Poster Presentation

DETERMINATION OF THE MINIMUM SAMPLE MASS OF U_3Si_2 TO BE USED AS CANDIDATE REFERENCE MATERIAL FOR CHEMICAL ANALYSES OF TOTAL URANIUM AND TOTAL SILICIDE

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Abstract

To guarantee the reliability and comparability of analytical data, the use of reference materials is essential. Uranium intermetallic compounds, in particular U_3Si_2, have been the preferred fuel materials for high flux research reactors. A method for the quantitative determination of the minimum representative sample mass of a candidate for reference material for determination of total uranium and silicide is described and illustrated in this paper. The analytical method used for determination of total uranium was the high precision potentiometric titration method of Davies and Gray, while total silicide was determined gravimetrically. The study was conducted according to ISO Guide 35. A preliminary test for homogeneity can be performed after homogenization as an integral part of the candidate reference material preparation.

1. INTRODUCTION

Uranium intermetallic compounds, in particular U_3Si and U_3Si_2, are the preferred choice of fuel materials for high flux research reactors. Uranium silicide fuel has been conventionally prepared by rolling or extruding the blended powders of uranium silicide and aluminum. The use of reference materials (RMs) and, where possible, certified reference materials (CRMs) enable a laboratory to provide the results of analytical measurements with an acceptable level of reliability [1, 2]. The preparation of these materials should consider not only all certification parameters (values and corresponding uncertainties) but also other information on the handling and use of a CRM. An extremely important part of this information is the 'minimum sample size' of a solid CRM [1–5]. Quantitative statements based on micro- or macro-homogeneity determinations are rarely made. As a direct result, most CRMs should not be used to calibrate or control micro-techniques. It is impossible to assess the uncertainty to be assigned to the certified value if samples smaller than the minimum sample size are used [4, 5]. Thus, this study was conducted according to ISO Guide 35 as a preliminary test to elucidate the minimum sample size to be used for a repeatable candidate reference material [3, 4, 6].

2. METHODS

2.1. Minimum sample mass

According to ISO Guide 35 [3] there are two ways to realize a minimum mass assay. A preliminary test for homogeneity can be performed after homogenization as an integral part of the CRM preparation process. Alternatively, by taking a vial to be used in the analysis, a 'sub-

sample' bottle with a different mass is made. As the size of this sub-sample is decreased, it can be determined whether this subdivision into progressively smaller sub-samples results in variations in the uncertainty mentioned in the certificate (typically for a 95% confidence interval), giving instead a range of statistical tolerances of 95% [3–6]. The size of the sample for a minimum amount of CRM corresponds to a sample mass m for which the uncertainty expressed in Eq. (1) becomes equal to that of Eq. (2).

$$UNC = \frac{\pm t_{1-\alpha} s}{\sqrt{n}} \tag{1}$$

where t is the Student t-factor at a probability level of $1-\alpha$, s is the experimental standard deviation and n is the number of measurements for certification, assuming for simplicity that n measurements are performed under the same conditions by an impartial method [4], and

$$\Delta = k'_2 s \tag{2}$$

where k'_2 is a factor for the tolerance limits of normal distributions for both sides, with at least a proportion p for a probability level of $1-\alpha$ and a series of n samples analysed during the study uniformity, s is the experimental standard deviation for the study homogeneity [4]. The second method is conducted by selecting an experimental mass range based on the analytical method used in the validation process.

2.2. Determination of total uranium by the high precision potentiometric titration method of Davies and Gray

The uranium titration method introduced by Davies and Gray [7] (and subsequently improved [8]) is the most widely used analytical method for the potentiometric titration of uranium from nuclear materials. It relies on the reduction of U (VI) to U (IV) followed by a subsequent titration of U (IV) with potassium dichromate. The result is given by the following equation:

$$\%U = 100 \times \frac{mg\ U\ found}{(1000) \times (solution\ aliquant\ wt,\ g) \times (DF)} \tag{3}$$

where DF is the dilution factor expressed as:

$$DF = \frac{g\ sample\ taken}{total\ g\ sample\ solution\ prepared} \tag{4}$$

2.3. Gravimetric determination of silicide

The total silicide is determined gravimetrically by an indirect method, dissolving an aliquot of the solid sample U_3Si_2, hydrofluoridization, and then insolubilization of silica. The result is obtained by measuring the mass of Si containing impurities ($m1$); volatilization of silicon tetrafluoride, measurement of the mass $m2$ of the residue containing impurities and finally the calculation of the percentage of pure Si in the sample, considering the difference between $m1$ and $m2$, and the mass ma of the solid sample [9]:

$$\%Si = \frac{(mi - mf) \times f_{Si} \times 100}{ma} \quad (5)$$

3. RESULTS AND DISCUSSION

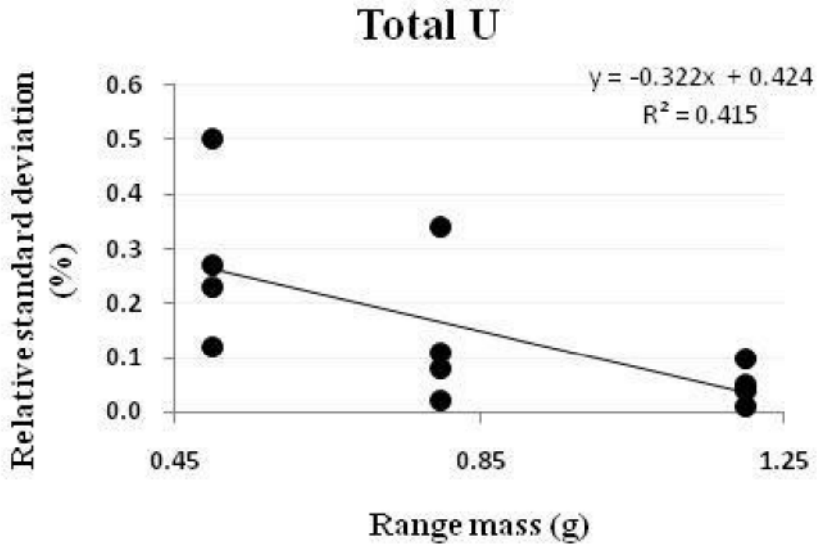
Bottle 11 was used for the study of homogeneity within the bottle. Three mass sub-samples containing 0.5, 0.8 and 1.2 g of U_3Si_2 were used for total uranium and silicide analysis. Dixon tests were used for evaluation of the results, Shapiro-Wilks for normal 95% confidence, and ANOVA for equality between the average percentages of the elements; F calculated was lower than the critical F for 95% confidence [4, 5]. There was no significant difference between the mean values in the variation of the mass of uranium elements and total silicide (see Table 1).

TABLE 1. PERCENTAGE OF TOTAL URANIUM MASS OBTAINED BY THE DAVIES AND GRAY METHOD AND TOTAL SILICON OBTAINED BY THE GRAVIMETRIC TECHNIQUE

	Total uranium (%)			Total silicide (%)		
	1.2 g	0.8 g	0.5 g	1.2 g	0.8 g	0.5 g
Average ± SD	91.84 ± 0.01	91.69 ± 0.02	91.58 ± 0.11	7.62 ± 0.02	7.63 ± 0.03	7.62 ± 0.01
RD	0.01	0.02	0.12	0.20	0.41	0.19
W	0.62	0.71	0.86	0.90	0.75	0.92
P-valor	0.0003	0.0005	0.11	0.45	0.012	0.46
Dcalc	0.12	0.16	0.06	0.18	0.06	0.3
Fcalc[a]	1.10	0.004	1.18	0.97	0.96	0.97
U (%)[b]	0.2	0.3	0.4	0.3	0.3	0.3

[a]Fcrit U total = 3.03; Fcrit Si = 5.41.
[b]*U(%)* – uncertainty.

The ideal minimum mass was estimated by comparison, in percentage form, DPR with the dispersion of individual RSD values and mean for each selected mass in repeatability conditions, with 8 replicates of titration and weighed at the same time and by the same analyst. A graphical comparison of the results for selected elements is shown in Fig. 1. It was observed that, for total uranium, the deviation ranged from 0.05 to 0.28%, with an average value of 0.16 ± 0.04%. For total silicide, the deviation ranged from 0.08 to 0.84%, with an average value of 0.35 ± 0.7%. Differences in the average values of the elements for the masses of 0.5, 0.8 and 1.2 g were not statistically significant. However, the individual results for the standard deviation were more widely dispersed. Thus 1.2 g was selected as the minimum mass of the sample for characterization of the material, since it resulted in individual values that were mutually compatible.



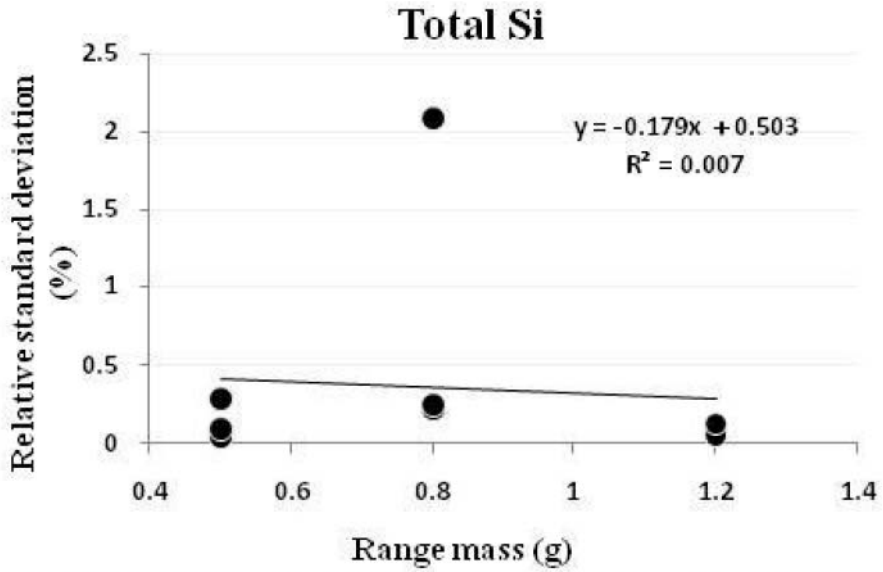


FIG. 1. Standard deviation in relative weight function for the study of homogeneity in the vial using Davies and Gray test for total uranium and gravimetric assay for total silicide.

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