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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 U_3Si_2 sample's recovery, which, in time, considering routinely analysis, may account for significant unusable uranium waste. An estimated average of 15 samples per month are expected to be analyzed by WDXRF, resulting in approx. 320 g of U_3Si_2 that wouldn't return to the nuclear fuel cycle. This not only impacts in production losses, but generates another problem: radioactive waste management. The purpose of this paper is to present the mathematical models that may be applied for the correction of systematic errors when H_3BO_3 sample holder is substituted by cellulose-acetate $\{[C_6H_7O_2(OH)_3\text{-}m(OOCCH_3)m]$, m = 0~3$\}$, thus enabling U_3Si_2 sample's recovery. The results demonstrate that the adopted mathematical model is statistically satisfactory, allowing the optimization of the procedure.

1. INTRODUCTION

The determination of Si, total U and impurities in low enriched uranium silicide (U_3Si_2, LEU 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 U_3Si_2 fuel samples, a potential recovery could represent the reduction of radioactive solid wastes generation by the reincorporation of the compound to the fuel cycle.

Sample preparation 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.

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.

Within this context, this study aims to evaluate the systematic errors in the determination of of Si, total U and impurities in LEU silicide (U_3Si_2) powder samples by WDXRF, when boric acid (H_3BO_3) is substituted by cellulose acetate {$[C_6H_7O_2(OH)_3$-m$(OOCCH_3)$m], m = 0~3}. This should not only take the boron out of the picture, but also favors the recovery of U_3Si_2.

2. EXPERIMENTAL

2.1. Sample preparation

A sample containing 12 g of U_3Si_2 powder was supplied by CCN. 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 instead. For each single sample, the following procedure was employed: 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 briquette of 25.01 ± 0.01 mm of diameter and 5.0 ± 0.2 mm of thickness is 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).

The parameters such as excitation, emission line (EL), divergence slit (Ds), diffracting crystal (Dc), detector (D), fixed counting time (t) and Bragg's positions (2θ) 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: Measurements condition to WDXRF

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_α	160	LiF(200)	SC	20	57.300	57.505	57.700
Co	Co-K_α	560	LiF(200)	SC	20	52.570	52.770	52.970
Ni	Ni-K_α	160	LiF(200)	SC	20	48.450	48.650	48.850
Cu	Cu-K_α	560	LiF(200)	SC	20	44.810	45.010	45.210
Zn	Zn-K_α	160	LiF(200)	SC	20	41.580	41.780	41.980
Mo	Mo-K_α	560	LiF(200)	SC	20	20.120	20.320	20.250
Cd (F-Zr)	Cd-K_α	560	LiF(200)	SC	20	15.110	15.300	15.500
Sn	Sn-K_α	160	LiF(200)	SC	20	13.830	14.030	14.230
Ba	Ba-L_α	560	LiF(200)	SC	20	86.930	87.130	87.330
Pb	Pb-L_α	560	LiF(200)	SC	20	33.710	33.915	34.111
U	U-L_α1-2nd	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 the sample's 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 briquettes, 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].

$$A_{i=\frac{W_{is}}{W_i}-1.0} \quad (1)$$

where $A_i \equiv$ correction coefficient; $W_{is} \equiv$ standard value; $W_i \equiv$ analyzed value.

2.4. Methodology evaluation

Samples were divided into 2 sub-groups: "Group A", prepared using the cellulose acetate as binder, and "Group B", using H_3BO_3. Each sample was 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 comparison of the Group A and B samples was performed by the Student "t" test, assuming different variances. The null hypothesis is accepted, when $t_{experimental} < t_{theoretical}$, what means there is no significant difference between methods [8].

3. RESULTS AND DISCUSSION

The results, accompanied by their standard deviations ($\bar{X}\pm\sigma$), followed by the relative standard deviation (RSD), calculated and critical "t" of Student values ("t-test" and "critical-t") and the systematic error coefficients (SEC) of the prepared samples from both "Group A" and "Group B" are displayed in Tab. 2.

Table 2: WDXRF analysis results for "Group A" and "Group B" samples.

Elements	A Group		B Group		t-test	critical-t	SEC
	$\bar{X}\pm\sigma$	RSD	$\bar{X}\pm\sigma$	RSD			
B (μg g^{-1})	2.212±0.004	0.2	2.20±0.03	1.5	1.37	2.31	0.014±0.004
Mg (μg g^{-1})	4.645±0.009	0.2	4.61±0.07	1.5	1.37	2.31	0.014±0.004
Al (μg g^{-1})	154.9±0.3	0.2	154±2	1.5	1.36	2.31	0.014±0.004
Si (%)	7.804±0.002	0.02	7.804±0.001	0.02	0.01	2.13	0.0002±0.0001
Ca (μg g^{-1})	8.63±0.02	0.2	8.6±0.1	1.5	1.36	2.31	0.014±0.004
V (μg g^{-1})	0.332±0.001	0.2	0.329±0.005	1.5	1.37	2.31	0.014±0.004
Cr (μg g^{-1})	13.16±0.02	0.2	13.1±0.2	1.5	1.37	2.31	0.014±0.004
Mn (μg g^{-1})	189.4±0.4	0.2	188±3	1.5	1.37	2.31	0.014±0.004
Fe (μg g^{-1})	204.8±0.4	0.2	203±3	1.5	1.37	2.31	0.014±0.004
Co (μg g^{-1})	0.332±0.001	0.2	0.329±0.005	1.5	1.37	2.31	0.014±0.004
Ni (μg g^{-1})	10.73±0.02	0.2	10.7±0.2	1.5	1.37	2.31	0.014±0.004
Cu (μg g^{-1})	21.01±0.04	0.2	20.9±0.3	1.5	1.37	2.31	0.014±0.004
Zn (μg g^{-1})	7.08±0.01	0.2	7.0±0.1	1.5	1.37	2.31	0.014±0.004
Mo (μg g^{-1})	2.76±0.01	0.2	2.75±0.04	1.5	1.37	2.31	0.014±0.004
Cd (μg g^{-1})	0.2212±0.0004	0.2	0.220±0.003	1.5	1.37	2.31	0.014±0.004
Ba (μg g^{-1})	0.2212±0.0004	0.2	0.220±0.003	1.5	1.37	2.31	0.014±0.004
Sn (μg g^{-1})	8.18±0.02	0.2	8.1±0.1	1.5	1.37	2.31	0.014±0.004
Pb (μg g^{-1})	5.53±0.01	0.2	5.49±0.08	1.5	1.37	2.31	0.014±0.004
U (%)	91.17±0.01	0.01	91.16±0.02	0.02	0.14	2.13	0.0002±0.0001

The results showed that all elements were quantified for both procedures. However, 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 acetated 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 ("critical-t"), demonstrating that there are no statistically significant differences between the samples of "Group A" and "Group B".

The systematic error coefficients (SEC) showed that for the elements Si and U, the influence of the major constituents are negligible (0.0002±0.0001), thus proving the hypothesis that there are no significant differences between both preparation methods. For the impurities, all elements exhibited the same significantly low value (0.014±0.004), showing that the differences are also negligible.

Visually, it was clear that the 3 samples prepared with cellulose acetate were easily removable from the base after the analysis (Fig. 1). 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.

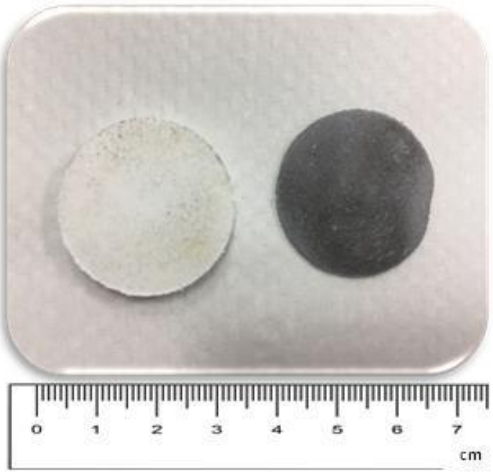

Figure 1: Cellulose base (left) and clear detached U_3Si_2 sample.

4. CONCLUSIONS

The results allowed concluding that the substitution of H_3BO_3 for cellulose acetate can be applied, since the same results are achieved statistically. Moreover, 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, in which 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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