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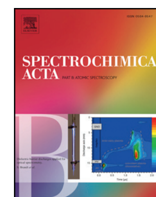
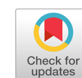


Analytical note

Total reflection X-ray Fluorescence determination of interfering elements rubidium and uranium by profile fitting



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A B S T R A C T

Systematic studies to assess the analytical parameters obtained in the total reflection X-ray fluorescence (TXRF) determinations of interfering elements Rb and U using profile fitting are reported in the present manuscript. The X-ray lines Rb Kα and U Lα having serious spectral interference (ΔE = 218 eV), have been used as analytical lines. The intensities of these X-ray lines have been assessed using profile fitting. In order to compare the analytical results of Rb determinations in presence of U, with and without U excitation, synchrotron radiation was tuned to energy just above and below the U L_{abs} edge. This approach shall excite both Rb Kα and U Lα simultaneously and Rb Kα selectively. Finally, the samples were also analyzed with a laboratory based TXRF spectrometer. The analytical results obtained in all these conditions were comparable. The authenticity of the results was assessed by analyzing U with respect to Rb in $Rb_2U(SO_4)_3$, a standard reference material for U. The average precision obtained for TXRF determinations was below 3% (RSD, n = 3, 1σ) and the percent deviation of TXRF values from the expected values calculated on the basis of sample preparation was within 3%.
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1. Introduction

Total reflection X-ray fluorescence (TXRF) is a frequently used analytical technique which finds applications in almost all branches of science for chemical characterization of materials. In TXRF analysis, only a few microlitres volume of the sample are pipetted out directly on highly polished smooth surfaces over which the total reflection of X-rays occurs. Due to the enhanced excitation in the TXRF geometry, one obtains elemental detection limits at ng/mL levels for most of the elements in the periodic table. In addition, it has simple quantification procedure using a single internal standard and is free from matrix and memory effects [1–5]. The XRF spectra, unlike the atomic spectra which are characterized by large number of spectral lines and are very complicated, are relatively simpler [6]. Though, the K, L and M X-ray lines of a particular element are the characteristic signature of that element, the spectral interferences in XRF arise because of interferences of K X-ray lines of lighter elements with the L or M X-ray lines of heavy elements present in the sample e.g. As Kα (10.54 keV) interferes with Pb Lα (10.55 keV), Rb Kα (13.396 keV) with U Lα (13.614 keV), etc. [7]. Further, the Kα and Kβ lines of nearby elements in periodic table interfere e.g. Cr Kα (5.41 keV) interferes with V Kβ (5.43 keV), etc. These spectral overlaps can produce severe errors in the corresponding XRF elemental quantifications, if proper corrections are not applied. Several studies are reported in literature on the use of various correction methods involving rigorous mathematical equations for the determinations of such interfering elements [7–10]. In TXRF, due to very small sample mass (~ng), the absorption enhancement effects are almost negligible. Hence, the matrix doesn't contribute to the change in the intensities of the elemental X-ray lines as severely as in the case of conventional XRF. So, while applying mathematical corrections for spectral interferences using TXRF, the contribution of matrix effect for change in their intensities can be neglected [9]. For TXRF quantification using empirical method, the basic requirement is to get the elemental sensitivity values using multielement standards. The area under the peak of an elemental X-ray line is calculated by deconvolution of the experimental spectra. For deconvolution of the experimental spectra many software packages are available. In our laboratory, TXRFACQ32 and EDXRF32 programs developed by ITAL structures, Italy for data acquisition and processing, respectively are used routinely [11]. The program EDXRF32 is a 32 bit-version software for quantitative processing of TXRF and EDXRF spectra generated by the spectrometer. It works on the files written in IAEA XRF spectra file format. In this program, the analysis session is divided into three phases: peak identification, area calculation followed by quantitative analysis. In case of peaks having interferences, the profile fitting of the X-ray peaks is performed. This involves separation of individual elemental X-ray lines using mathematical procedure which is based on nonlinear least-squares fitting using Marquardt algorithm.

Uranium and its compounds are technologically important materials having a variety of applications in the form of catalysts, magnetic

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Table 1
Details of samples used for TXRF measurements. (All concentration are in μg/mL).

Samples	Rb concentration	U concentration	Co concentration	Rb % in (U + Rb)
Rb-U-1	19.93	1.90	20	91.30
Rb-U-2	9.96	4.76	20	67.66
Rb-U-3	9.96	9.52	20	51.13
Rb-U-4	4.98	9.52	20	34.34
Rb-U-5	1.99	19.05	20	9.46
Rb-U-6	1.99	36.19	20	5.21

materials, electrodes and most important nuclear fuel [12,13]. Alkali metal uranates such as Na, K, Rb and Cs have been extensively studied because these uranates are likely to be formed by fission product – fuel, fuel – coolant interactions in a nuclear reactor during its operating or in transient conditions [14–16]. Rubidium is an important fission product formed during fuel irradiation and therefore many rubidium uranates are reported in the literature. Mono and di uranates of rubidium are well established compounds. Also a variety of polyuranates of rubidium, i.e. $Rb_2U_4O_{13}$, $Rb_2U_6O_{19}$ and $Rb_2U_7O_{22}$ have been reported in the literature [17,18]. The physical, chemical as well as compositional characteristics of such compounds need to be studied to understand the fuel behavior inside the reactor. Rubidium uranium (IV) trisulphate, i.e., $Rb_2U(SO_4)_3$, is a standard reference material for uranium, developed in our Division a few years back. It is an anhydrous compound having high purity and stability required for standard reference materials [19]. For compositional accuracy of these compounds, accurate determinations of their Rb and U contents are essential. Also environmental samples like soil, water, rocks etc. from uranium ore sites, are prone to be contaminated with uranium, and may even contain Rb from earth crust. Hence, a technique that can simultaneously determine U and Rb will be very useful for the rapid compositional characterization of samples obtained from all the areas mentioned above. Techniques such as mass spectrometry and gravimetry have been used for the determination of U and Rb, respectively in $Rb_2U(SO_4)_3$ [20,21]. Simultaneous XRF determination of U and Rb in presence of each other is difficult due to the strong interference of X-ray peaks of Rb Kα (13.396 keV) with U Lα (13.614 keV) especially in EDXRF. The second order lines (n = 2) of U Lα and Rb Kα are well

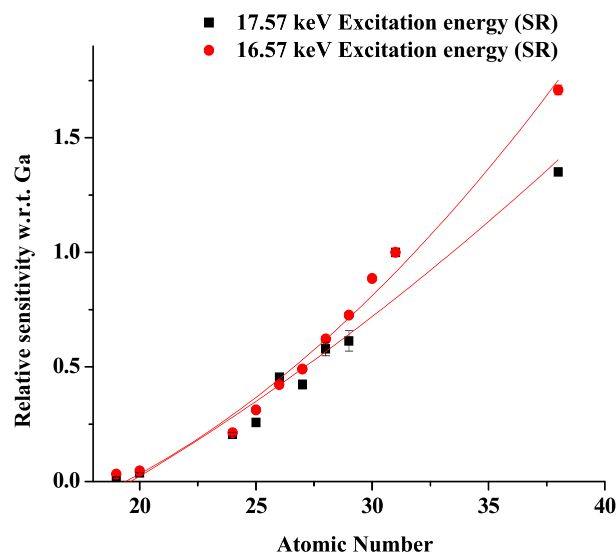

Fig. 2. Plot of relative sensitivities for K lines vs. atomic number for two different excitation energies using synchrotron radiation excitation (error bar represents ± 1σ for n = 4).

separated from each other in WDXRF and have been used for Rb determination in presence of U [21]. Simultaneous EDXRF determination of Rb and U having energy difference of (ΔE = 218 eV) can be a beneficial approach for such determinations by profile fitting and requires a careful study. However, no such systematic study using EDXRF is reported in literature for U and Rb as far as we know.

Due to above reasons, a comparison of the analytical results for the TXRF determinations of Rb and U, in presence of each other using different excitation sources were made. Synchrotron radiation (SR), which has the advantage of energy tunability with high brilliance, can be used for selective excitation of the element of interest [22,23]. Rb Kα can be selectively excited (Rb K_{abs} = 15.202 keV) leaving U Lα unexcited (U L_3 = 17.166 keV) by choosing an X-ray energy in between 15.20 keV to 17.17 keV whereas an excitation energy above 17.17 keV will excite both U and Rb, simultaneously. Hence, the TXRF analytical results obtained by profile fitting of the X-ray peaks of Rb and U excited

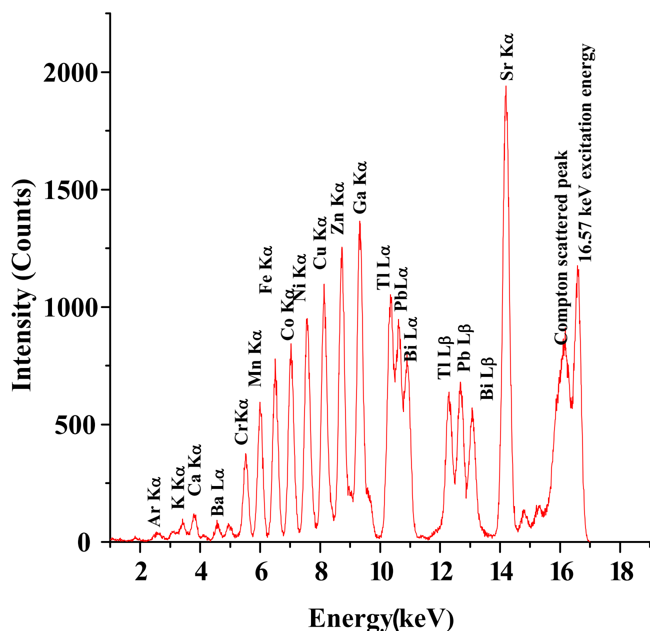

Fig. 1. TXRF spectrum of a multi elemental standard solution with elemental concentration of 16 μg/mL obtained using 16.57 keV SR excitation.

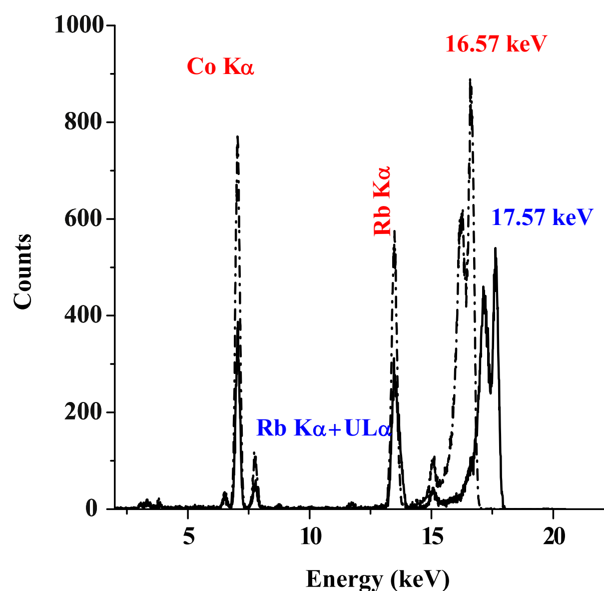

Fig. 3. TXRF spectra of U-Rb sample containing Co internal standard obtained using 16.57 keV (dashed) and 17.47 keV (solid) synchrotron radiation excitation.

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