

STUDY OF RESOLUTION ENHANCEMENT METHODS FOR IMPURITIES QUANTITATIVE ANALYSIS IN URANIUM COMPOUNDS BY XRF

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ABSTRACT

X-ray fluorescence analysis is a technique widely used for the determination of both major and trace elements in a large variety of materials. The modern X-ray spectrometers have devices which reduce undesirable effects related to interaction between the sample and radiation, allowing direct and nondestructive analysis. However, in uranium matrices these devices are inefficient because the characteristic emission lines of elements like S, Cl, Zn, Zr, Mo and other overlap characteristic emission lines of uranium. Thus, chemical procedures to separation of uranium are needed to perform this sort of analysis. In this paper the deconvolution method was used to increase spectra resolution and correct the overlaps. The methodology was tested according to NBR ISO 17025 using a set of seven certified reference materials for impurities present in U₃O₈ (New Brunswick Laboratory - NBL). The results showed that this methodology allows quantitative determination of impurities such as Zn, Zr, Mo and others, in uranium compounds. The detection limits were shorter than 50 μg g⁻¹ and uncertainty was shorter than 10% for the determined elements.

1. INTRODUCTION

U, Th and Pu in their different forms have been used as fuel for research and power reactors. During fuel fabrication operations, e.g. grinding, pelletizing and others, fuel material gets contaminated with various trace elements. For the efficient operation of a reactor stringent quality control by means of determination of trace elements present in the nuclear fuel is necessary before the fuel is put in a nuclear reactor [1].

The concentration of these impurities is specific to each kind of fuel [1,2,3]. Various analytical techniques as Atomic Absorption Spectroscopy (AAS), Spark Source Mass Spectrometry (SSMS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Neutron Activation Analysis (NAA) are usually used to for the trace element determination in the nuclear fuels.

These techniques have satisfactory robustness and accuracy as soon as lower limit of quantification (ng g⁻¹ to μg g⁻¹). However, preliminary chemical treatment as dissolution, digestion and separation of matrix are needed in sample preparation. Procedures like these make the analysis costly and lengthy, and still generate waste which requires specific procedures for disposal or proper storage environment [4, 5, 6].

The literature has also reported the use of Total Reflection X-ray Fluorescence (TXRF) spectrometry has been used for trace elemental determinations in different industrial and research areas, but preliminary chemical treatments in sample preparation also are required to minimize the matrix effects [1,7].

In case of conventional X-ray fluorescence (XRF), interelements effects such as absorption and / or intensification and the overlap [8,9,10], constitute the principal interference. However, modern spectrometers of X-ray Fluorescence (XRF), especially wavelength dispersion (WDXRF), have accessories, like scintillation detectors (SC), flow proportional (SPF), crystals diffraction, filters and others, and still coupled software which minimize and correct these effects, allowing direct and nondestructive testing.

In this paper the calculation correction coefficient method using regression was applied to increase impurities detection in U_3O_8 with the objective of performing direct and non-destructive chemical analysis. The methodology was evaluated in accordance with ISO/IEC 17025:2005. A WDXRF spectrum of U_3O_8 sample is shown in Fig. 1

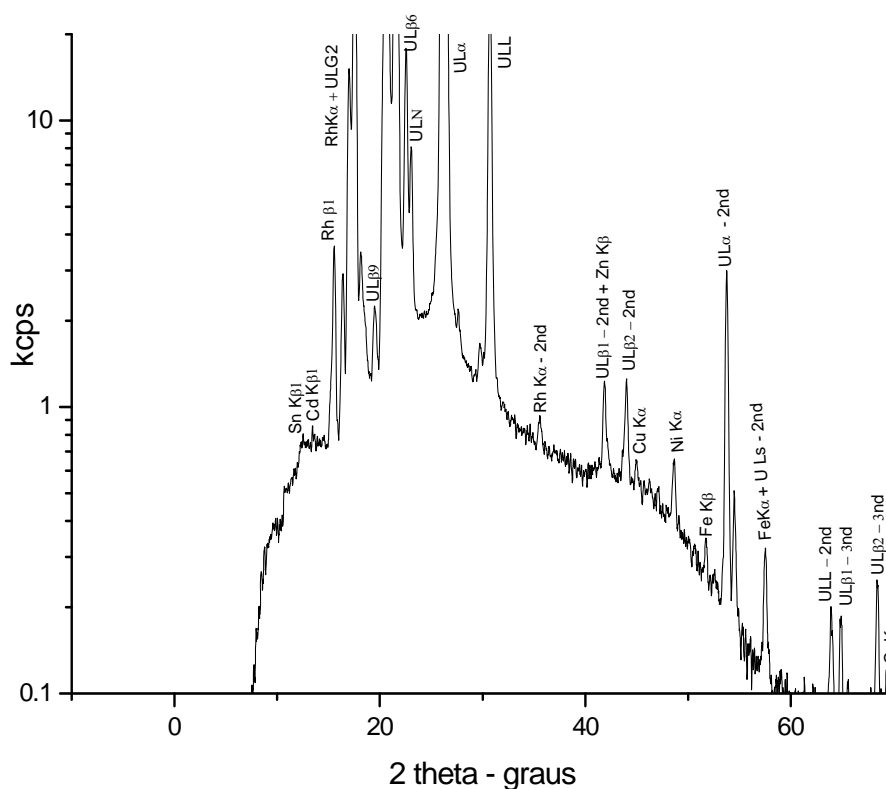


Figure 1. WDXRF spectra from U_3O_8 sample and impurities (CRM 124 - NBL).

2. EXPERIMENTAL

2.1. Sample preparation

The pressed powdered samples were prepared according to the following steps: 1.5 g of sample plus 0.5 g of wax (wax C micro powder, Hoechst) were transferred into a polyethylene bottle (5 cm³) and homogenized in a mechanical mixer for 5 min (Spex Mixer / Mill). The mixture was compacted into a hydraulic press (Herzog) using a pressure of 20 MPa for 1 second, on a basis of boric acid (H₃BO₃ PA), previously compressed with 100 MPa for 10 seconds, obtaining pressed samples of 25.01 ± 0.01 mm diameter and 5.0 ± 0.2 mm in thickness.

2.2. Instrumental parameters condition

The experiments were carried out using a WDXRF spectrometer (RIGAKU Co. model RIX 3000, which comprised the following primary devices: one 3 kW Rh X-ray tube, 6 positions sample, 4 positions for Al, Ti, Ni and Zr filters, 3 collimators, 8 crystal analyzers, 2 detectors (scintillation and flow-proportional counters). The parameters such as voltage, current, collimator, analyzing crystal, detector and fixed counting time for Mg, Si, Ca, Cr, Fe, Ni, Cu, Zn, Zr, Mo and Sn characteristic emission line were selected. (Tab. 1).

Table 1 – Measurements condition to WDXRF spectrometer RIX 3000

Excitation: 40kV x 40mA - * 50kV x 40mA						
<i>Element</i>	<i>Spectrum</i>	<i>Collimator</i>	<i>Analyzing Crystal</i>	<i>Detector</i>	<i>Counting time (s) Peak</i>	
Mg	K α	560 μ m	TAP	SFP	40	
Si	K α	560 μ m	PET (111)	SFP	40	
Ca	K α	560 μ m	Ge (111)	SFP	40	
Cr	K α	560 μ m	LiF (200)	SC	20	
Fe	K α	480 μ m	LiF (200)	SC	20	
Ni	K α	480 μ m	LiF (200)	SC	20	
Cu	K α	560 μ m	LiF (200)	SC	20	
Zn	K α	480 μ m	LiF (200)	SC	20	
Zr* (F-Ni)	K α	480 μ m	LiF (200)	SC	20	
Mo (F-Zr)	K β	560 μ m	LiF (200)	SC	20	
Sn (F-Zr)	K α	560 μ m	LiF (200)	SC	20	

TAP: thallium phosphate - LiF: lithium fluorite - Ge: germanium
SC: scintillation detector - NaI/Tl - FPC: flow-proportional counter.
F-Ni: Ni filter; F-Zr: Zr filter

2.3. Absorption/Excitation (Matrix) correction and overlap correction

A set of six certified reference materials CRM 123 (1-6) from New Brunswick Laboratory (NBL) – multi-element, were prepared according to the procedure described in 2.1 item for building calibration curve.

In the regression program, software coupled at spectrometer, matrix correction coefficients and overlap correction coefficients as well as calibration curves coefficients were calculated for Mg, Si, Ca, Cr, Fe, Ni, Cu, Zn, Zr, Mo and Sn.

The corrections for the coexisting elements were made using Eq.1.

$$W_i = (aI_i * bI_i + c)(1 + k + \sum A_{ij}F_j + \sum Q_{ij}F_jF_k + \sum \frac{R_{ij}F_j}{1+W_i}) + \sum B_{ij}F_j + \sum D_{ijk}F_jF_k + c \quad (1)$$

W_i \equiv Quantification value;

a, b, c \equiv Calibration curve coefficients;

I_i \equiv X-ray intensity;

K \equiv Constant term;

A_{ij} \equiv Absorption/excitation correction coefficient;

F_j \equiv Analysis value or X-ray intensity of correcting component;

Q_{ij} \equiv Absorption/excitation correction coefficient (secondary correction);

R_{ij} \equiv Excitation correction coefficient;

B_{ij} \equiv Overlap correction coefficient;

D_{ij} \equiv Absorption/excitation correction coefficient;

C \equiv Constant term.

2.4. Methodology evaluation

The methodology was evaluated using CRM 124-1 - multi-element standard from New Brunswick Laboratory. Three samples were prepared and six measurements for each element were carried out. The experimental fluorescent intensities were interpolated in the calibration curve for their determination. The following statistical tests were applied for performance evaluation.

The precision was calculated in terms of relative standard deviation (% RSD) and accuracy in terms of percentage relative error (%RE) and standard error (E_n), Eq. 2 [11]

$$E_n = \frac{(X_{lab} - X_{CRM})}{\sqrt{U_{lab}^2 + U_{CRM}^2}} \quad (2)$$

E_n \equiv standard error;

X_{lab} \equiv experimental average;

X_{CRM} \equiv certificate value;

U_{lab}^2 \equiv experimental variance;

U_{CRM}^2 \equiv certificate variance.

The limit detection (LD) was calculated according to Eq. 3 [12].

$$LD = 2 * \sqrt{\frac{I_B}{T_B}} \quad (3)$$

I_B \equiv Background intensity

T_B \equiv time of the background measurement

The limit quantification (LQ) was calculated according to Eq. 4 [12].

$$LQ = 2 * \sqrt{\frac{\sum_{ii}^N (C_i - \bar{C})^2}{N - 1}} \quad (4)$$

C_i \equiv Individual measured value;

\bar{C} \equiv Average;

N \equiv Repetition number

3. RESULTS

In Tab. 2, the experimental and certified values for Ca, Ni, Zn, Cr, Mo, Sn, Zr, Fe, Si, Mg and Cu (average and uncertainty) of the CRM 124 - NBL- multi-element standard are listed. In the same table, the relative standard deviation (%RSD), relative error (%RE), detection limits and quantification limits are also presented.

The precision of the results evaluated by % RSD values, showed a satisfactory repeatability for Ca, Ni, Zn, Cr, Mo, Sn, Zr, Fe, Si determination (less than 13 %); exception was observed for Mg determination, which showed 17,3 % RSD values, however can be accept because the X-ray fluorescence spectrometry presents difficulty in determining low atomic number elements ($Z < 20$).

The results evaluated by %RE values, e.g. comparing the certified and determined values, shows that the proposed methodology is satisfactory for Ca, Ni, Zn, Cr, Mo, Sn and Mg because the relative errors are less than 10 % (0.6 to 12.8 %), questionable for Zr (30,1%) and Cu (28,8%), because the uncertainty of these elements in CRM 124 is circa the 30% and 18% respectively and unsatisfactory for the Fe and Si (54,8-55,7%).

The detection limits (LD - $\mu\text{g g}^{-1}$) show that the proposed methodology is sensitive to detect trace elements in U_3O_8 , therefore direct chemical analysis and nondestructive can be performed. The quantification limits (LQ - $\mu\text{g g}^{-1}$) are sufficient for impurities determination in U_3O_8 .

Table 2 – Determined and calculated values for CRM 124 - NBL

Element	$X_{cert} \pm \sigma$	$X_{det} \pm \sigma$	RDS (%)	RE (%)	LD ($\mu\text{g g}^{-1}$)	LQ ($\mu\text{g g}^{-1}$)
Ca	200±36	194±11	5.8	3.3	0.4	13
Ni	202±17	191±1	0.6	5.3	0.3	2
Zn	202±57	198±25	12.8	1.9	0.4	29
Cr	102±14	108±8	7.1	5.8	0.3	13
Mo	100±6	92±5	5.1	8.1	0.3	8
Sn	51±7	55±3	5.0	7.0	0.3	6
Zr	200±61	260±33	12.7	30.1	2.0	66
Fe	210±24	95±10	10.9	54.8	0.2	21
Si	202±58	89±4	4.9	55.7	0.2	9
Mg	101±13	105±22	17.3	1.0	0.2	36
Cu	50±9	64±7	11.4	28.8	0.3	34

In Fig. 2 the standard error values (En) calculated for the determined elements are showed. When $|En| \leq 1$ the result of the laboratory can be considered satisfactory [11].

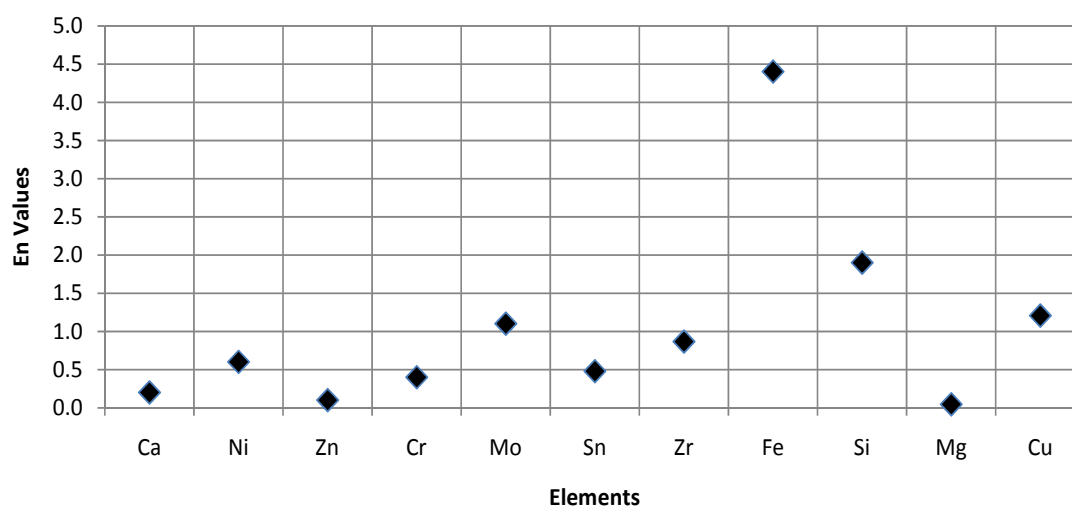


Figure 2. Standard error values (En) calculated from CRM 124-1 - NBL

According with test, the results obtained are satisfactory for the Ca, Ni, Zn, Cr, Mo, Sn, Zr, Mg and Cu ($En \leq 1$) thus, the proposed methodology is efficient for direct and not destructive analysis in U_3O_8 , except Fe (4.4) and Si (1.9), however in the routine analysis this elements can be expressed as indicative.

4. CONCLUSIONS

The results showed that the mathematical algorithms used for absorption/excitation (Matrix) correction and overlap correction are efficient demonstrating increase in resolution was achieved. Thus, direct and not destructive chemical analysis by WDXRF without chemical separation of uranium can be performed for the Ca, Ni, Zn, Cr, Mo, Sn and Mg with precision and accuracy adequate. The elements Fe and Si despite being rejected by statistical tests provide indicating results.

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