

## Uncertainty estimation for the determination of uranium by titrimetric method Davies & Gray

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**Abstract:** The aim of this work is to reporting a complete estimation of the uncertainty in uranium determination by the modified potentiometric titration method of Davies & Gray. The uncertainty of the measurement is estimated according to the parameters established in the Eurachem Guide to Quantifying Uncertainty in Analytical Measurement. The accuracy of method was evaluated using a series of 9 measurements of CRM 112A: Uranium oxide ( $U_3O_8$ ). The most relevant sources of uncertainty result from those associated with the sample mass used and the analyst's accuracy. In conclusion, the adopted Davies & Gray method fully meets the expected objectives.

**Keywords:** Uranium, Davies & Gray, titrimetric.

### 1. INTRODUCTION

Currently uranium and silicon compounds such as  $U_3Si$  and  $U_3Si_2$  have received the most attention as fuel for MTR type research reactors due to the high uranium content per unit volume, mainly  $U_3Si_2$  because of its good friability and low rate of swelling. In Brazil has started production in 2002 at the IPEN (Nuclear Combustion Plant) IPEN-CNEN / SP (Institute of Energy and Nuclear Research - National Nuclear Energy Commission/São Paulo) by powder metallurgy by means of the conversion of the enriched national  $UF_6$  produced by CTMSP (Marine Technology Center from São Paulo) [1, 2].

In order to achieve the best performance of the fuel element the  $U_3Si_2$  powder manufacturer should be responsible for establishing and maintaining a quality assurance program to control the quality of the final product. In this context, CNEN has established a technical cooperation agreement with the New Brunswick Laboratory (NBL), an international laboratory that

produces and supplies certified uranium reference materials. Therefore, one of the points consisted in the implementation of the modified Potentiometric Titration Method of Davies & Gray, also known as "titrimetric method NBL" which is used by the NBL manually. In addition, this paper describes the application of a strategy to estimate the uncertainty of uranium determination method in  $U_3Si_2$  samples [2].

### 2. MATERIALS AND METHODS

#### 2.1 Instrumentation

Balance Analytical analysis of 5 houses, (Sartorius, Brazil), analytical precision 0.00001 g; Digital pH meter PG2000 sensitivity 99.9%, accuracy of 0.05%, electrode with reference system Ag / AgCl (GEHAKA LTDA, Brazil).

#### 2.2 Reagents

All reagents are analytical grade Merck. hydrochloric acid (HCl); A. phosphoric acid ( $H_3PO_4$ ); nitric acid ( $HNO_3$ ); amino sulfuric acid

(NH<sub>2</sub> SO<sub>3</sub>H); sulfuric acid (H<sub>2</sub>SO<sub>4</sub>); High purity water, with resistivity of 18.2 MΩ cm at 25 °C, Barnstead Thermolyne, ammonium molybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O); ferrous sulphate (FeSO<sub>4</sub>); (VOSO<sub>4</sub>); Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>); CRM 112A: Uranium oxide (U<sub>3</sub>O<sub>8</sub>) from Of New Brunswick Laboratory, United States Atomic Energy Commission: Sample: 1,580 kg of U<sub>3</sub>Si<sub>2</sub> powder, lot EULAB , Identification: UNSI05-15, manufactured by CCN IPEN-CNEN / SP on 12/09/2015.

## 2.2. Sample preparation

Firstly, it was weighed 1.2 g of uranium silicide in Erlenmeyer glass coupled to a glass condensate. After that, the material was dissolved with a solution of nitric acid and hydrochloric acid (3: 1) on a hot plate for 30 minutes after cooling 5 mL of H<sub>2</sub>SO<sub>4</sub>. Then it was added and returned to the hot plate for an additional 15 minutes moreover the material was added to 30 mL and filtered to remove silica. Thus, the filter paper was washed with 30 mL of 0.5 N H<sub>2</sub>SO<sub>4</sub> solutions. After the silica analysis by gravimetric, the platinum crucible containing the final uranium residue was washed with 0.5 N H<sub>2</sub>SO<sub>4</sub> solution 90mL final and stored in a polyethylene bottle to be titrated. Thereby an aliquot was added to the contents of the bottle of uranium solution into 400 mL beakers for potentiometric titration with potassium dichromate solution [2].

## 2.3. Determination of uranium by ferrous reduction in phosphoric acid and manual titration with dichromate "titrimetric method NBL"

The uranium is reduced to U(IV) with ferrous sulfate in a concentrated phosphoric acid medium. Excess ferrous ion is removed by molybdate catalyzed oxidation with nitric acid. Sulfamic acid is added to remove nitrites which may be formed during oxidation with nitric acid, and which might interfere with uranium reduction.

The sample is diluted with a vanadyl solution which improves the rate of the titration reaction; U(IV) is titrated to U(VI) with potassium dichromate of appropriate strength. While a single titration can be completed in ten minutes, elapsed time including sample preparation for a single sample is usually 1-2 hours [2].

## 2.4. Identification of sources of uncertainty

The identification of the sources of uncertainty was performed through the equation of the measurand. The parameters controlling the result are shown in Eq. (1).

$$\%U = ((mdx\text{fd}) \div \text{maliq} \div 1000)x(\text{msol} \div \text{ma})x100 \quad (1)$$

Where: md = Potassium dichromate solutions mass used for titration; fd = equivalency factor of a standardized potassium dichromate solution; m aliq = aliquot mass for titration; m sol = final dilution uranium mass; ma = sample mass.

Indeed, the uncertainties associated with these parameters will contribute to the overall uncertainty at the final result.

### 2.4.1 Estimate the uncertainty

The uncertainty associated with the Uranium content is calculated by established in the Eurachem Guide [3].

## 3. RESULTS AND DISCUSSION

The sources of uncertainty identified in the cause-and effect of diagram were calculated and the values of the magnitude for uncertainty components were obtained. The table 1 shows the uncertainty values calculated for each source.

### 3.1 Potassium dichromate solutions mass for trition, md

The dichromate mass and the final dilution mass were weighed the same time in a short period of time. Thus, the calculated standard uncertainty in the final dilution mass is equal to the uncertainty

of the (initial) dichromate mass; the mass of dichromate used was 2.940 g. The uncertainty associated with the standard deviation of the control plot is 0.0001 g, the uncertainty associated with the calibration certificate is 0.002 g. Combining these values, the uncertainty of the final mass of the sample,  $u(mf)$ , is [3]:

$$\mu_{(m)} = \sqrt{(u1)^2 + (u2)^2} \quad (2)$$

$$\mu_{(m)} = \sqrt{(0.002)^2 + (0.0001)^2} = 0.001 \quad (3)$$

### 3.2 Factor of a standardized potassium dichromate solution, $fd$

This uncertainty depends on the purity of the potassium dichromate oxide, mass standard, recuperation of CRM and the mass of the liquid in which it is dissolved. In addition, the titrant equivalency factor is determined against an NBL-certified primary standard uranium material such as CRM 112-A, CRM 129A, or equivalent. The factor is calculated by equation [2].

$$fd = \frac{W_{dbc}}{W_{s+v} - W_v} \quad (4)$$

Where:  $W_{dbc}$  = buoyancy – and purity-corrected weight of  $K_2Cr_2O_7$ , g;  $W_{s+v}$  weight of volumetric flask and solution, g;  $W_v$  = weight of volumetric flask, g [2].

#### 3.2.1 Purity

The purity of the potassium dichromate oxide is quoted in the supplier's certificate as 99.99%  $\pm$  0.0044%.  $P$  is therefore  $0.9999 \pm 0.00044$ . The standard uncertainty  $u(P)$  of the potassium dichromate oxide, is obtained the assumption of a rectangular distribution, is obtained dividing 0.00044 by  $\sqrt{3}$ , and using the equation [3]:

$$\mu_p = \frac{0.00044}{\sqrt{3}} = 0.000025 \quad (5)$$

#### 3.2.2 Mass standard, mass of liquid for dilution of dichromate, mass aliquot, and final dilution uranium mass

All the samples are prepared and diluted on w/w basis. The contributions to the uncertainty associated with these mass, are the uncertainty about of standard deviation of balance control chart, uncertainty of calibration certificate and repeatability of the balance [4]. Therefore, all the mass were obtained by difference between the tare and gross weights taken on the same balance, and then balance "zero bias" is canceled. The uncertainty associated with the mass is  $u(\text{mass}) = 0.001$ .

#### 3.2.3 Recovery, $R$

The estimate of  $R$  and  $u(R)$  was obtained from standards prepared of a certified reference material of uranium CRM 129-A Uranium Assay (Mass Fraction) [3]. The concentration of  $U$  in this material is certified as  $(84.7698 \pm 0.09) \%U$ . The uncertainty,  $u(C_{CRM})$ , in the aliquot sample, is obtained by multiplying the uranium factor in the solution by the root of the uncertainty of the CRM certificate + the uncertainty of the balance, factor = 4.879 [3].

$$\mu(C_{CRM}) = 4.879x \sqrt{\left(\frac{0.09}{84.768}\right)^2 + (0.01)^2} = 0.007 \quad (6)$$

$R$  is calculated using equation (7) [3]:

$$R_m = \frac{U_{obs}}{U_{CRM}} \quad (7)$$

Where  $C_{obs}$  is the mean of the results obtained from the replicate analysis of the solution and  $C_{CRM}$  is the concentration of the solution in the certified reference material. For this analysis,  $R = 1.05$ . The uncertainty associated with  $R$ ,  $u(R)$ , is obtained by combining the uncertainty in the reference value,  $u(C_{CRM})$ , obtained from solution of the certified reference material with the uncertainty in the mean of the observations [3]:

$$u_{Rm} = Rmx \sqrt{\left(\frac{u_{sol}}{U_{sol}}\right)^2 + \frac{u_{obs}^2}{nx U_{obs}^2}} \quad (8)$$

Where  $C_{CRM}$  is the concentration of aliquot sample measured,  $S_{obs}$  is the standard deviation obtained from the replicate analyses of the solution and  $n$  the number of replicates. Then, the uncertainty  $u(R)$  is:

$$u_{Rm} = 1.05x \sqrt{\left(\frac{0.09}{84.768}\right)^2 + \frac{(0.029)^2}{5x(84.7698)^2}} = 0.015 \quad (9)$$

Combining the intermediate standard uncertainties, above presented, the standard uncertainty of the titrant solution ( $t_{sol}$ ) of potassium dichromate can be calculated by:

$$u_{t_{sol}} = f d_{t_{sol}} x \sqrt{\left(\frac{u_p}{P}\right)^2 + \left(\frac{u_{mp}}{mp}\right)^2 + \left(\frac{u_{CRM}}{CRM}\right)^2} \quad (10)$$

$$u_{t_{sol}} = 0.00147x \sqrt{\left(\frac{0.00003}{0.999}\right)^2 + \left(\frac{0.001}{2.94}\right)^2 + \left(\frac{0.0015}{84.77}\right)^2} \quad (11)$$

=  $5.01E^{-07}$

### 3.3 Analyst precision - Pa

The uncertainty was calculated from the standard deviation of a 9 series of CRM titration samples.

$$u_{(Pa)} = \frac{s}{\sqrt{n}} \quad (12)$$

$$u_{(Pa)} = \frac{0.02}{\sqrt{9}} = 0.006 \quad (13)$$

### 3.6 Calculation of standard combined uncertainty

The combined standard uncertainty is calculated from the root sum of squares of the individual components, according to the rules set out in the Eurachem Guide [3].

$$uU = C_{ij} x \sqrt{\left(\frac{u_{ms}}{ms}\right)^2 + \left(\frac{u_{msolU}}{msolU}\right)^2 + \left(\frac{u_{md}}{md}\right)^2 + \left(\frac{u_{Pa}}{n}\right)^2 + \left(\frac{u_{malig}}{malig}\right)^2} \quad (14)$$

$$uU = 91.8x \sqrt{(6.8^{-7})^2 + (1.1^{-7})^2 + (1.2^{-7})^2 + (5.3^{-7})^2 + (2.2^{-7})^2} = 0.12 \quad (15)$$

### 3.6 Calculation of expanded uncertainty

The combined standard uncertainty is calculated from the root sum of squares of the individual components, according to the rules set out in the Eurachem Guide table 1 [3].

**Table 1.** Summary of contributions to the measurement uncertainty for Davies & Gray

Parameter	Relative standard uncertainty
Dichromate mass	1,2E-07
Dichromate factor	1,2E-07
Aliquot mass	2,2E-07
Solution mass	1,1E-10
Sample mass	6,8E-07
Analyst precision	5,3E-07

$$U(CU) = u(C_{ij})xk = 0.12x2 = 0.24 \% \quad (16)$$

The result of relative standard uncertainty was = 0.12 %. According to International Target Values 2010, this method achieves a relative combined standard uncertainty of 0.28 % rel. for U alloys [3]. Furthermore, expanded uncertainty was calculated using a coverage factor of two, with a level of confidence of approximate 95%, thus the expanded uncertainty was 0.24 %.

## 4. CONCLUSION

The result of the Davies & Gray method ( $91.83 \pm 0.24$ ) %, demonstrated that the analytical method is adequate, sensitive and provides an overall estimate of uncertainty. The components that contributed most to the uncertainty budget were the sample mass and the analytical precision [3].

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## 5. REFERENCES

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