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X-ray fluorescence spectrometry: An alternative technique for analysis of waste

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ABSTRACT

This study aims to develop reliable analytical methodology that is, cost-effective, and requires minimal sample quantity to quantify uranium content in nuclear waste and others. The Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) technique was used, and a rigorous comparison was made between the fundamental parameters (FP) method and the empirical (EMP) method. Statistical evaluation of results demonstrated that the FP method showed a satisfactory level of confidence for precision and limit of quantification.

Keywords: **uranium, X-ray, EDXRF.**

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1. INTRODUCTION

Nuclear technology has been playing an important role in several science areas, such as medicine, agriculture, materials and others. The advancements in this technology are represented by the work of researchers, students and technicians at Universities, Research Institutes, and other institutions worldwide. The uranium waste can be produced in experiments or processes using uranium compounds. Despite specific standards and guidelines storage and identification [1,2], it may be required to confirm uranium content in waste. Therefore, an analytical technique efficient and efficacy for uranium content determination in waste is of great value.

The X-ray fluorescence spectrometry (XRF) is an instrumental analytical technique. It has been applied in different areas of knowledge, such as nuclear, nanotechnology, environmental, health, forensic and others [3-7]. XRF technique compared with atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and others has been highlighted for allowing direct and non-destructive, i.e., element identification and quantification without previous sample chemical treatments [7].

Qualitative analysis is efficient because irradiated sample by X-rays generate photons with characteristic energies of the elements present in the sample [8,9]. However, satisfactory quantitative results are obtained using certified reference materials (CRMs), i.e. of chemical composition similar to the unknown sample. The high cost or absence of CRMs have motivated researchers and technique users to develop methodologies to decrease the use of specific CRMs. Fundamental Parameters Method (FP) has been most applied and current [10]. This method, also known as "Standardless Quantitative Analysis" allows the emission intensity of each element's characteristic photons to be calculated using parameters such as primary spectral distribution (polychromatic source), absorption coefficients (photoelectric and mass), fluorescence yield, and others, providing a multivariate calibration curve [6].

Thus, this study aimed to develop a robust and reliable analytical methodology that is cost-effective and requires minimal sample quantity to quantify uranium content in wastes by EDXRF. The methodology is expected to assist in safeguarding and waste management area for quantifying uranium content in unknown samples.

2. MATERIALS AND METHODS

A set of six U_3O_8 CRMs from National Nuclear Security Administration (NBL - C123-1, C123-3, C123-4, C124-1, C124-3, C124-4) [11,12] and one CRM from Johnson Matthey Chemical Limited (JMC – U3O8 – Spectrographically Standardized) was used for the fundamental parameters (FP) method and the empirical (EMP) Method. The C123 -1,3 and 4 CRMs were used for calibration curve and C124 -1,3 and 4 for evaluation, according to the guidelines on analytical methodology validation.

The U_3O_8 concentration was converted to U_{Total} according to equation 1:

$$U_{Total}(\%) = \left(100 - \sum_{i=0}^{n} \left(\frac{Imp_e}{1000}\right)\right) \times 0{,}848 \tag{1}$$

where,

Imp_e ≡ total mass of impurities according to the certificate [11,12];

0,848 g ≡ gravimetric factor for converting U_3O_8 to U_{Total}.

Circa 30-50 mg (one spatula tip) C123-1, C123-3, C123-4, C124-1, C124-3 and C124-4 CRMs were placed within XRF X-Cell™ Sample Cups (Spex-31 mm), using polypropylene film (Spex SamplePrep 3520 Polypropylene) as a support.

Data acquisition was performed using a Shimadzu Co. model 720 Energy Dispersive X-ray Fluorescence (EDXRF) Spectrometer, configured with an X-ray tube and Rh anode (250W), Si (Li) semiconductor detector, cooled with liquid N_2 and 3-millimeter collimator. The instrumental set up were: voltage 50 keV, auto adjustable current of max. 1 mA and vacuum atmosphere between 30-10 Pa. For each CRM, 2048 points were measured, from 0.00 to 40.96 keV, with a 0.02 keV interval, exposure time for 100s and detector "dead time" (DT) 39%.

Under established conditions acquisition of the count rate (cps μA^{-1}) for U-L_α using FP method (ROI ≡ 13.6-14.2 keV) were registered in EDX-720 software and obtained concentration for U_{total}. The U_{total} concentration by EMP method was obtained using count rate (cps µA-1) and OriginPro8 Software. Applying Gauss Fit single peak (ROI ≡ 13.6-14.2 keV), normal probability density, according to equation 2:

$$y = y_0 + \frac{A}{w \times \sqrt{\frac{\pi}{2}}} e^{-2\frac{(x-x_c)^2}{w^2}} \qquad (2)$$

where,

$y_0 \equiv$ cps µA^{-1} in the beginning of the curve;

A ≡ area;

w ≡ half height width;

$x_c \equiv$ average cps µA^{-1}.

The correlation between count rates (cps µA-1) versus U_{Total} concentration was calculated by least squares method for FP and EMP methods. Precision was evaluated in terms percent relative standard deviation (RSD%) using Horwitz equation as acceptability criterion. Accuracy in terms of relative error (RE%) using Z-score test [13] as acceptability criterion. The limit of quantification (LOQ) was calculated for 95% confidence level [13]. Comparison between FP and EMP methods was performed using t-test, considering mean of two paired samples.

3. RESULTS AND DISCUSSION

The following parameters are shown in Table 1: concentration (%) and standard deviation for nominal U_{Total} (± σ) and determined by FP method (± σ); relative standard deviation (RSD%) and calculated values for acceptability of precision (HorRat); relative error (RE%) and Z-score values, calculated for acceptability of accuracy to following NBL CRMs - C123-1, C123-3, C123-4, C124-1, C124-3, C124-4 and JMC CRM.

Table 1: Parameters determined for the FP Method.

CRM (%)	**U_{Total} (nominal) ($\bar{x} \pm \sigma$)**	**U_{Total} FP ($\bar{x} \pm \sigma$)**	**RSD%**	**HorRat**	**RE%**	**Z-Score**
NBL-123-1	82.7 ± 0.1	83.0 ± 0.2	0.3	0.1	0.4	1.1
NBL-123-3	84.31 ± 0.05	82.2 ± 0.2	0.3	0.1	2.5	8.4
NBL-123-4	84.58± 0.05	86.4 ± 0.2	0.3	0.1	2.1	7.6
NBL-124-1	82.5 ± 0.8	81.4 ± 0.2	0.3	0.2	1.3	1.4
NBL-124-3	84.2 ± 0.1	81.7 ± 0.2	0.3	0.1	3.0	9.2
NBL-124-4	84.5 ± 0.1	79.7 ± 0.3	0.3	0.2	5.8	17.5
JMC	84.8 ± 0.1	85.5 ± 0.2	0.3	0.1	0.8	2.7

$\bar{x}$ = average of measurements in triplicate; σ = standard deviation.

Results showed that precision in terms of RSD% for FP method was satisfactory once it HorRat test values are lesser than < 2 [13]. Regarding accuracy four CRMs were rejected (NBL 123-3,123-4, 124-3 and 124-4), as values, it is > 3. JMC presented Z = 2.7 indicating a questionable result [13].

The following parameters are shown in Table 2: concentration (%) and standard deviation for nominal U_{Total} (± σ) and determined by EMP method (± σ); relative standard deviation (RSD%) and calculated values for acceptability of precision (HorRat); relative error (RE%) and Z-score values, calculated for acceptability of accuracy to following NBL CRMs - C123-1, C123-3, C123-4, C124-1, C124-3, C124-4 and JMC CRM.

Table 2: Parameters determined for the EMP Method.

CRM	**U_{Total} (nominal) ($\bar{x} \pm \sigma$)**	**U_{Total} EMP ($\bar{x} \pm \sigma$)**	**RSD%**	**HorRat**	**RE%**	**Z-Score**
NBL-123-1	82.7 ± 0.1	84 ± 2	2.0	1.0	1.2	0.6
NBL-123-3	84.31 ± 0.05	80 ± 2	2.2	1.1	5.5	2.6
NBL-123-4	84.58± 0.05	89 ± 2	1.8	0.9	5.3	2.9
NBL-124-1	82.5 ± 0.8	75 ± 2	2.5	1.2	8.6	3.5
NBL-124-3	84.2 ± 0.1	77 ± 2	2.4	1.2	8.6	4.0
NBL-124-4	84.5 ± 0.1	67 ± 2	3.1	1.6	21.0	8.5
JMC	84.8 ± 0.1	97 ± 1	1.5	0.7	14.0	8.2

$\bar{x}$ = average of measurements in triplicate; σ = standard deviation.

Results showed that precision was also satisfactory for the EMP method once it HorRat test values are lesser than < 2 [13]. Regarding accuracy, four CRMs were rejected (NBL C124-1, C124-3, C124-4 and JMC), as values, it is > 3. Results are questionable for C 123-3 and C123-4 (Z= 2.6 and 2.9, respectively).

Tables 1 and 2 agreement shows in terms of precision for FP and EMP methods. With regard to accuracy showed disagreement according to the Z-score test. Thus, the methodology is precise, but not accurate.

The comparison of FP and EMP methods result by t-test (mean of two paired samples) showed the following values: $t_{calculated} = 0.58$ and $t_{critical} = 2.45$. Thus, it was verified that FP and EMP results are statistically similar.

Regarding the Limit of Quantification (LOQ) it was observed that Method FP = 1.2% and EMP = 1.6%. The comparison by t-test showed the following values: $t_{calculated} = 0.58$ and $t_{critical} = 2.45$. Thus, it was verified that LOQs for FP and EMP methods are statistically similar.

This study allowed verifying that FP and EMP methods are statistically similar for uranium determination. Although accuracy to have been unsatisfactory, fact that little sample using not require chemical treatments in sample preparation and provides results fast, show applicability for semi-quantitative analyses in uranium determination.

4. CONCLUSIONS

The necessity for chemical analysis of nuclear materials and waste pose challenges for analytical experts. The proposed methodology proved to be an interesting alternative technique, in the way it demands minimum handling and sample amounts, as it also eliminates the need of previous chemical treatments for the identification and quantification of uranium content in unknown samples. The results provided by the FP method showed applicability for semi-quantitative analyses evidencing uranium content in wastes.

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