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Application of bias correction methods to improve U_3Si_2 sample preparation for quantitative analysis by WDXRF

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ABSTRACT

The determination of silicon (Si), total uranium (U) and impurities in uranium-silicide (U_3Si_2) samples by wavelength dispersion X-ray fluorescence technique (WDXRF) has been already validated and is currently implemented at IPEN's X-Ray Fluorescence Laboratory (IPEN-CNEN/SP) in São Paulo, Brazil. Sample preparation requires the use of approximately 3 g of H_3BO_3 as sample holder and 1.8 g of U_3Si_2. However, because boron is a neutron absorber, this procedure precludes the recovery of U_3Si_2 from the samples, preventing its use as nuclear fuel. Consequently, a significant amount of uranium is wasted in this process. An estimated average of 15 samples per month is expected to be analyzed by WDXRF, resulting in approx. 320 g of U_3Si_2 that wouldn't return to the nuclear fuel cycle. The purpose of this paper is to present a new preparation method, replacing H_3BO_3 by cellulose acetate $\{[C_6H_7O_2(OH)_3\text{-}m(OOCCH_3)m],\ m = 0\sim3\}$, thus enabling the recovery of the boron-free U_3Si_2 from the samples. The results demonstrate that the suggested sample preparation approach is statistically satisfactory, allowing the optimization of the procedure.

Keywords: U_3Si_2, XRF, WDXRF.

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1. INTRODUCTION

The determination of Si, total U and inorganic impurities in low enriched uranium silicide (U_3Si_2, 19.9% of ^{235}U) powder samples by wavelength dispersion X-ray fluorescence (WDXRF) is carried out by a validated procedure at IPEN's X-Ray Fluorescence Laboratory (IPEN-CNEN/SP) in São Paulo, Brazil [1,2]. WDXRF is able to perform non-destructive simultaneous multielement determinations with good precision and accuracy [3], thus preserving the original sample. Since routine analyses are to be required for the qualification of the U3Si2 fuel samples, a potential recovery could represent the reduction of radioactive solid wastes generation by the reincorporation of the compound to the fuel cycle.

IPEN's Nuclear Fuel Center (CCN-IPEN/SP) is responsible for the yearly production of 60 nuclear fuel elements for the Brazilian Multipurpose Reactor ("*Reator Multipropósito*", RMB) [4]. The expected amount of U_3Si_2 samples to undergo fluorescence analysis could then reach 324 g per year, once each reading is performed in triplicate to ensure the reliability of the results.

The current sample preparation method requires an amount of 1.8 g of U_3Si_2, which is supported by an approx. 3 g of H_3BO_3, used as sample holder. This step is used to facilitate sample's handling [2]. However, boron (^{10}B) is a neutron absorber (neutron poison) because of its high neutron capture cross section, thus disabling sample's recovery after the analysis, since boron contamination may impair the fuel's performance in the nuclear reactor.

Within this context, this study proposed a new preparation method for the determination of Si, total U and inorganic impurities in U_3Si_2 powder samples by WDXRF, replacing boric acid (H_3BO_3) by cellulose acetate $\{[C_6H_7O_2(OH)_3\text{-}m(OOCCH_3)m], m = 0\sim3\}$. Systematic errors were evaluated in order to demonstrate that the proposed method presents no significant analytical impact.

2. MATERIALS AND METHODS

2.1. Sample preparation

A candidate sample for reference material containing 12 g of U_3Si_2 powder was supplied by the Nuclear Fuel Center (CCN) at IPEN (CNEN/SP). Sampling was performed in order to obtain 6 sub-fractions of 2.0 g each. 3 of these sub-fractions were prepared using H_3BO_3 as sample holder and the other 3 were prepared using cellulose acetate. For each single sample, the following procedure it was used: 1.8 g of U_3Si_2 and 0.2 g of wax (Hoechst wax C micro powder, Merck Millipore, MA, USA) were transferred to a polyethylene flask (approx. 5 cm^3) and homogenized in a mechanical mixer for 5 min (Spex CertiPrep, NJ, USA). The mixture was compacted in a hydraulic press (Herzog, Osnabruck, Germany) employing a 2 kN pressure. A pressed pellet of 25.01 ± 0.01 mm of diameter and 5.0 ± 0.2 mm of thickness was obtained for each sub-fraction.

2.2. Instrumental parameters

The experiments were carried out using a WDXRF spectrometer (RIGAKU Co., Tokyo, Japan), model RIX 3000, comprising the following primary devices: one 3 kW (Rh target) X-ray tube, 6 positions sample, 8 crystal analyzers and 2 detectors (scintillation and flow-proportional counters). Analytical program parameters such as excitation, emission line (EL), divergence slit (Ds), diffracting crystal (Dc), detector (D), fixed counting time (t) and Bragg's positions (2θ) - peak and background (BG1 and BG3) readings - for B, Mg, Al, Si, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Sn, Ba, Pb and U are shown in Tab. 1 [5].

Table 1: Analytical program measurements conditions of WDXRF spectrometer

Excitation: 50 kV x 50 mA						2θ (degrees)		
E	**EL**	**Ds (μm)**	**Dc**	**D**	**t(s)**	**BG1**	**peak**	**BG3**
B	B-K_α	560	RX70	FPC	200	44.000	49.280	56.000
Mg	Mg-K_α	560	TAP	FPC	200	44.850	45.190	45.650
Al	Al-K_α	560	PET	FPC	40	144.440	145.220	145.240
Si	Si-K_α	560	PET	FPC	40	108.30	109.235	109.630
Ca	Ca-K_α	560	Ge	FPC	40	60.860	61.260	61.660
V	V-K_α	560	LiF(200)	SC	40	76.710	76.910	77.110
Cr	Cr-K_α	560	LiF(200)	SC	20	69.130	69.330	69.530
Mn	Mn-K_α	560	LiF(200)	SC	20	62.750	62.950	63.150

Fe	Fe-K$_{\alpha}$	160	LiF(200)	SC	20	57.300	57.505	57.700
Co	Co-K$_{\alpha}$	560	LiF(200)	SC	20	52.570	52.770	52.970
Ni	Ni-K$_{\alpha}$	160	LiF(200)	SC	20	48.450	48.650	48.850
Cu	Cu-K$_{\alpha}$	560	LiF(200)	SC	20	44.810	45.010	45.210
Zn	Zn-K$_{\alpha}$	160	LiF(200)	SC	20	41.580	41.780	41.980
Mo	Mo-K$_{\alpha}$	560	LiF(200)	SC	20	20.120	20.320	20.250
Cd (F-Zr)	Cd-K$_{\alpha}$	560	LiF(200)	SC	20	15.110	15.300	15.500
Sn	Sn-K$_{\alpha}$	160	LiF(200)	SC	20	13.830	14.030	14.230
Ba	Ba-L$_{\alpha}$	560	LiF(200)	SC	20	86.930	87.130	87.330
Pb	Pb-L$_{\alpha}$	560	LiF(200)	SC	20	33.710	33.915	34.111
U	U-L$_{\alpha}$1-2nd	560	LiF(200)	SC	20	53.560	53.765	53.960

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.

2.3. Systematic error coefficient (SEC)

Systematic errors, which affect the accuracy of the results, have identifiable causes and can be eliminated [6]. In X-ray fluorescence spectrometry, systematic errors are usually related to sample preparation. For instance, metallic samples require surface treatment using abrasives. Abrasive change, or even the employment of a new batch, may lead to systematically divergent results (above or under the results obtained for the original abrasive). Considering pressed pellets, the substitution of the binder or support base, as described in this study, may also conduct to systematically divergent results.

Because of this, X-ray fluorescence spectrometers' manufacturers provide mathematical tools, enabling the correction of the systematic errors through the calculation of these coefficients. This is a very valuable tool, since these coefficients allow the analysis of samples prepared by different procedures using a calibration curve obtained by a determined procedure. In this study, Eq. 1, available in the software Simultix 14 of the Rigaku spectrometer, was employed [7].

$$A_i = \frac{Wis}{Wi} - 1.0 \tag{1}$$

where *Ai* = correction coefficient; *Wis* = standard value; *Wi* = analyzed value.

2.4. Methodology evaluation

Samples were divided into 2 sub-groups: “Group A”, prepared using the cellulose acetate as holder, and “Group B”, using H_3BO_3. Each sample was randomly analyzed 3 times under the established instrumental conditions, resulting in a set of 18 measurements for each element and the data were evaluated statistically [2]. The Fisher-Snedecor F-test was applied to compare the variances of groups A and B at a 95% confidence level. When the calculated values of F were below their critical value (0.05), the hypothesis of different variances was accepted. The Student t-test was applied to compare the average values (means), assuming different variances for a 95% confidence level. For calculated values of “t” below their critical value (2.13), the difference between the mean values can be assumed as statistically insignificant. Both tests were performed using the Software Microsoft Excel (2013 version).

3. RESULTS AND DISCUSSION

The results for “Group A” and “Group B” are presented in Tab. 2 comprising elemental contents and standard deviations ($\bar{X}\pm\sigma$), followed by the relative standard deviations (RSD), calculated values of F and t, both for a 95% confidence level, and systematic error coefficients (SEC) calculated according Eq. 1.

Table 2: WDXRF analysis results for “Group A” and “Group B” samples

Elements	**A Group**		**B Group**		**F-test**	**t-test**	**SEC**
	$\bar{X}\pm\sigma$	**RSD**	$\bar{X}\pm\sigma$	**RSD**			
B ($\mu g\ g^{-1}$)	2.212±0.004	0.2	2.20±0.03	1.5	0.02	1.37	0.014±0.004
Mg ($\mu g\ g^{-1}$)	4.645±0.009	0.2	4.61±0.07	1.5	0.02	1.37	0.014±0.004
Al ($\mu g\ g^{-1}$)	154.9±0.3	0.2	154±2	1.5	0.02	1.36	0.014±0.004
Si (%)	7.804±0.002	0.02	7.804±0.001	0.02	1.69	0.01	0.0002±0.0001

Ca (µg g^{-1})	8.63±0.02	0.2	8.6±0.1	1.5	0.02	1.36	0.014±0.004
V (µg g^{-1})	0.332±0.001	0.2	0.329±0.005	1.5	0.02	1.37	0.014±0.004
Cr (µg g^{-1})	13.16±0.02	0.2	13.1±0.2	1.5	0.02	1.37	0.014±0.004
Mn (µg g^{-1})	189.4±0.4	0.2	188±3	1.5	0.02	1.37	0.014±0.004
Fe (µg g^{-1})	204.8±0.4	0.2	203±3	1.5	0.02	1.37	0.014±0.004
Co (µg g^{-1})	0.332±0.001	0.2	0.329±0.005	1.5	0.02	1.37	0.014±0.004
Ni (µg g^{-1})	10.73±0.02	0.2	10.7±0.2	1.5	0.02	1.37	0.014±0.004
Cu (µg g^{-1})	21.01±0.04	0.2	20.9±0.3	1.5	0.02	1.37	0.014±0.004
Zn (µg g^{-1})	7.08±0.01	0.2	7.0±0.1	1.5	0.02	1.37	0.014±0.004
Mo (µg g^{-1})	2.76±0.01	0.2	2.75±0.04	1.5	0.02	1.37	0.014±0.004
Cd (µg g^{-1})	0.2212±0.0004	0.2	0.220±0.003	1.5	0.02	1.37	0.014±0.004
Ba (µg g^{-1})	0.2212±0.0004	0.2	0.220±0.003	1.5	0.02	1.37	0.014±0.004
Sn (µg g^{-1})	8.18±0.02	0.2	8.1±0.1	1.5	0.02	1.37	0.014±0.004
Pb (µg g^{-1})	5.53±0.01	0.2	5.49±0.08	1.5	0.02	1.37	0.014±0.004
U (%)	91.17±0.01	0.01	91.16±0.02	0.02	0.62	0.14	0.0002±0.0001

F-critical = 0.05 – t-critical = 2.13

The results showed that all elements were quantified for both procedures. The calculated values of F were lower than the critical value (F-critical = 0.05) for all elements, demonstrating that the difference between the variances of Groups “A” and “B” are statistically insignificant, except for Si (1.69) and U (0.62). The relative standard deviation (RSD) values were significantly lower for the samples of “Group A” (0.2 %) compared to those of “Group B” (1.5 %). Thus, the repeatability of the overall results for the samples prepared with cellulose acetate was more satisfactory than for the samples prepared with H_3BO_3.

The calculated values for the “t” Student test (“t-test”) for all the elements were lower than the critical values (2.13), demonstrating that there are no statistically significant difference between the samples of “Group A” and “Group B”.

For Si and U, the systematic error coefficients (SEC) showed that the influence of the major constituents were lower (0.0002±0.0001) when compared to the other elements (0.014±0.004). However, the SEC values can be disregarded for all the elements, when the correction is applied, because the variation in the concentration values is smaller than the standard deviation. Thus, the hypothesis can be accepted, that there are no statistically significant differences between both methods.

It was visually evident that the 3 samples prepared with cellulose acetate were easily removable from its base after the analysis (Fig. 1), thus ensuring boron-free U_3Si_2 pellets. The probable hypothesis for this is that the cellulose acetate had undergone some sort of decomposition after the irradiation in the spectrometer, favoring the detachment of the sample from its base.

Figure 1: *Cellulose base (left) and clear detached U_3Si_2 sample.*

Source: author

4. CONCLUSION

The results allowed concluding that the substitution of boric acid for cellulose acetate in the preparation of pressed pellets for elemental analysis by WDXRF can be applied, since statistically equivalent results are achieved in both cases. Indeed, the cellulose acetate proved to be more suitable than the H_3BO_3, because it allowed an effortless recovery of the sample. Thus, the aim of this study was achieved, as an effective alternative preparation procedure for U_3Si_2 analysis by WDXRF was proposed. In addition, using cellulose acetate as support base allows a simple and complete recovery of the U_3Si_2 samples.

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