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Uncertainty Measurement Evaluation of WDXRF and EDXRF Techniques for the Si and U_{total} Determination in U_3Si_2 used as Nuclear Fuel Material

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ABSTRACT

Uranium silicide (U_3Si_2), 20% ^{235}U enriched powder, is an intermetallic compound used as nuclear fuel material; that is the state-of-the-art among nuclear fuel materials used in modern research reactors. It is produced by IPEN and used as nuclear fuel of the IEA-R1 reactor (IPEN/CNEN, São Paulo, Brazil); U_3Si_2 has 92.3%wtU and 7.7%wtSi. The qualification of this material requires chemical and physical tests such as Si and U_{total} content, isotope ratio, impurities, density, specific surface area and particle size determination. The Si and Utotal determination were made by gravimetric and volumetric procedures at the Environment Chemistry Center (CQMA-IPEN/CNEN). Usually, these classical methods require a long time for analyses and are expensive. The objective of this study was to establish a fast and efficient analytical method to meet ISO/IEC 17025:2005 requirements in the Si and Utotal determination. The X-ray fluorescence techniques (XRF) were chosen to allow a direct and non-destructive testing, what is a principal advantage faced to other instrumental techniques, since previous chemical treatments are not necessary. In this study, the performance of the wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X- ray fluorescence techniques was evaluated. Furthermore, two different sample preparation procedures, plain powdered and pressed powdered were evaluated. Statistical tools were used to evaluate the results and a comparison between these results and the conventional methods was done.

1. INTRODUCTION

Aiming the autonomy in the radioisotopes production for nuclear medicine and for the recommencement of the Brazilian Nuclear Program, researchers from the Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN, São Paulo, Brazil) are proposing a project to build the Brazil Multipurpose Reactor, the largest research nuclear reactor in Latin America.

The Multipurpose Reactor operation is expected to increase, significantly, medical radioisotopes production for nuclear medicine. Thus, the increase in nuclear fuel element production is expected, too.

The modern research reactors use, as nuclear fuel, powdered uranium silicide (U_3Si_2) enriched 20% in ^{235}U, which is an intermetallic compound with 92.3 wt% U and 7.7 wt% Si. It is produced by magnesiothermic reaction and pure silicon, dispersed in aluminum [1]. The qualification of this material requires chemical and physical tests such as Si and U_{total} content, isotope ratio (U^{235}/U^{238}), impurities, density, specific surface area and grain size determination.

The Si and U_{total} determinations have been performed by gravimetric and volumetric procedures at the Centro de Química e Meio Ambiente (CQMA-IPEN). These analyses take a long time and are expensive. Furthermore, they produce great quantities of waste during the sample preparation steps.

The aim of this study was establishing a fast and efficient analytical method for the Si and U_{total} determination, according to requirements of the ISO/IEC 117025:2005. In addition, to produce a smaller amount of radioactive waste as well as to carried out the analyses in a short time.

The X-ray fluorescence techniques were chosen because perform direct and non-destructive testing, which lead advantage when compared to other instrumental techniques, once the previous chemical treatments are not necessary, resulting in a less time of contact with samples, besides to reduce the sample amounts, consequently, of waste.

In this study, the performance of the wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence techniques was evaluated. Furthermore, two different sample preparation procedures, plain powdered (PL) and pressed powdered (PR), were evaluated using the Fundamental Parameters (FP) and Calibration Curve (CC) methods [2, 3]. The evaluation and comparison with conventional methods by statistical tools were carried out.

2. MATERIALS AND METHODS

2.1. Pelletizing

The pressed powdered samples (grain size ≅ 106 μm) 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 cm^3) 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 (H_3BO_3 PA), previously compressed with 100 MPa for 10 seconds, obtaining pressed samples of 25.01 ± 0.01 mm diameter and 5 ± 1 mm in thickness.

2.2. EDXRF Analysis

A Shimadzu Co. X-ray fluorescence spectrometer, model EDX-720, was used, following the operating conditions: X-ray tube: Rh (3.0kW); Excitation: 15 kV for Si Kα and 50 kV for ULα ; Current:1 mA, maximum ; Collimator: 10 mm ; Detector: Si (Li) cooled with liquid N_2; Measurement time: 100 s for Si Kα and 50 s for ULα, with Ag filter.

The loose powered samples (*circa of* 2.0 g of sample were placed in the powder sample holder) were analyzed using the fundamental parameters method, that correlates the theoretical (calculated by software coupled to the Shimadzu spectrometer) and experimental intensity. The curve fitness by means of twelve measurements from one certified reference material (provided by the Centro do Combustível Nuclear, CCN/IPEN) was carried out.

The pressed samples using the calibration curve method were analyzed. The Si and U curves by three measurements for each of the six references samples (SE 006/04, SE 007/04, SE 003/07, SE 010/08, L 1008-1 and L 1008-2), were obtained.

2.3 WDXRF Analysis

A Rigaku Co. X-ray fluorescence spectrometer, model RIX 3000, was used. The measurement condition for SiKα (K-L_3) and ULα (L_3-M_5) lines are presented in Table 1.

Table 1. WDXRF spectrometer measurement condition (Rigaku Co., model RIX 3000)

	SiKα	ULα
Collimator	160 µm	160 µm
Analyzing crystal	LiF (200)	PET (111)
Detector	FPC	SC
Counting time (s)	40	20
Bragg position (2θ)	109,025	26,125
Excitation (kV vs mA)	40 X 30	40 X 30

LiF: lithium fluorite – PET: pentaerythritol - SC scintillation detector –NaI/Tl - FPC: flow-proportional counter.

The same pressed samples, used for EDXRF analysis, were used to obtain Si and U calibration curves. For each of the six references samples, three measurements were carried out and the matrix effects were corrected by Eq. 1, using software coupled to the spectrometer.

$$W_i = (aI_i * bI_i + c)\,(1 + K + \sum AijFj + \sum QijFjFk + \sum \frac{RijFj}{1+W_i}) + \sum BijFj + \sum DijkFjFk + C \qquad (1)$$

W_i ≡ Quantification value;
a, b,c ≡ calibration curve coefficients;
I_i ≡ X-ray intensity;
K ≡ Constant term;
Aij ≡ Absorption/excitation correction coefficient;
Fj ≡ Analysis value or X-ray intensity of correcting component;
Qij ≡ Absorption/excitation correction coefficient (secondary correction);
Rij ≡ Excitation correction coefficient;
Bij ≡ Overlap correction coefficient;
Dij ≡ Absorption/excitation correction coefficient;
C ≡ Constant term.

2.4 Quality control

The methodologies (PF and CC) and the all procedure were evaluated using the AR reference sample (U_3Si_2, enriched 20% in ^{235}U), supplied from CCN/IPEN. The sample six times, for 3 consecutive days, obtaining a set of 18 measurements for each element was analyzed. The following statistical tests were applied, for accuracy evaluation [4, 5, 6, 7].

At first, the Chauvenet's test to detect of outliers was applied, according to Eq. 2 [4]

$$|X_i - \bar{X}| > k_n . s \qquad (2)$$

Where,
X_i ≡ measured value;
$\bar{X}$ ≡ average;
k_n ≡ Chauvenet's coefficient;
s ≡ standard deviation.

Afterwards, uncertainty test to evaluate the precision was applied, using the Eq. 3 [7]

$$U = \pm t_{n-1(\frac{\alpha}{2})} * \frac{s}{\sqrt{n}} \qquad (3)$$

Where,
n ≡ repetitions number;
s ≡ standard deviation;
$t_{n-1(\frac{\alpha}{2})}$ ≡ t-Student value.

The accuracy assessment using the percentage relative error (RE %), assuming as true values the results obtained by conventional methods, (gravimetric for Si and volumetric for U_{total}) was carried out, according to Eq 4

$$RE\,\% = \frac{\overline{X}_{lab} - X_{\upsilon}}{X_{\upsilon}} * 100 \qquad (4)$$

Where,
$\overline{X}_{lab}$ ≡ experimental average;
X_{υ} ≡ value accepted as true (RM value);
s ≡ standard deviation (uncertainty of the RM);

The limit of quantification, considering the results as true values (results obtained by conventional methods) was calculated, according to Eq 5 [8]

$$2 * \sqrt{\frac{\sum_{il}^{N}\left(Ci - \overline{C}\right)^2}{N-1}} \qquad (5)$$

Where,
Ci ≡ measured value;

$\overline{C}$ ≡ value accepted as true (RM value);
N ≡ repetition number

The ruggedness evaluation using t-Student test (paired two-sample t-tests), at 0.5 significance level (Eq. 6) for 9 pressed sample set and a 7 loose powder sample set, was carried out.

The results obtained by EDXRF and WDXRF analyses were compared with those obtained by gravimetric (for Si) and volumetric (for the U_{total}) methods. For the null hypothesis, the $t_{experimental} < t_{teorethical}$ is accepted, what means that there is no significant difference between methods.

$$t_{experimental} = \frac{(d - d_0)}{\frac{sd}{\sqrt{n}}} \quad (6)$$

Where,
d ≡ sample mean;
d_0 ≡ tested the mean value of differences in populations;
sd ≡ standard deviation of diferences in populations;
n ≡ size sample of differences.

For the comparison study among all the procedures and methodologies, the Cluster analysis, with Ward's method by Statistica, 6.0, was applied.

3. RESULTS AND DISCUSSION

In Tab. 2 are presented the Si and U_{total} values (average and uncertainty) determined for AR reference sample by gravimetric and volumetric methods ($X_{V/G}$). These values were considered like reference values. The results for EDXRF (PL_{PF}: loose powdered sample with fundamental parameters method and PR_{CC}: pressed powered samples with calibration curve method) and for WDXRF (PR_{CC}: pressed powered with calibration curve method) are shown, too. Furthermore, the relative standard deviation (RSD%), relative error (RE%) and limit of quantification (QL) values are presented.

Table 2. Determined values, RSD%, RE% and LQ for AR reference sample

Method/element	Mass Fraction (%)	RSD%	RE(%)	LQ(mg g^{-1})
$X_{V/G}$				
Si	7.6±0.1	***	***	***
U_{total}	92.2±0.1	***	***	***
$PL_{ED/FP}$				
Si	7.9±0.3	0.35	3.2	0.27
U_{total}	92.1±0.3	0.03	0.3	0.09
$PR_{ED/CC}$				
Si	7.709±0.002	0.02	1.4	0.08
U_{total}	90.14±0.06	0.06	2.2	1.8
$PR_{WD/CC}$				
Si	7.771±0.002	0.05	2.3	0.25
U_{total}	90.926±0.01	0.01	1.3	1.8

*** - not calculated; $X_{V/G}$:: volumetric/gravimetric method; $PL_{ED/FP}$: plain powered samples with EDXRF/PF method; $PR_{ED/CC}$: pressed powered samples with EDXRF/CC method; $PR_{WD/CC}$: pressed powered samples with WDXRF/CC method.

The accuracy assessment, in relation to RSD% values, the three XRF methods showed satisfactory repeatability. According to INMETRO recommendation [6], the RSD% values above 10% are considered unsatisfactory. The XRF techniques showed lower values, where $PR_{WD/CC}$ method reveals better repeatability, presenting a lower RSD% values for Si (0.05%) and U_{total} (0.01%) determination, exhibiting that WDXRF technique has improved repeatability. In the accuracy evaluation, related to RE% values, the three XRF methods showed a value less than 3.2% for Si and 2.2% for U_{total} where these values also sustain the satisfactory accuracy. The limits of quantification calculated for the three methods showed adequate values, what means that these values are 10 to 100 times lower than determined values.

In Tab. 3, the t-Student test results, for a set of 7 samples by $PL_{ED/FP}$ method and a set of 9 samples by $PR_{ED/CC}$ and $PR_{WD/CC}$ methods are presented. Based on the null hypothesis, $PL_{ED/FP}$ method, for Si determination, is refused since $t_{experimental} > t_{theoretical}$ (2.6>2.5), demonstrating that the result is considered different from those obtained by gravimetric method. The $PR_{ED/CC}$ and $PR_{WD/CC}$ methods did not show significant difference in relation to the gravimetric method. Therefore, it could be concluded that the pressed powered samples are more appropriate than the loose powered samples. In accordance with, the null hypothesis, for three XRF methods presented adequacy for U_{total} determination, showing no significant differences between those values in relation to volumetric values. The Pearson correlation showed, for $PR_{ED/CC}$ method, the lowest values (0.08) in Si and (0.06) in U_{total} determination, showing no linear relation between established methods (Tab.3).

Table 3. Student's t-test values for the $PL_{ED/FP}$, $PR_{ED/CC}$ and $PR_{WD/CC}$ methods

		Si	
	$PL_{ED/FP}$	$PR_{ED/CC}$	$PR_{WD/CC}$
Average	7.78	7.46	7.50
Variance	0.44	0.18	0.09
Pearson correlation(r)	0.9	0.08	0.7
$g\vert$	6	8	8
stat t	2.6	2.1	0.3
t-critical	2.5	2.3	2.3
		U_{total}	
	$PL_{ED/FP}$	$PR_{ED/CC}$	$PR_{WD/CC}$
Average	91.55	93.64	91.07
Variance	0.57	11.58	0.23
Pearson correlation(r)	0.6	0.06	0.7
$g\vert$	6	8	8
stat t	0.79	2.11	0.7
t-critical	2.4	2.3	2.3

Significance level: 0.05; degrees of liberty ($g\vert$); t-Sudent experimental (stat t); t-Sudent theoretical (t-experimental).

In Fig.1, the Cluster analysis used for similarity evaluation between XRF ($PL_{ED/FP}$, $PR_{ED/CC}$, $PR_{WD/CC}$) and classic methods ($X_{v/G}$) are shown. The results show that $PR_{WD/CC}$ groups with $X_{v/G}$ method, revealing its adequacy for Si and U_{total} determination in U_3Si_2 fuel elements.

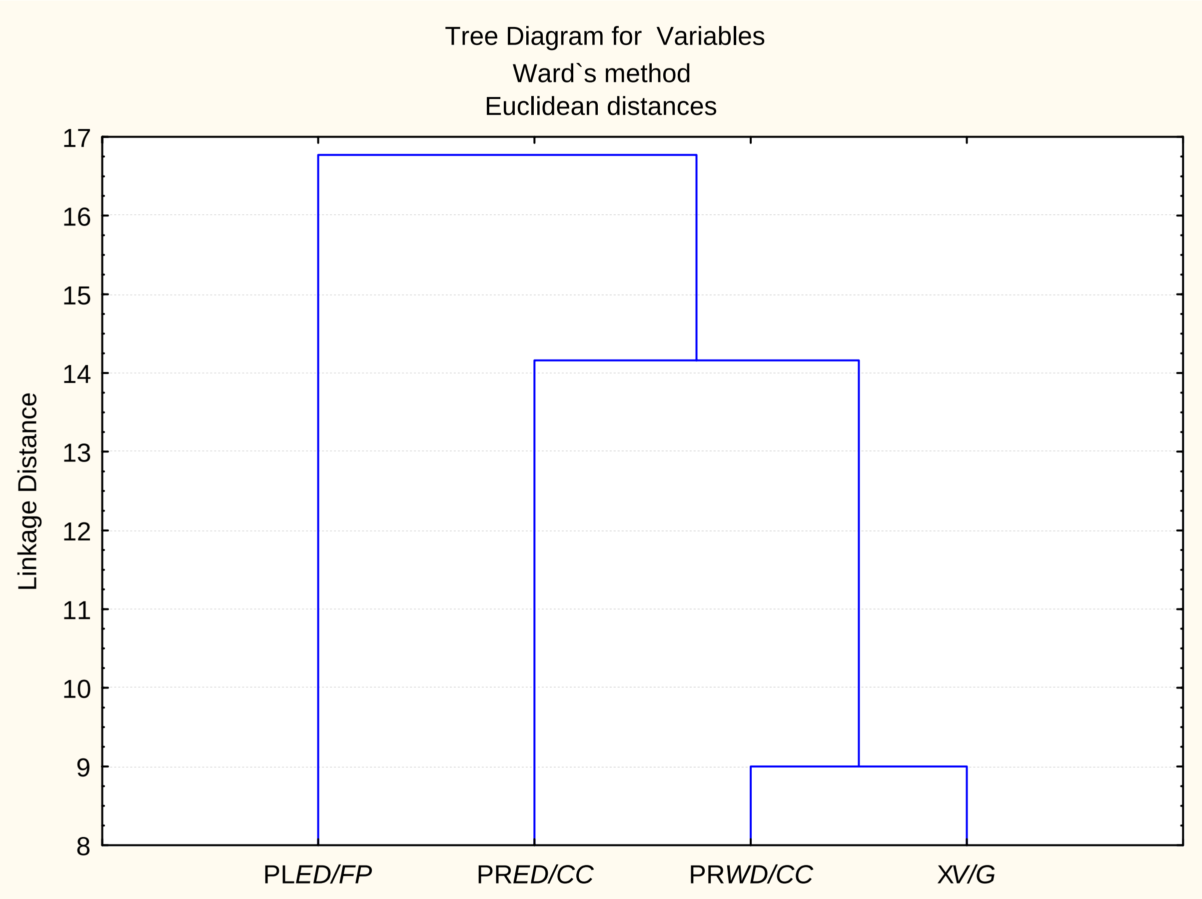

Figure 1. Cluster Diagram (Ward`s method Euclidean distances)

4. CONCLUSIONS

The results showed that WD-EDXRF techniques have adequate performance for Si and U_{total} quantitative determination in U_3Si_2 nuclear fuel, demonstrating appropriate precision and accuracy. The WDXRF analysis, using calibration curve plus powered pressed samples, showed closer values to the conventional methods.

REFERENCES

1. A. M. Saliba Silva, M. Durazzo, E. F. U. Carvalho, H. G. Riella. *Proceeding of International Latin-American Conference on Powder Technology*, Buzios, RJ, 7th, Nov. 2-10, (2007).
2. D. M. Müller, *Spectrochemical analysis by X-ray fluorescence*. New York, Plenum, (1972).

3. R. Tertian, F. Claisse. *Principles of quantitative X-ray fluorescence analysis,* London, Heyden, (1982).
4. M. A. Scapin. *Aplicação da Difração e Fluorescência de Raios X (WDXRF): Ensaios em Argilominerais*, Dissertação (Mestrado) - Instituto de Pesquisas Energéticas e Nucleares, São Paulo, "http://www.teses.usp.br/teses/disponiveis/85/85134/tde-07052007-161852/" (2003).
5. Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO); *Guia para a expressão da incerteza de medição*. 2 ed. Rio de Janeiro, ABNT, INMETRO, SBM, pp. 121 (1998).
6. Instituto Nacional de Metrologia, Normalização e Qualidade Industrial (INMETRO), *Orientações sobre validação de métodos de ensaios químicos*. DOQ-CGCRE-008, São Paulo, "*http://www.inmetro.gov.br/Sidoq/Arquivos/*CGCRE*/DOQ/DOQ-CGCRE-8_02.pdf*" (2003).
7. M. A. SCAPIN. *Estudo de remoção de elementos inorgânicos e degradação de compostos orgânicos por radiação gama em óleos lubrificantes usados*, Tese (Doutorado) - Instituto de Pesquisas Energéticas e Nucleares, São Paulo, "http://pintassilgo2.ipen.br/biblioteca/teses/24240.pdf" (2008).
8. R. Rousseau, "Detection limit and estimate of uncertainty of analytical XRF results", *The Rigaku Journal*, **Vol. 18**, (2001).