

MAJOR CONSTITUENT QUANTITATIVE DETERMINATION IN URANIUM ALLOYS BY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY AND X RAY FLUORESCENCE WAVELENGTH DISPERSIVE SPECTROMETRY

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ABSTRACT

A wavelength-dispersive X-ray fluorescence (WD-XRF) spectrometric method for determination of major constituents elements (Zr, Nb, Mo) in Uranium/Zirconium/Niobium and Uranium/Molybdenum alloy samples were developed. The methods use samples taken in the form of chips that were dissolved in hot nitric acid and precipitate particles melted with lithium tetraborate and dissolved in hot nitric acid and finally analyzed as a solution. Studies on the determination by inductively coupled plasma optic emission spectrometry (ICP OES) using matched matrix in calibration curve were developed. The same samples solution were analyzed in both methods. The limits of detection (LOD), linearity of the calibrations curves, recovery study, accuracy and precision of the both techniques were carried out. The results were compared.

1. INTRODUCTION

Uranium alloys are presently considered as advanced nuclear fuel for compact power and research reactors due to they exhibit superior combined features such as high density fissile material and high thermal conductivity, besides low cost manufacturing [1]. There are considerable amounts of work aiming to develop uranium alloys [2–10]. U–Mo and U–Zr–Nb alloys were selected based on screening of the potential candidates over gamma stability irradiation behavior [11–14]. The first alloy systems considered were the binary one having a high degree of solubility within the gamma-U phase. Thereafter ternary alloys were developed in order to improve certain desirable properties such as gamma phase retention, high ductility and low capture cross-section for thermal neutrons. Nuclear industry has been interested in trace, minor and major metallic constituents characterization, especially for support fuel development programs.

The direct excitation of these matrices for trace-impurity determinations is not acceptable owing to severe spectral interferences found in the complex atomic optic emission spectrum of these materials. Consequently, separation procedures are commonly used to enhance impurity signals in spectroscopy analyses. The widely used carrier distillation methods for trace impurities in refractory materials [15] are not practical, because standardization with closely matched matrices is generally required for satisfactory results. Solvent extraction

employing various extractants or alternatively the ion-exchange technique [16-17] have been utilized, wherein the major matrix is first separated from the impurity elements and the aqueous fraction thus obtained is analyzed by inductivity coupled plasma optic emission spectrometer (ICP OES).

X-ray fluorescence spectrometry (XRF) is widely used for major, minor and trace elements analysis. Among many other important features, the ability to analyze directly solid samples (avoiding complicated acid-digestion procedures) and the inherent multi-elemental capability have made it a mature analytical tool in this field [18]. Direct XRF analysis of liquid samples, however, entails technical difficulties and the results are characterized by errors. Direct analysis of solutions is usually performed with a non-evacuated XRF setup using a few milliliters of sample in a cup with a thin film (Mylar, polyethylene, Kapton) bottom liquid samples usually produce a high background level of X-ray scatter, resulting in a poor signal to noise ratio [19]. Several analytical methods have been used XRF for analysis of alloy samples such as direct measurement of liquids in special cups, measurement of semi-liquid samples after evaporation from foil or other substrates, evaporation from filter disks, solidification of the sample using agar, starch, saccharose, or an organosilicon polymer [20-26].

In this work is described two analytical methods for major constituents determination (Zr, Nb and Mo) in uranium alloys using ICP OES and WD-XRF. The limits of detection (LOD), linearity of the calibration curves, recovery study, accuracy and precision of the both were carried out. For both methods chips samples were dissolved in nitric acid and precipitated particles melted with lithium tetraborate, dissolved again in hot nitric acid and finally analyzed as a solution. The results were compared.

2. EXPERIMENTAL AND RESULTS

2.1 Instrumental

The equipments used in this work are summarized below (table 1).

Table 1: Experimental system

ICP OES Equipment brand	Spectroflame Modula - SPECTRO
WD-XRF Brand	Tigger 8 - BRUKER
Fusion machine brand	Fluxana HD Elektronik Vulcan

2.2. Standards, and reagents

The standards for ICP OES were prepared by dilutions from 1000 mg/L analyte stock solutions in nitric acid 5.0 % v/v. The concentrations for calibration were ranged from 0.0 to 100 mg/L for the analytes. Standards were prepared in a matrix uranium standard solution, obtained by dissolution of high purity uranium oxide.

The standards to WD-XRF were prepared by accuracy weight of the high purity oxides (Zr, Nb, and Mo) and in matrix uranium obtained as the same for ICP OES. The oxides were

melted in lithium tetraborate in the fusion machine and the after this dissolved in nitric solution. The concentration for calibration curves were from 0.0 to 200 mg/L in nitric acid 5.0% v/v.

2.3. Sample preparation

The sample preparation was carried out by weighted about 0.7 g of the chips. The chips samples were dissolved in hot nitric acid (about 100°C). The solution was filtered in filter paper to remove the precipitated particles. The filter paper plus precipitated particles were melted with lithium tetraborate in fusion machine. The fusion product was dissolved in hot nitric acid and added in filtrated solution. The volume was completed until 100 mL, and this solution was diluted in suitable estimate concentration for the calibrations curves. The blank was carried out.

2.4 Analytical wavelengths selection for ICP OES

At least six theoretical analytical wavelengths were selected by using Boumans Tables [17] for each analyte. Several criteria were applied for the selection: sensitivity (intensity of the line), selectivity, and limits of detection (LOD). All of selected lines were tested by using individual 0.1 mg/L standards solutions in 5.0 % v/v HNO₃, searching the peak-center in a first step. Then profiles of the 100 mg/L solution (Nb, Zr, Mo) and 1000 mg/L of the uranium matrix were obtained for each line in order to evaluate the influence of the other elements and the matrix on the analyte signal. These profiles allow comparing on the signal for different selected analytical lines of each element and choosing those with better sensibility and less interference. The peak to background intensities ratio was the essential parameter to compare the behaviour of different wavelengths. In this way, free-interference lines were finally selected for each analyte, those being selected showing high sensitivities with the lowest inter element interferences, not only on the peak position but also on the background measurements positions. Selected spectral lines are presented in Table 2 with their respective backgrounds position. The operation parameter used for ICP OES analyses are shown in table 3.

Table 2: Selected lines and backgrounds of each element

Element	Spectral line	Background Position*
Zr	339.160	-0.064
Nb	309.418	-0.038
Mo	281.615	-0.044
* (-) distance to the left of the peak		

Table 3: Operation parameters for ICP OES

Frequency	27.12 MHz
Operating power	1.2 kW
Plasma gas flow	25 L/min
Aerosol flow	0.8 L/min
Nebulizer type	Cross flow
Spray Chamber type	Scott

2.5 Operation parameters for WD-XRF

For WD-XRF analysis, a portion of the solution was added to a special cup with a bottom made of 6- μm polypropylene foil. This container was tightly filled with prepared solution. The diameter of the analyzed area was 34 mm. The operation parameter used for WD-XRF analyses are shown in table 4.

Table 4: Operation parameters for WD-XRF of each element

Elements	Nb	Zr	Mo
High voltage (kV)	30	40	50
Current (mA)	135	80	80
Peak angle ($^{\circ}$)	81.717	22.521	76.385
Spectral line ($^{\circ}$) 2θ	Nb $L\alpha_1$	Zr $K\alpha_1$	Mo $L\alpha_1$
Detector counter type	Flow	Scintillation	Flow
Analyzer crystal type	PET	LiF (200)	PET
Counting time (sec.)	60	30	60
Collimator aperture ($^{\circ}$)	1.0	0.23	0.23
Xray Tube type	Rh	Rh	Rh

2.6 Sensitivity

Sensitivity in the context of quantitative analysis is the ability to measure small differences in concentration of an analyte species. Sensitivities in this work were calculated using the net intensities of the peak (dI) divided by the concentration (dC) of the solution. The equation to compute sensitivity is shown in equation 1 and the results are presented in the table 5:

$$\text{Sensitivity} = dI/dC \quad (1)$$

Table 5. Sensitivities of the analytes of each technique

ANALYTE	ICP OES	WD-FRX
Mo	1272	1.06
Zr	33562	1.07
Nb	15679	0.008

The sensitivities for ICP OES technique were biggest than WD-FRX for all analytes.

2.7 Limits of detection (LOD)

In this study the sensitivities of the analytes were used to determine the smallest concentration of an analyte that can be detected, in the other words the limits detection. The principle is the ability to measure a signal representative of the concentration of the analyte comparable in magnitude to the blank (absence of analyte) signal. The LOD of the analytes were calculated according to equation 2. The results are shown in figure 1.

$$LOD=3C\times\frac{SD}{S} \quad (2)$$

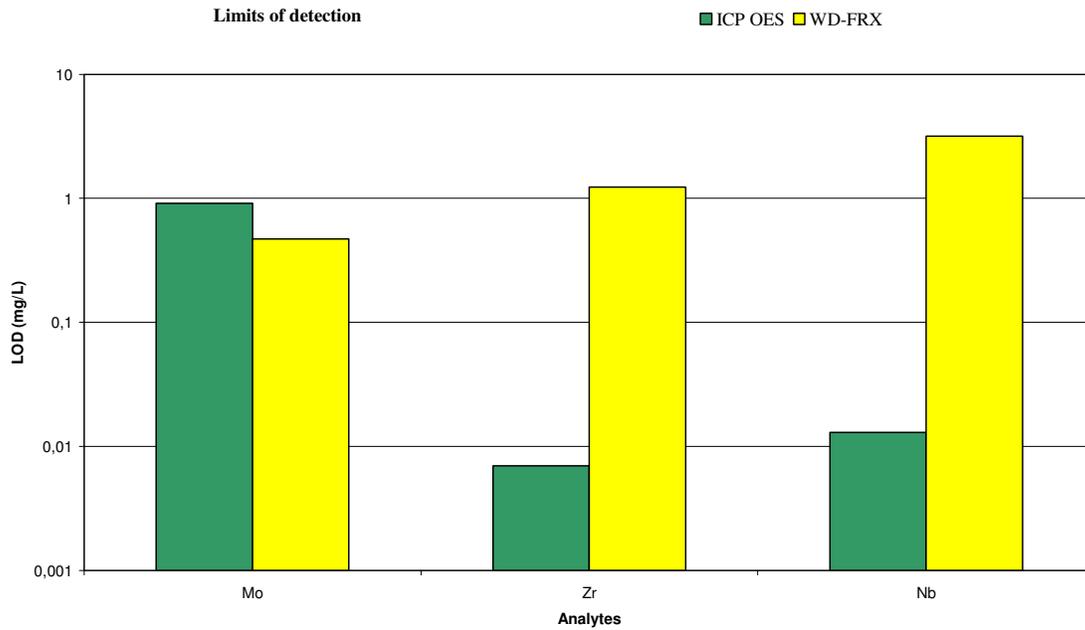


Figure 1. Limits of Detection

The ICP OES yield the lowest LOD, except for Mo. The limits of detection of the Zr and Nb in ICP OES were significantly lowest than WD-XRF. The LOD is an important parameter in the choice of the analytical methodology because defined is suitable or not to the requested limits for evaluation the real samples.

2.8 Linearity of the calibration curves

The linear analytical ranges used for calibration curves construed were 0 to 200 mg/L for WD-XRF and 0 to 100 mg/L for ICP OES. The correlation coefficients of the linear fit for each analyte are presented in figure 2.

Analysis with the WD-XRF instrument produced good linear fit within the experimental analytical range (0–200 mg/L) for all analytes (minimum correlation figure 0.9720 for Nb). Analysis with the ICP OES presents the best linear fits (minimum correlation figure 0.9991 for Nb) in the analytical range (0-100 mg/L) than WD-FRX. Both techniques presented results are very acceptable.

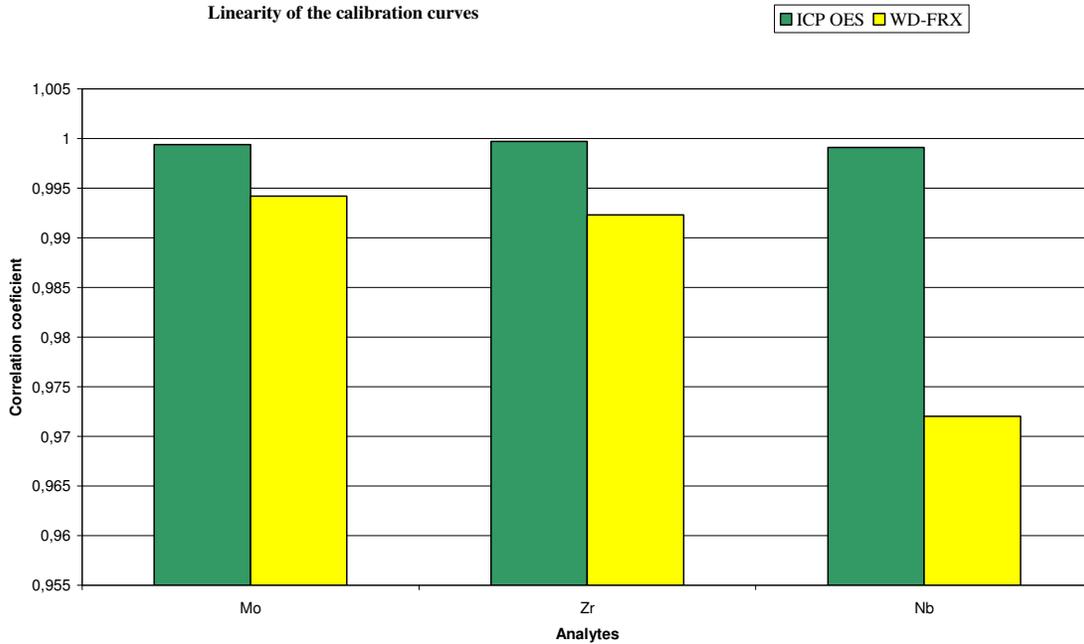


Figure 2. Linear fits of the calibration curves

2.9 Recovery study, accuracy and precision

For recovery study seven replicates of high pure U_3O_8 oxide were spiked with high pure oxides of the analytes Mo, Zr and Nb. The spiked and non-spiked samples were analyzed by ICP OES and WD-FRX in order to evaluate the recovery factor. The recovery factor (RF) is the numerical percentage of the analytical error or loss and it is calculated using equation 3.

$$RF = (\text{Spiked sample conc.} - \text{Non-spiked sample conc.}) \times 100 / \text{Spike concentration} \quad (3)$$

The agreement's degree between a well-known analyte concentration in a standard reference material and the analyzed concentration on the same material is a measure of the analysis accuracy and can be calculated by equation 4. The precision is the measure of replicate analyses reproducibility. Because reproducibility determined in this manner is considered to be random in nature and hence has a normal distribution, the standard deviation is used as a measure of the precision's magnitude. To normalize the standard deviation and make it possible to compare between different magnitudes of measurements, the relative standard deviation is used. The relative standard deviation is expressed on a percentage basis and called percent relative standard deviation (% RSD) [28]. It is calculated using equation 5.

$$\text{Accuracy} = \text{Spiked conc.} \times 100 / \text{measured conc.} \quad (4)$$

$$RSD = \text{measured standard deviation} \times 100 / \text{measured average} \quad (5)$$

In the lake of the suitable certified references materials (CRM) the accuracy and precision parameters can be evaluated using of the recovery results [28]. In this way the accuracy and recovery factor has the same mean, and RSD of the measurements is a precision. In this work we used the recovery study for evaluate that parameters. The results of the recovery factor or accuracy and precision are shown in figs. 3 and 4.

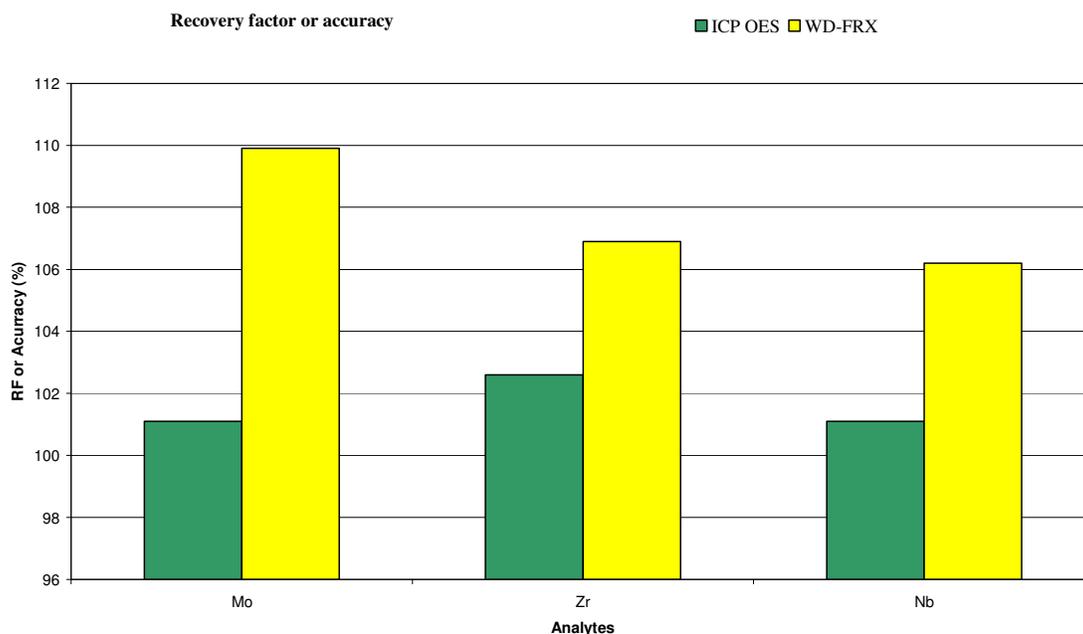


Figure 3. Recovery factors or accuracy

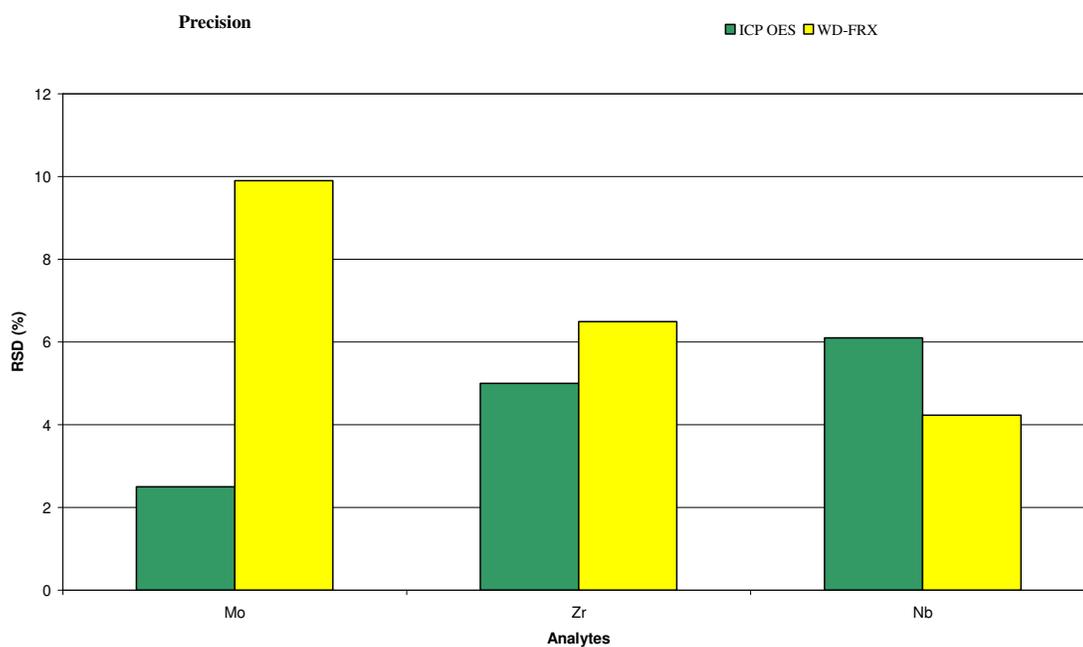


Figure 4. Precision (RSD-Relative standard deviation)

All the analytes in ICP OES yields a relative accuracy of nearly 102%, whereas WD-FRX accuracy were minimum 106.2% to Nb and maximum 109.9% to Mo. ICP OES yield more acceptable results on precision values (nearly 5%) for Mo and Zr, whereas WD-FRX yield more acceptable result on precision value for Nb (lower than 5%).

2.10 Real sample characterization

The comparison of the two techniques or two sequence series results for the same analysis can be evaluated and considered the same in the required confidence level by the student test (t-student) [29]. Seven replicates of the U-Nb-Zr alloy sample and seven replicates of the U-Mo alloy sample were prepared and suitable diluted in range concentration of the calibration curves in both studied techniques. The analyses were carried out and the results obtained were compared by the t-student using the averages, standard deviation, and number of the measurements of the each technique in 95% of the confidence level. The results are present in table 6.

Table 6. Averages and standard deviations of the analytes concentration (%) of each technique. Experimental and theoretical t-student

Analyte	ICP OES	WD-FRX	Experimental t-student	Theoretical t-student
Mo	9.62 ± 0.49	10.26 ± 0.56	0.67	2.18
Zr	1.54 ± 0.17	1.42 ± 0.03	0.22	2.18
Nb	2.22 ± 0.06	2.24 ± 0.36	0.22	2.18

Based on this statistical test two results series can be consider the same, and the analytical methods equivalents.

3. Conclusions

We have present two analytical methods (by ICP OES and WD-FRX) for Mo, Zr and Nb determination in uranium alloys such as major constituents. Both techniques presented had acceptable results parameters for this application. In the statistical test the technique are considered equivalents. Thus, these technique could potentially be used to provide real-time data necessary to guide critical field decisions concerning in the uranium alloy's field.

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