± 0.3 |
| ANT | P-based P_2O_5 | 6.0 ± 0.1 |
| LAWN | N-P-K fertilizers | Not detected |

4. Conclusion

The study has demonstrated that trace amounts of uranium in fertilizer samples can be determined using TXRF. However, before this technique is applied for such determinations on routine basis, more such fertilizer samples should be analysed by TXRF and the results should be compared with other techniques.

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