

Application of multivariate calibration for simultaneous determination of major and minor constituents in U_3Si_2 by WDXRF technique

Marcos A. Scapin · Clayton P. Silva ·
Marycel E. B. Cotrim · Maria Ap. F. Pires

Received: 4 February 2014
© Akadémiai Kiadó, Budapest, Hungary 2014

Abstract The aim of this work was to implement and to validate the multivariate calibration for simultaneous determination of major and minor constituents in uranium nuclear fuel by WDXRF technique. The method is non-destructive and involves no chemical treatments thus is possible to perform fast chemical analysis and produces no hazardous waste. The precision and accuracy achieved are statistically comparable to others sensitive techniques like ICP-OES for impurities determination.

Keywords U_3Si_2 · Elemental analysis · Wavelength dispersive X-ray fluorescence · Multivariate calibration

Abbreviations CAS

MTR	Material testing reactor
FP	Fundamental parameters
SDV	Singular value decomposition method
NBL	New brunswick laboratory
IPEN/ CNEN-SP	Instituto de Pesquisas Energéticas e Nucleares
ICP-OES	Inductively coupled plasma optical emission spectrometry
RMB	Brazilian multipurpose reactor
FAAS	Flame atomic absorption spectrometry
PDCA	Pyridine-2,6-dicarboxylic acid
WDXRF	Wavelength dispersion X-ray fluorescence
ISO/IEC 17025	General requirements for the competence of testing and calibration laboratories

CRM	Reference materials characterized for uranium matrix impurities
RSD	relative standard deviation
RE	relative error
Z	Z-score
LoQ	Limit of quantification
MATLAB	Matrix laboratory
PC	Principal component
PLS	Partial least square
PCA	Principal component analysis

Introduction

The first multi-purpose research nuclear reactor in Brazil (RMB) will become operational in 2018. As its name implies, the equipment, estimated at US \$500 million, has multiple purposes. These purposes include production of radioisotopes for use in nuclear medicine for cancer exams/treatment and for research in the fields of nuclear technology, energy, agriculture, industry, materials science, and environment [1]. The technology to manufacture fuel for the RMB is already in place. The fuel will be plate type MTR, with an U_3Si_2 base, and produced at the IPEN/CNEN-SP [1, 2]. Currently, the production of MTR fuel begins by mixing aluminum with uranium silicide powder enriched to 20 wt% ^{235}U , in proportions predetermined. After, the mixture is compressed as briquettes and degassed under vacuum. Finally, one set of U_3Si_2 -Al briquettes is mounted on laminate to constitute the fuel core, which is then encased in a frame with two revetments of aluminum (top and nether). To ensure quality, stringent tests are applied at all process stages [3]. Although not an innovative technology, U_3Si_2 , with 4.8 g U cm^{-3} , is currently the world's most advanced commercial fuel [3]. Its performance in reactors depends on

M. A. Scapin (✉) · C. P. Silva · M. E. B. Cotrim ·
M. Ap. F. Pires
Instituto de Pesquisas Energéticas e Nucleares, IPEN – CNEN/
SP, Av. Prof. Lineu Prestes 2242 – Cidade Universitária,
05508-000 São Paulo, SP, Brazil
e-mail: scapin@usp.br

the chemical composition and absence of impurities. Lack of impurities is a requisite for good neutron economy, because their presence compromises the fuel energy density. Elements with a high neutron capture cross section, such as B and Cd, absorb thermal neutrons. The alkali, alkaline earth, and transition metals can form oxides, modifying the metal to oxygen ratio in a fuel matrix. Moreover, when combined with even ultra-trace levels of rare earth elements, such as Sm, Eu, Gd, and Dy, a decrease in energy density is caused, since radionuclides can be produced after reactor irradiation [4]. There are many techniques to determine impurities in uranium compounds. Spectroscopic methods are used most often because they allow for simultaneous determination using a small sample amount. These methods present advantages and disadvantages based on spectral interferences, accuracy, cost, type of sample (solid or liquid), and equipment used for analysis. The method must take into consideration the detection limit, sample preparation, and steps required for pre-concentration [4]. No single analytical technique is ideal for determination of all the elemental impurities since most of the elements are present in ultra-traces levels, and sometimes techniques do not possess the detection limit required for determination of the analytes. Low concentrations of the impurities, in the range of mg g^{-1} to $\mu\text{g g}^{-1}$, associated with uranium complex matrices as UO_2 , U_3Si_2 , U_3O_8 , and U–Mo, need to be determined, and compatible analytical methodologies must to be validated [4].

Thus, there is a need to develop rapid and simple methods for chemical characterization of materials used as nuclear fuel. In this context, the aim of this work is to evaluate the potential of WDXRF technique for chemical characterization of nuclear materials in accordance with technical specifications for nuclear fuels made of U_3O_8 and U_3Si_2 . The overall goal is to establish and validate a method for a non-destructive, inexpensive, and rapid quantitative chemical analysis, in addition to minimizing the generation of waste from simultaneous determination of the major constituents U_{total} and Si and impurities B, Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, and others present in U_3O_8 and U_3Si_2 in accordance with ISO/IEC 17025.

Materials and methods

Sample preparation

The pressed powdered samples were prepared according to the following steps: 1.8 g of sample and 0.2 g of wax (wax C micro powder, Hoechst) were transferred to a polyethylene bottle (5 cm^3) and homogenized in a mechanical mixer for 5 min (Spex Mixer/Mill). The mixture was

compacted by a hydraulic press (Herzog) using a pressure of 20 MPa for 2 s on a base of boric acid (H_3BO_3 PA) previously compressed with 100 MPa for 10 s. This gave pressed samples $25.01 \pm 0.01 \text{ mm}$ in diameter and $5.0 \pm 0.2 \text{ mm}$ in thickness.

Instrumental parameters

The experiments were carried out using a WDXRF spectrometer RIGAKU Co., model RIX 3000 with X-ray tube a Rh anode, a $75 \mu\text{m}$ Be window, and a 60 kV maximum acceleration voltage, scintillation detector NaI(Tl) and flow-proportional counter. A deconvolution method was applied to correct for overlap U-L β 1-2nd with Zn-K α , UL β 1 with Mo-K α . Zr-filter for separation of the Rh-K β 1 from Cd-K α X-rays. The FP method was applied for correction of the absorption/excitation effects. The parameters such as excitation, emission line, divergence slit, diffracting crystal, detector, fixed counting time, and Bragg's positions for B, Mg, Al, Si, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sn, Ba, Pb, and U are shown in Table 1.

Reference materials

The two sets of reference materials characterized for uranium matrix impurities were from the New Brunswick Laboratory (NBL) and labeled CRM 123 (1–7) and CRM 124 (1–7) and one set of the sixteen U_3Si_2 reference samples 20 % enriched in ^{235}U from the Nuclear Fuel Center of IPEN/CNEN-SP.

Univariate calibration

First, a qualitative analysis was performed on CRM-124 (1) to check for interferences and set up instrumental conditions. The overlaps were corrected using filters and a deconvolution method with software coupled to the spectrometer.

$$I_{ic} = I_i \sum L_{ij} I_{ij} \quad (1)$$

where I_{ic} is the intensity after overlap correction, I_i intensity before overlap correction, L_{ij} overlap correction coefficient for element j , and I_{ij} is the intensity of element j .

The matrix correction coefficients (absorption/excitation) were calculated by the FP method [5] using software coupled to the spectrometer.

$$W_i = (aI_i * I_i + bI_i + C) \left\{ 1 + K + \sum A_{ij} F_j + \sum Q_{ijk} F_j F_k + \sum \frac{R_{ij} F_j}{1 + W_1} + \sum B_{ij} F_j + \sum D_{ijk} F_j F_k + C \right\} \quad (2)$$

Table 1 Measurement conditions for WDXRF-Excitation: 50 kV × 50 mA

Elements	Emission line	Divergence slit (μm)	Diffracting crystal	Detector	Time (s)	Bragg's positions (°)
B	B-K _α	560	RX70	FPC	200	49.280
Mg	Mg-K _α	560	TAP	FPC	200	45.190
Al	Al-K _α	560	PET	FPC	40	145.220
Si	Si-K _α	560	PET	FPC	40	109.235
Ca	Ca-K _α	560	Ge	FPC	40	61.260
V	V-K _α	560	LiF(200)	SC	40	76.910
Cr	Cr-K _α	560	LiF(200)	SC	20	69.330
Mn	Mn-K _α	560	LiF(200)	SC	20	62.950
Fe	Fe-K _α	160	LiF(200)	SC	20	57.505
Co	Co-K _α	560	LiF(200)	SC	20	52.770
Ni	Ni-K _α	160	LiF(200)	SC	20	48.650
Cu	Cu-K _α	560	LiF(200)	SC	20	45.010
Zn	Zn-K _α	160	LiF(200)	SC	20	41.780
Mo	Mo-K _α	560	LiF(200)	SC	20	20.320
Cd (F-Zr)	Cd-K _α	560	LiF(200)	SC	20	15.300
Sn	Sn-K _α	160	LiF(200)	SC	20	14.030
Ba	Ba-L _α	560	LiF(200)	SC	20	87.130
Pb	Pb-L _α	560	LiF(200)	SC	20	33.915
U	U-L _α 1-2nd	560	LiF(200)	SC	20	53.765

TAP thallium acid phtalate, PET pentaerythritol, LiF lithium fluoride, Ge germanium, SC scintillation detector, NaI(Tl): FPC flow-proportional counter, F-Zr Zr primary X-ray filter

where W_i is the quantification value, a , b , and c are calibration curve coefficients, I_i is the X-ray intensity, K constant term, A_{ij} absorption/excitation correction coefficient, F_j analysis value or X-ray intensity of correction 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.

After setting up the instrumental conditions, seven measurements for B, Mg, Al, Si, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, Mo, Cd, Sn, and Pb were performed on CRM-123 (1–7). The net intensities of each element were related to their respective concentrations, and using linear regression the coefficients of each curve were calculated.

The methodology was evaluated using CRM-124 (1). Three samples were prepared, and six measurements for each element were performed. The statistical tests were then applied.

At first, Chauvenet's test was applied for detection of outliers [5].

$$|X_i - \bar{X}| > k_n * s \tag{3}$$

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 calculated in terms of relative standard deviation (RSD) and accuracy in terms of relative error (RE) and Z-score (Z) [6].

$$Z = \frac{(\bar{X}_{Lab} - \bar{X}_{CRM})}{\sqrt{U_{Lab}^2 - U_{CRM}^2}} \tag{4}$$

where Z is the standard error, \bar{X}_{Lab} experimental average, \bar{X}_{CRM} certificate value, U_{Lab}^2 experimental variance, and U_{CRM}^2 is the certificate variance.

The limit of quantification (LoQ) was calculated according to Eq. 5 [6].

$$LoQ = 2 * \sqrt{\sum_{m=1}^n \frac{(C_m - \bar{C})^2}{n - 1}} \tag{5}$$

where C_m is the individual measured value, \bar{C} average, and n is the repetition number.

Multivariate calibration

Under predetermined instrumental conditions, CRM-123 (1–7) samples were measured in 2θ scan mode. The spectra and concentration of each element were organized in a matrix, X and Y, respectively. The mean vector; original matrix of autoscaled data; standard deviations vector of X variables; original matrix of autoscaled data; loadings matrix; scores matrix; singular values; vector regression parameters were calculated using MATLAB 7.0.1 [8]. The vector regression provided the multivariate calibration curve for U₃O₈ samples. The methodology was evaluated using CRM-124 (1); three samples were prepared and six measurements were performed for each cited element. The same statistical tests described in Univariate calibration were applied.

The same process was applied to the U₃Si₂ samples, and a multivariate calibration curve was obtained. The

Table 2 Certified and determined values for CRM 124 (1) of the univariate calibration curves

Elements	Xcert ± σ (μg g ⁻¹)	Xdet ± σ (μg g ⁻¹)	RSD (%)	RE (%)	LoQ (μg g ⁻¹)	Z	r ²
B	5.1 ± 1.0	ND	NC	NC	NC	NC	0.01
Mg	101 ± 13	105 ± 22	21	4	36	0.3	0.98
Al	205 ± 37	ND	NC	NC	NC	NC	0.81
Si	202 ± 58	89 ± 4	5	56	9	1.9	0.96
Ca	200 ± 36	194 ± 11	6	3	13	0.2	1.00
V	50.0 ± 7.2	ND	NC	NC	NC	NC	0.06
Cr	102 ± 14	108 ± 8	7	6	13	0.4	0.98
Mn	51.0 ± 7.6	ND	NC	NC	NC	NC	0.75
Fe	210 ± 24	95 ± 10	11	55	21	4.8	0.91
Ni	202 ± 17	191 ± 1	1	5	2	0.6	1.00
Cu	50.0 ± 9.4	64 ± 7	11	29	34	1.5	0.99
Zn	202 ± 57	198 ± 25	13	2	29	0.1	1.00
Mo	100.0 ± 5.5	92 ± 5	5	8	8	1.5	0.99
Cd	5.20 ± 0.88	ND	NC	NC	NC	NC	0.17
Sn	51.0 ± 6.9	55 ± 3	6	7	6	0.5	1.00
Pb	51 ± 15	ND	NC	NC	NC	NC	0.81

Xcert ± σ certified values, Xdet ± σ determined values, RSD relative standard deviation, RE relative error, LoQ limit of quantification, Z Z-score, r² correlation coefficients, ND not determined, NC not calculated

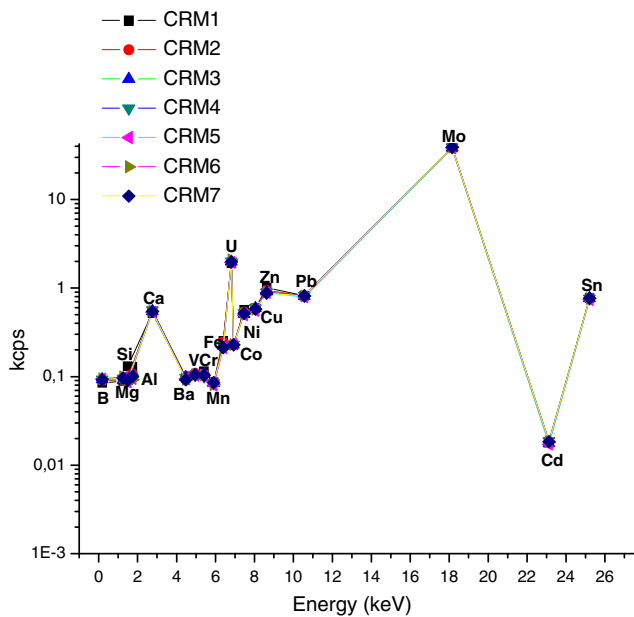


Fig. 3 Intensity versus energy plot used to obtain an X matrix with U₃O₈ CRMs

Multivariate calibration with U₃O₈ CRM

The calibration model was constructed using the same set of MRC-123 (1–7) with the instrumental conditions presented in Table 1 using the 2θ scan method. The X matrix (intensity matrix) was obtained by averaging seven replicates for each element from all CRM measurements according to their respective energy (Fig. 3), resulting in a 7 × 19 matrix. Using MATLAB 7.0.1 software, the mean

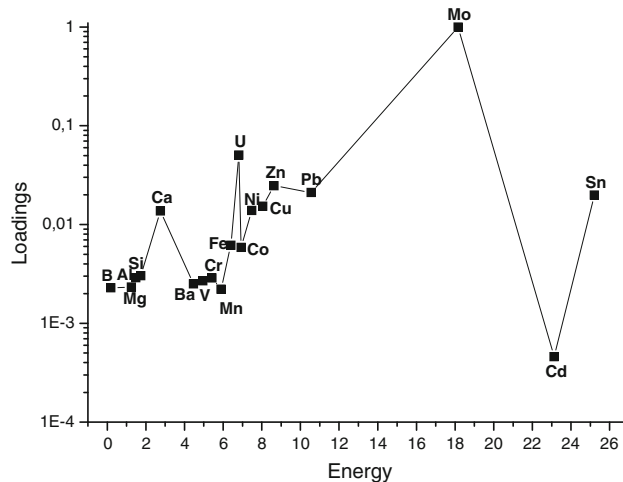


Fig. 4 Loading versus energy plot principal component PC1 in U₃O₈ CRMs

values and deviations pertaining to the centering matrix were calculated. Subsequently, a principal component analysis was performed to determine the number of components needed to describe data set. The results showed a main component is sufficient (PC1 = 99.9999, PC2 = 0.0001 %) [10]. In Fig. 4, loading versus energy, calculated for PC1, is shown. Comparison of Figs. 3 and 4 indicates that one component is sufficient to describe the whole set. The calibration model was obtained using the partial least square (PLS) method [10], and statistical test validation was applied to CRM 124 (1).

In Table 3, certified and determined values, RSD, RE, LoQ, and Z-score are presented for CRM 124 (1) of the multivariate calibration. The precision assessment, in

Table 3 Certified and determined values for CRM 124 (1) of the multivariate calibration

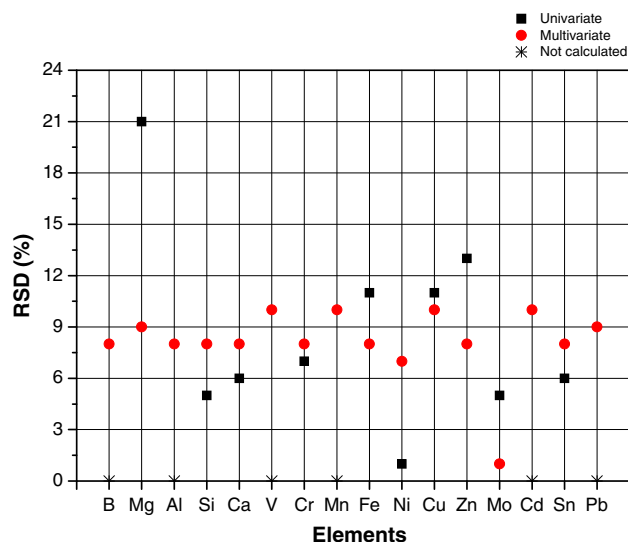
Elements	$X_{cert} \pm \sigma$ ($\mu\text{g g}^{-1}$) ($\mu\text{g g}^{-1}$)	$X_{det} \pm \sigma$ ($\mu\text{g g}^{-1}$)	RSD (%)	RE (%)	LoQ ($\mu\text{g g}^{-1}$)	Z
B	5.1 ± 1.0	4.8 ± 0.4	8	6	2.6	0.3
Mg	101 ± 13	82 ± 7	9	19	43	1.5
Al	205 ± 37	166 ± 14	8	19	81	1.1
Si	202 ± 58	197 ± 16	8	3	99	0.1
Ca	200 ± 36	176 ± 14	8	12	87	0.7
V	50.0 ± 7.2	40 ± 4	10	20	22	1.4
Cr	102 ± 14	85 ± 7	8	17	43	1.2
Mn	51.0 ± 7.6	42 ± 4	10	18	21	1.2
Fe	210 ± 24	173 ± 13	8	18	80	1.5
Ni	202 ± 17	169 ± 12	7	16	77	1.9
Cu	50.0 ± 9.4	42 ± 4	10	16	22	0.8
Zn	202 ± 57	179 ± 15	8	11	88	0.4
Mo	100.0 ± 5.5	85 ± 1	1	15	40	1.9
Cd	5.20 ± 0.88	4.2 ± 0.4	10	10	2	1.1
Sn	51.0 ± 6.9	38 ± 3	8	25	20	1.8
Pb	51 ± 15	35 ± 3	9	21	18	1.1

$X_{cert} \pm \sigma$ certified values,
 $X_{det} \pm \sigma$ determined values,
 RSD relative standard deviation,
 RE relative error, LoQ limit of
 quantification, Z Z-score

relation to the RSD, showed satisfactory repeatability for all elements determined ($RSD \leq 10\%$). According to the INMETRO recommendation, RSD values above 10 % are considered unsatisfactory. The process was reproducible [9]. The accuracy evaluation, in relation to the Z-score, had values less than ≤ 1.9 , making it satisfactory [6]. The limits of quantification also showed adequate values once they were lower than $3 \mu\text{g g}^{-1}$ for B and Cd. Those elements are of great interest because of their high cross sections. Furthermore, for all other elements the LQ is less than $90 \mu\text{g g}^{-1}$, with the exception of Si ($99 \mu\text{g g}^{-1}$).

Univariate and multivariate calibration comparison

The comparison between univariate and multivariate calibrations was made based on precision (RSD), accuracy (Z-score), and LoQ calculated for CRM 124 (1). The RSD (Fig. 5) for both methods is less than 10 %, except for Mg (21 %). Thus, it can be stated that the precision of the two methods is comparable. However, multivariate calibration has a higher precision for B, Mg, Al, V, Mn, Cd, and Pb determination. The Z-score values (Fig. 6) for both methods are < 2 , except for Cu ($Z = 2.1$) and Fe ($Z = 4.8$) using the univariate calibration. The results show that the accuracy of both methods is comparable; however, for Cu and Fe determination, multivariate calibration provides more reliable results (exact). Furthermore, for B, Al, V, Mn, Cd, and Pb, multivariate calibration has a greater accuracy. The LoQ (Fig. 7) is lower for Univariate calibration, except for Cu. However,

**Fig. 5** RSD comparison of univariate and multivariate calibrations

multivariate calibration also has LoQ values sufficient for impurity determination in U_3O_8 matrices.

Multivariate calibration using U_3Si_2 reference samples

The calibration model based on the U_3Si_2 samples was built in the same manner as the model for U_3O_8 , i.e. the instrumental conditions presented in Table 2 using the 2θ scan method. The X matrix (intensity matrix) was also obtained by averaging seven replicas from each sample for each element, according to its respective energy (Fig. 8), resulting in a

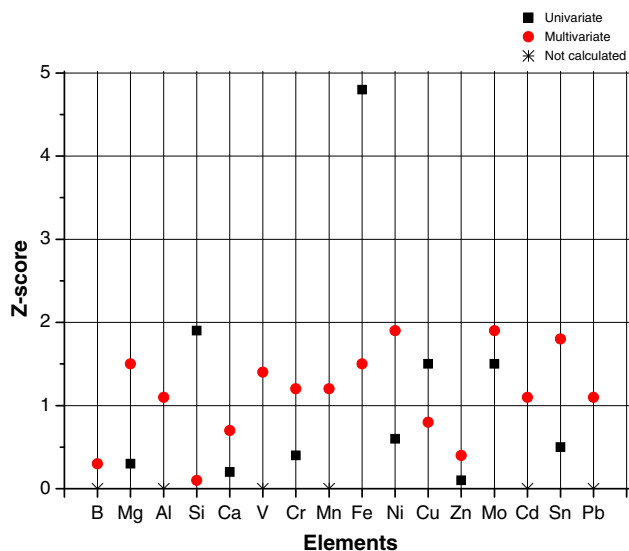


Fig. 6 Comparison of the Z-score values for univariate and multivariate calibration

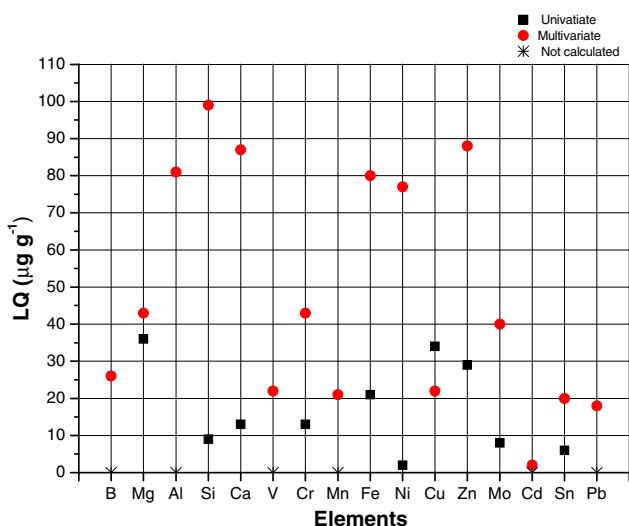


Fig. 7 LoQ comparison for univariate and multivariate calibration

16 × 19 matrix. The PCA analysis revealed two principal components (PC1 = 99.982; PC2 = 0.016 %); however, PC1 is sufficient to describe the calibration model because it has the highest weight (~ 100 %). Loading versus energy is calculated for PC1 and shown in Figs. 9. 8 and 9 have similarities, proving that one component is sufficient to describe the whole range of the U₃Si₂ samples, similar to U₃O₈. In Table 4, the U_{total} and Si values were determined by conventional methods (\bar{X}_V : volumetric; \bar{X}_G : gravimetric). The B, Mg, Al, Si, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Ba, Sn, and Pb values were determined by ICP-OES ($\bar{X}_{ICP-OES}$) and

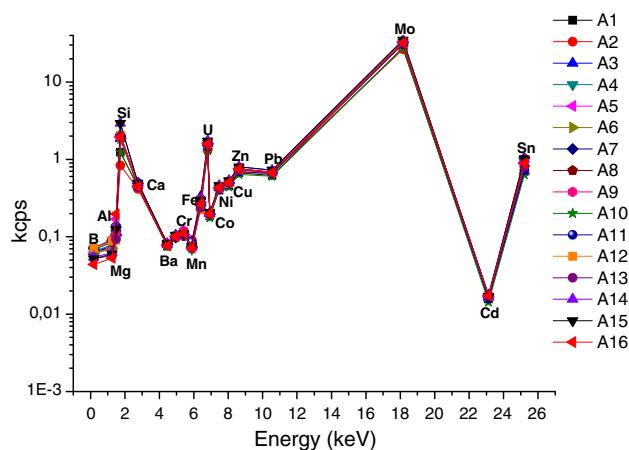


Fig. 8 Intensity versus energy plot used to obtain an X matrix with U₃Si₂ samples

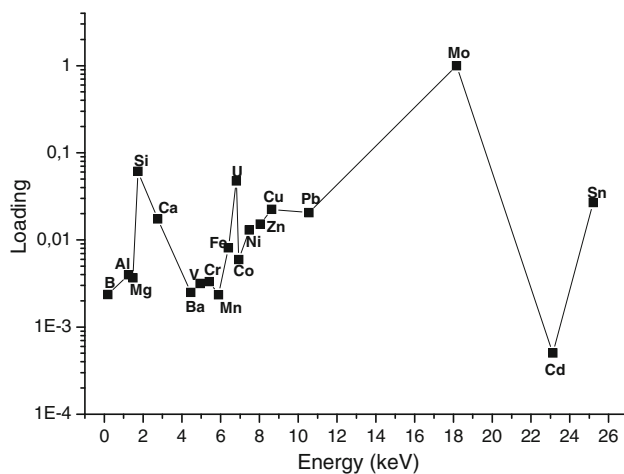


Fig. 9 Loading versus energy plot for principal component PC1 in U₃Si₂

WDXRF ($\bar{X}_{MC-WDXRF}$) by multivariate calibration. Also, LoQ, F-distribution ANOVA, and the student *t* test to compare the difference in outcomes are all presented. The precision assessment, in relation to ANOVA, showed the three methods (\bar{X}_V : volumetric, \bar{X}_G : gravimetric, \bar{X}_{WDXRF}) to be statistically equal. The F-distribution ANOVA calculated values were less than critical F-values for all the elements except Sn ($F = 10.03$, $F_{critical} = 4.96$). The student *t* test for all the elements was also less than the critical *t* values. For the elements where the statistical tests did not apply B, Mo, Cd, and Ba, because the values were lower than the LoQ, a visual assessment demonstrated their compliance. The LoQ calculated for the multivariate calibration is sufficient for impurity determination in U₃Si₂ and meets the specifications of U₃Si₂ nuclear fuel.

Table 4 U_{total} , Si and impurities values for U_3Si_2 reference samples

Element	\bar{X}_V (%)	σ^2	$\bar{X}_{MC-WDXRF}$ (%)	σ^2	LoQ ($\mu\text{g g}^{-1}$)	F	F _{critical}	t	t _{critical}	n
U	91.3	0.2	91.8	5.6	1	0.6	4.5	0.8	2.1	16
Element	\bar{X}_G (%)	σ^2	$\bar{X}_{MC-WDXRF}$ (%)	σ^2	LQ ($\mu\text{g g}^{-1}$)	F	F _{critical}	t	t _{critical}	n
Si	7.79	0.02	7.82	0.04	1	0.2	4.2	0.5	2.1	16
Elements	$\bar{X}_{ICP-OES}$ ($\mu\text{g g}^{-1}$)	σ^2	$\bar{X}_{MC-WDXRF}$ ($\mu\text{g g}^{-1}$)	σ^2	LQ ($\mu\text{g g}^{-1}$)	F	F _{critical}	t	t _{critical}	n
B	1.5	1.6	<4	NC	4	NC	NC	NC	NC	10
Mg	12.4	188.3	7.1	10.5	1	2.2	4.2	1.6	2.1	16
Al	260	128936	260	25022	23	0.1	4.2	0.1	2.1	16
Ca	11.8	147.2	10.0	42.4	1	0.3	4.2	0.7	2.1	16
V	1.8	5.8	1.8	1.4	2	0.1	4.2	0.2	2.1	16
Cr	25	836	15	46	2	1.9	4.2	1.6	2.1	16
Mn	56	3688	80	2591	8	0.2	4.2	1.0	2.1	16
Fe	283	53059	188	8647	12	2.3	4.2	0.1	2.1	16
Co	14	2	18	2	1	0.2	4.6	0.4	2.4	8
Ni	22	336	30	290	3	1.4	4.2	1.5	2.2	14
Cu	27	264	39	648	4	2.4	4.2	1.7	2.1	16
Zn	14	310	10	40	3	0.6	4.2	0.9	2.1	16
Mo	<3.0	NC	<1	NC	1	NC	NC	NC	NC	16
Cd	<0.1	NC	<2	NC	2	NC	NC	NC	NC	12
Ba	<0.2	NC	<10	NC	10	NC	NC	NC	NC	14
Sn	39	698	78	214	1	10.03	4.96	2.4	2.8	5
Pb	7.9	5.6	9.4	0.4	1	1.3	7.7	1.1	4.3	3

\bar{X} Average, σ^2 Variance, \bar{X}_V determined by volumetric method, \bar{X}_G determined by gravimetric method, $\bar{X}_{ICP-OES}$ determined by ICP-OES method, \bar{X}_{WDXRF} determined by WDXRF methods, LoQ limit of quantification, F F-distribution value, t student t test value, n number of observations, NC not calculated

Conclusions

The methodology proposed in this work would allow agencies to meet the requirements for nuclear materials control in relation to U_{total} and impurities in nuclear fuel that is based on U_3Si_2 , enriched by 20 wt% ^{235}U , and U_3O_8 , in accordance with ISO/IEC 17025. The method has minimal waste production, reducing analysis time and cost significantly. It also has promise as a method for chemical characterization of materials in nuclear fuel.

Acknowledgments The authors would like to thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq-Edital Universal) n. 479106/2010-0, Brazil; Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES-PNPD n. 02889/2009-9), and Comissão Nacional de Energia Nuclear (CNEN), Brazil (PCI n. 680.020/2008-0) for financial support.

References

1. Brasil Nuclear (2013) Informativo da Associação Brasileira de Energia Nuclear. <http://www.aben.com.br/Arquivos/48/48.pdf>. Accessed 30 Sept 2013
2. The RMB Project Development Status (2011) International conference on research reactors: safe management and effective utilization. http://www.pub.iaea.org/MTCD/Publications/PDF/P1575_CD_web/datasets/abstracts/C6Perrotta.html. Accessed 30 Sept 2013
3. Saliba-Silva AM, Durazzo M, Carvalho EFU, Riella HG (2008) Fabrication of U_3Si_2 powder for fuels used in IEA-R1 nuclear research reactor. Mater Sci Forum. doi:10.4028/www.scientific.net/MSF.591-593.194
4. Souza AL, Cotrim MEB, Pires MAF (2012) An overview of spectrometric techniques and sample preparation for the determination of impurities in uranium nuclear fuel grade. J Microchemical. doi:10.1016/j.microc.2012.06.015
5. Scapin MA, Salvador VLR, Cotrim MEB, Pires MAF, Sato IM (2011) Uncertainty measurement evaluation of WDXRF and EDXRF techniques for the Si and U_{total} determination in U_3Si_2 nuclear fuel. J Radioanal Nucl Chem. doi:10.1007/s10967-010-0897-6
6. Instituto Nacional de Metrologia, Normalização e Qualidade Industrial-INMETRO (2010) Orientação sobre validação de métodos analíticos (DOQ-CGRE-008). http://www.inmetro.gov.br/sidoq/arquivos/cgcre/doq/doq-cgcre-8_03.pdf. Accessed 30 Sept 2013
7. Rousseau R (2001) Detection limit and estimate of uncertainty of analytical XRF result. Rigaku J. <http://www.rigaku.com/downloads/journal>. Accessed 30 Sept 2013
8. Ferreira MMC, Antunes AM, Melgo MS, Volpe PLO (1999) Quimiometria I: calibração multivariada, um tutorial". Quim Nova 22:724–731

9. EURACHEN/CITAC GUIDE, 2^a Edit (2011) Quantifying uncertainty in analytical measurement. http://eurachem2011.fc.ul.pt/pdf/QUAM2011_DIS1.pdf. Accessed 30 Sept 2013
10. Parreira TF (2003) Utilização de métodos quimiométricos em dados de natureza multivariada. <http://biq.iqm.unicamp.br/arquivos/teses/vtIs000317484.pdf> Accessed 30 Sept 2013