J Radioanal Nucl Chem (2011) 287:807–811
DOI 10.1007/s10967-010-0897-6

Uncertainty measurement evaluation of WDXRF and EDXRF techniques for the Si and U_{total} determination in U_3Si_2 nuclear fuel

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Received: 24 August 2010 / Published online: 16 December 2010

Abstract Uranium silicide (U_3Si_2), 20% ^{235}U enriched powder, is an intermetallic compound used as nuclear fuel material, which 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 wt% U_{total} and 7.7 wt% Si. 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 U_{total} were determined by gravimetric and volumetric procedures. 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 U_{total} determination. The X-ray fluorescence techniques (XRF) were chosen to allow a direct and non-destructive analysis, what is the main advantage compared 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.

Keywords U_3Si_2 · Nuclear fuel material · Wavelength dispersive X-ray fluorescence · Energy dispersive X-ray fluorescence · Fundamental parameters

Abbreviations

WDXRF	Wavelength dispersion X-ray fluorescence
EDXRF	Energy dispersive X-ray fluorescence
FP	Fundamental parameters method
PL	Plain powdered
PR	Pressed powdered
CC	Calibration curve
Xv	Volumetric method
Xg	Gravimetric method
IPEN	Instituto de Pesquisas Energéticas e Nucleares
CQMA	Centro de Química e Meio Ambiente
CCN	Centro do Combustível Nuclear
PLPF	Loose powdered sample with fundamental parameters method
PRCC	Pressed powered samples with calibration curve method
RSD%	Relative standard deviation
ER%	Relative error
QL	Limit of quantification

Introduction

Aiming the autonomy in the radioisotopes production for nuclear medicine and for the recommencement of the Brazilian Nuclear Program, a project to build the Brazil

Presented in the 2009 International Nuclear Atlantic Conference, held in Rio de Janeiro, Brazil, September 27 to October 2.

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Multipurpose Reactor, the largest research nuclear reactor in Latin America, is under development.

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

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

At IPEN, the Si and U_{total} have been determined by gravimetric and volumetric procedures. These analyses are long time-consuming and expensive, besides producing considerable quantities of waste during the sample preparation.

The objective of this study was to establish a fast and efficient analytical method for Si and U_{total} determination, to meet ISO/IEC 117025:2005 requirements, also producing less radioactive waste and less exposure time for the analyst.

The X-ray fluorescence techniques were chosen to allow direct and non-destructive analysis without previous chemical treatments, what is the major advantage compared with classical methods. So, the analytical procedure results in a short contact time with samples, requiring less amount of samples to analyze and also produce less quantity of waste [2, 3].

In this study, the performance of the wavelength dispersive (WDXRF) and energy dispersive (EDXRF) X-ray fluorescence techniques was evaluated. Furthermore, two sample preparation procedures (plain powdered, PL and pressed powdered, PR) were evaluated using the fundamental parameters (FP) and calibration curve (CC) methods. The results were compared with conventional methods data, using statistical tests tools. The application of Pearson correlation and Cluster analysis to evaluate different analytical methodologies is unique once in earlier studies, such studies were not available in literature.

Materials and methods

Sample preparation

The pressed powdered samples (PR) were prepared according to the following steps: 1.5 g of sample plus 0.5 g of wax (wax C micro powder, Hoechst) was 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 using a pressure of 20 MPa for 1 s on a boric acid base (1.5 g of H_3B0_3, previously compressed with 100 MPa for 10 s); obtaining pressed samples with 25.01 ± 0.01 mm diameter and 5 ± 1 mm thick.

The plain powdered samples (PL) consist of the 2.0 g U_3Si_2 sample (grain size <106 μm) placed in the spectrometer sample holder.

EDXRF analysis

A Shimadzu Co., model EDX-720 X-ray fluorescence spectrometer was used, using the following operating conditions: X-ray tube: Rh (3.0 kW); 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 plain powered samples (PL) were analyzed using the fundamental parameters method. The instrumental sensitivity curve was obtained by the theoretical and experimental intensity relation using six secondary reference materials (RM), from CCN/IPEN (Nuclear Fuel Center/IPEN).

The pressed powered samples (PR) were analyzed using the calibration curve method. The individual calibration curves for Si and U were also obtained using six secondary reference materials (RM). For each material three measurements for SiKα and for ULα lines were obtained.

WDXRF analysis

A Rigaku Co., model RIX 3000 X-ray fluorescence spectrometer was used. The measurement conditions for SiKα and ULα lines are presented in Table 1.

The same six pressed powered samples, used for EDXRF analysis, were used to obtain Si and U calibration curves by WDXRF. For each sample three measurements for SiKα and ULα were obtained and the matrix effect was

Table 1 WDXRF spectrometer measurement conditions (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 × 30	40 × 30

LiF lithium fluorite, *PET* pentaerythritol, *SC* scintillation detector—NaI/Tl, *FPC* flow-proportional counter

corrected by Eq. 1, with software coupled to the spectrometer.

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

where W_i is the quantification value, a, b, c calibration curve coefficients, I_i X-ray intensity, K constant term, A_{ij} absorption/excitation correction coefficient, F_j analysis value or X-ray intensity of correcting component, Q_{ij} absorption/excitation correction coefficient (secondary correction), R_{ij} excitation correction coefficient, B_{ij} overlap correction coefficient, D_{ij} absorption/excitation correction coefficient, and C is the constant term.

Methodologies evaluation

The fundamental parameters (PF) and calibration curve (CC) methodologies were evaluated using 20% enriched U_3Si_2 secondary reference material (CERCA) from CERCA/AREVA, France. The material was analyzed six times, for three consecutive days, obtaining a set of 18 measurements for each element and the data were evaluated statistically [4–7]. At first, the Chauvenet's test was applied to outliers detection, according to Eq. 2 [4]

$$|X_i - \bar{X}| > k_n \cdot s \quad (2)$$

where X_i is the individual measured value, $\bar{X}$ average, k_n Chauvenet's coefficient, and s is the standard deviation.

The precision was evaluated by repeatability (R), calculated by Eq. 3 [7]; and the percentage relative standard deviation (RSD%) were calculated using R values.

$$R = \pm t_{n-1\left(\frac{\alpha}{2}\right)} * \frac{s}{\sqrt{n}} \quad (3)$$

where n is the repetitions number, s standard deviation and $t_{n-1\left(\frac{\alpha}{2}\right)}$ is the Student t value.

The accuracy was evaluated by percentage relative error (RE%), calculated according to Eq. 4. Values determined by conventional methods were considered true values; Si was determined by gravimetric method and U_{total} by volumetric method in CERCA material.

$$RE\% = \frac{\bar{X}_{lab} - X_v}{X_v} * 100 \quad (4)$$

where, $\bar{X}_{lab}$ is the experimental average and X_v is the true value.

The limit of quantification (LQ) was calculated according to Eq. 5 [8].

$$LQ = 2 * \sqrt{\frac{\sum_{il}^{N} (C_i - \bar{C})^2}{N - 1}} \quad (5)$$

where, C_i is the individual measured value, $\bar{C}$ average, and N is the repetition number.

The ruggedness was evaluated using Student's t test (paired t-tests) at 0.5 significance level (Eq. 6) using a data set from nine pressed powered samples and a seven plain powdered samples, prepared with CERCA reference material.

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

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

where d is the sample mean, d_0 the mean value of differences in populations tested, sd standard deviation of differences in populations, and n is the sample size.

The comparative study among all the procedures and methodologies was carried out by the Cluster analysis, with Ward's method using Statistica, 6.0.

Results and discussion

In Table 2, Si and U_{total} determined values (average and uncertainty) by conventional methods (G/V: gravimetric/volumetric), EDXRF ($ED_{PL/PF}$: plain powdered samples analyzed by fundamental parameters method and $ED_{PR/CC}$:

Table 2 Determined values, RSD%, RE% and LQ for CERCA reference material

Method/element	Determined values (%)	RSD%	RE%	LQ (mg g^{-1})
G/V				
Si	7.6 ± 0.1	–	–	–
U_{total}	92.2 ± 0.1	–	–	–
$ED_{PL/FP}$				
Si	7.9 ± 0.3	3.8	3.2	0.27
U_{total}	92.1 ± 0.3	0.3	0.3	0.09
$ED_{PR/CC}$				
Si	7.709 ± 0.002	0.03	1.4	0.08
U_{total}	90.14 ± 0.06	0.07	2.2	1.8
$WD_{PR/CC}$				
Si	7.771 ± 0.004	0.03	2.3	0.25
U_{total}	90.93 ± 0.01	0.01	1.3	1.8

–, Not calculated

V/G volumetric/gravimetric method, *$ED_{PL/FP}$* plain powered samples with EDXRF/PF method, *$ED_{PR/CC}$* pressed powered samples with EDXRF/CC method, *$WD_{PR/CC}$* pressed powered samples with WDXRF/CC method

pressed powered samples analyzed by calibration curve method) and WDXRF ($WD_{PR/CC:}$ pressed powered samples analyzed by calibration curve method), for CERCA reference material, are given. Also, the relative standard deviation (RSD%), relative error (RE%) and limit of quantification (QL) values are presented.

The precision assessment, in relation to RSD%, the proposed three XRF methods ($ED_{PL/PF}$, $ED_{PR/CC}$ and $WD_{PR/CC}$) showed satisfactory repeatability for Si and U_{total} determination (RSD%: 0.01–0.35). According to INMETRO recommendation [6], the RSD% values above 10% are considered unsatisfactory. The $WD_{PR/CC}$ method showed better repeatability, once presented lower RSD% values for Si (0.03%) and U_{total} (0.01%) determination, showing that WDXRF technique has better repeatability.

As to accuracy evaluation, in relation to RE%, the three XRF methods showed ER% values less than 3.2% for Si and less than 2.2% for U_{total} determination, showing satisfactory accuracy.

The Si and U limits of quantification, for the three XRF methods, also showed adequate values, once these values are circa 100 times lower than the determined values (Table 2).

In Table 3, the Student's *t* test results for a set of seven plain powdered samples (prepared with CERCA material) and analyzed by $ED_{PL//FP}$ method and a set of nine pressed powered samples (prepared with CERCA material) and analyzed by $ED_{PR/CC}$ and $WD_{PR/CC}$ methods are given.

The Si determination by $ED_{PL/FP}$ method presented $t_{experimental} > t_{theoretical}$ (2.6 > 2.5), that means, based on the null hypothesis, this result is considered different from gravimetric method. The $ED_{PR/CC}$ and $WD_{PR/CC}$ methods did not show significant difference in relation to the gravimetric method once $t_{experimental} < t_{theoretical}$ (2.1 and 0.3 < 2.3 and 2.3 for $ED_{PR/CC}$ and $WD_{PR/CC}$, respectively). Therefore, it could be concluded that the powered pressed samples are more appropriate than the plain powered samples.

The U_{total} determination presented for null hypothesis $t_{experimental} < t_{theoretical}$ (0.79, 2.11 and 0.7 < 2.4, 2.3 and 2.3 for $ED_{PL/FP}$, $ED_{PD/CC}$ and $WD_{PR/CC}$, respectively), showing that there is no significant differences between XRF methods and volumetric method. Therefore, the three XRF methods could be considered adequate for U_{total} determination.

The Pearson correlation showed, for $ED_{PR/CC}$ method, the lowest values for Si (0.08) and U_{total} (0.06) determination, showing low correlation. The $ED_{PL/PF}$ and $WD_{PR/CC}$ presented better correlation near 1 (Si: 0.9 and U: 0.6 for $ED_{PL/PF}$ and Si: 0.7 and U: 0.7 for $WD_{PR/CC}$). Therefore, Student's *t* test leads to the conclusion that $ED_{PL/PF}$ and $WD_{PR/CC}$ methods correspond to the volumetric method.

In Fig. 1, the cluster analysis used for similarity evaluation between XRF methods and conventional methods are shown. The results presented isolated groups for $ED_{PL/FP}$ and $ED_{PD/CC}$, and one group composed by $WD_{PR/CC}$ and G/V methods, showing that $WD_{PR/CC}$ method is equivalent to the G/V methods for Si and U_{total} determination in U_3Si_2 nuclear fuel.

Table 3 Student's *t*-test values for the $ED_{PL/FP}$, $ED_{PR/CC}$ and $WD_{PR/CC}$ methods

	$ED_{PL/FP}$	$ED_{PR/CC}$	$WD_{PR/CC}$
Si			
Average	7.78	7.46	7.50
Variance	0.44	0.18	0.09
Pearson correlation (*r*)	0.9	0.08	0.7
g|	6	8	8
Stat *t*	2.6	2.1	0.3
t-Critical	2.5	2.3	2.3
U_{total}			
Average	91.55	93.64	91.07
Variance	0.57	11.58	0.23
Pearson correlation (*r*)	0.6	0.06	0.7
g|	6	8	8
Stat *t*	0.79	2.11	0.7
t-Critical	2.4	2.3	2.3

g degrees of liberty; *stat t* Student *t* (experimental), *t-critical* Student *t* (theoretical)

Conclusions

Statistical tests, such as RSD% and RE% showed that EDXRF ($ED_{PL/PF}$: plain powdered samples analyzed by fundamental parameters method and $ED_{PR/CC}$: pressed

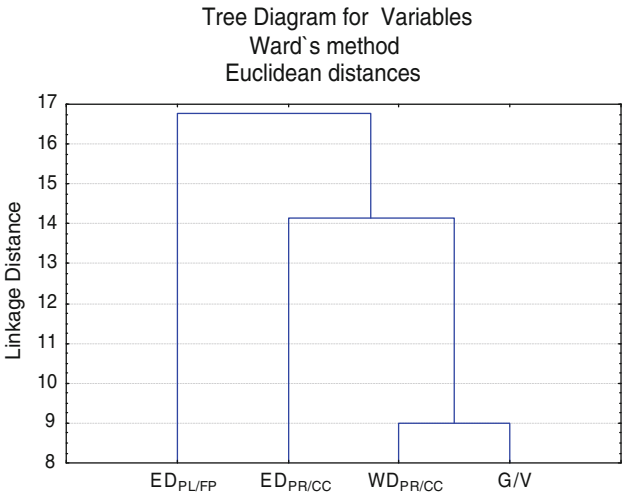

Fig. 1 Cluster Diagram (Ward's method Euclidean distances)

powered samples analyzed by calibration curve method) and WDXRF ($WD_{PR/CC:}$ pressed powered samples analyzed by calibration curve method) present appropriate precision and accuracy for Si and U_{total} determination.

The use of statistical tests such as Pearson Correlation and Cluster Analysis allowed concluding that pressed powered samples present less dispersion than plain powered samples.

The Pearson Correlation showed that $ED_{PL/PF}$ and $WD_{PR/CC}$ methods could be considered more similar to conventional methods.

The Custer Analysis showed that $WD_{PR/CC}$ method is equivalent to gravimetric and volumetric methods for Si and U_{total} determination in U_3Si_2 nuclear fuel.

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