

Uranium Determination in U-Al Alloy with Statistical Tools Support

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ABSTRACT

ICP-OES was used to quantify total uranium in natural UAl_x powder alloy. A simple solubilisation procedure using diluted HNO_3/HCl was successfully applied. Only 100 mg of sample were used which is an advantage over the volumetric methodologies. Only two dilutions were needed to reach measurable concentration. No other treatment was applied to the solutions. Calibration curves of three uranium lines (367.007, 385.958 and 409.014 nm) were evaluated using ANOVA. Comparing the indicators, the 367.007 nm line was the poorer one but exhibiting a $R^2 = 0.998$ and 0.9996 and 0.999 for the other two lines. No significant difference was found between these two lines. If needed, the 385.958 nm line could be used to quantify uranium in very low concentrations but with few advantages over the 409.014 nm line, if so. The average uranium concentration found was $0.80 \pm 0.01 \mu g \cdot g^{-1}$, as expected for a predominant UAl_2 phase alloy. Higher uranium concentrations are also expected to be successfully quantified using these lines. In order to verify possibly inhomogeneity due to the high uranium concentration, one-way ANOVA was applied to 3 replicates. Homogeneity was confirmed measuring in both 385.958 and 409.014 nm lines. The uncertainty of solution homogeneity was estimated also in these two emission lines giving 0.006 and $0.005 \mu g \cdot g^{-1}$, respectively. These two values are in compliance with the standard deviation of the average.

1. INTRODUCTION

In Nuclear Fuel Cycle, uranium determination is carried out in several steps during the entire process. Regarding to the reliability of the nuclear fuel, chemical analysis has a particular importance in the uranium compounds production cycle being such processes subject to an increasing international agreements and protocols of quality and control.

The Project of Development of the Mo-99 Production Process Using Irradiated Uranium Targets demands the production of 20 UAl_x -Al targets as considered in the Brazilian Nuclear Program, PNB, scope being related to the new Brazilian Multipurpose Reactor, RMB. The Mo-99 production process has to be qualified considering local and international norms and recommendations to support actions of the new RMB.

Considering the high uranium content in such targets, methodologies based on Davies & Gray approach are available. In this work, it will be considered the uranium determination by ICP-OES. This technique has been used in nuclear industry since its launch, even to quantify total uranium or its impurities. Combination of separations processes is also a common in these application practices by using ion exchange resins, liquid-liquid extraction, and so on. It is well known that in such atomic emission analytical technique, uranium has a rich emission spectrum. For a practical purpose, only few lines are considered to be used in analytical measurements. A combination of sample solution dilution and proper line selection is being considered to initiate this work. Fortunately, the most common elements interfering in the uranium lines (calcium, iron, vanadium and zirconium,) are not expected to be present in significant levels.

Initially, a procedure using acid dissolution and ICP-OES measurement will be discussed. The literature reports an eventual initial difficult with the acidic dissolution (boiling nitric acid) route and, fortunately, a chemical solution to overcome this problem, mercuric ion (mercury nitrate) presence. Depending on the uranium compound, the acid dissolution, mostly based on nitric acid, can use hydrochloride, sulfuric, phosphoric and hydrofluoric acids. Previous experience stated that the powder amount used to solubilize, the sequence of reagents to be added, their concentrations and the dilution applied are crucial to obtain a proper medium.

Although major elements can be quantified in alloys using ICP-OES, a statistical study will be used to assure the homogeneity of the high concentrated solubilized solution. A simple assumption that uranium is homogeneously distributed in high uranium content solutions cannot be enough when dilutions are applied to high concentrated solutions. This can eventually point out or establish the minimum amount of samples and aliquots.

Working with U-Al powder, homogeneity can be evaluated within-bottle and between-bottle. In the first situation, after proper solubilisation, the homogeneity can be evaluated by obtaining the dispersion of replicates results in sequential aliquots withdrawn. In the second situation, discrete amounts of powder are solubilized and analyzed. The dispersion between these amounts is evaluated to establish the homogeneity or non-homogeneity of the sample. The homogeneity of the initial material/powder is not a subject of the present work and will be considered in details in another paper.

2. EXPERIMENTAL

Finely grinded natural uranium-aluminum (UAl_x , mostly UAl_2) alloy powder was used in this study. The sample color was a deep gray looking like some U_3O_8 in color. Solubilisation procedure was tested using four sample masses (4x100 mg, weighted in a 0.1 mg precision balance) and a mixture of HNO_3 and HCl . These masses were withdrawn from the “as received” sample and no specific homogenization step was performed in the analytical

laboratory. Each amount was taken from the surface, avoiding an eventual sample loose. This simple step is given as follow:

- 1- Masses were weighted in 100 mL glass beaker;
- 2- 20 mL of water were added;
- 3- 5 mL of concentrated HNO₃ were added;
- 4- Beakers were heated up on a hot plate to a nearly boiling temperature;
- 5- When reaction comes to calm, beakers were taken out the plate and;
- 6- 2 mL of concentrated HCl were gently added;
- 7- Beakers were heated again until total sample solubilisation (clear solution).

At room temperature, solutions were transferred to 100 mL glass volumetric flasks and made up to the mark with water. Then, each solution was diluted (1mL of solution to a 25 mL glass volumetric flask) to be measured.

All reagents used were of analytical grade. Purified water was used throughout this study. Class A volumetric glass flasks were used when possible.

All measurements were carried out using a Spectro M120 Inductively Coupled Plasma Optical Emission Spectrometer, Spectro, Germany. Initially, the 367.007, 385.96 and 409.014 nm uranium emission lines were tested. For the present work, detection limit is not a significant figure of merit as the uranium concentration intended to measure are in $\mu\text{g.mL}^{-1}$ level.

Due to its simple atomic emission spectrum, spectral interferences from the presence of aluminum were not verified. As a complete clear solution was obtained and two dilutions were applied, no physical (changing in viscosity, for example) interferences were also considered.

2.1. Analysis of Variance (ANOVA)

In the present study the calibration curve (regression) was evaluated not only using the R^2 but the indicators obtained using analysis of variance, say maximum percentage of explainable variation and the percentage of the explained variation. The second one is equivalent to R^2 .

Homogeneity was also evaluated using analysis of variance (one-way ANOVA), as the approach considers the variances between group and within group, by establishing a proper set of sub-samples and replicates.

2.1.1. Calibration curve (Regression)

In this study, calibration curve was evaluated with attention to the concentrations interval and the highest concentration of the curve, linearity range, sensitivity or slope, and stability or dispersion behavior of the curve. ANOVA was applied to evaluate the proper fitting of the model (least-squares linear fitting). Good fitting is expected when small residuals are obtained after regression. The requirements for ANOVA application are shortly discussed latter. Table 1 shows equations concerned to the ANOVA regression.

Table 1: General equations to regression ANOVA [3].

| Source of Variation | Sum of Square | df | Mean Square | F test |
|---------------------------------|--|---|-------------------------------------|----------------------------|
| Regression | $SS_R = \sum_i^m \sum_j^{n_i} (\hat{y}_i - \bar{y})^2$ | $p - 1$ | $MS_R = \frac{SS_R}{p - 1}$ | $\frac{MS_R}{MS_r}$ |
| Residual | $SS_r = \sum_i^m \sum_j^{n_i} (y_{ij} - \hat{y}_i)^2$ | $n - p$ | $MS_r = \frac{SS_r}{n - p} = s^2$ | $\frac{MS_{lof}}{MS_{pe}}$ |
| Lack of Fit | $SS_{lof} = \sum_i^m \sum_j^{n_i} (\hat{y}_i - \bar{y}_i)^2$ | $m - p$ | $MS_{lof} = \frac{SS_{lof}}{m - p}$ | |
| Pure Error | $SS_{pe} = \sum_i^m \sum_j^{n_i} (y_{ij} - \bar{y}_i)^2$ | $n - m$ | $MS_{pe} = \frac{SS_{pe}}{n - m}$ | |
| Total | $SS_T = \sum_i^m \sum_j^{n_i} (y_{ij} - \bar{y})^2$ | $n - 1$ | | |
| % EXPLAINED variation | $R^2 = \frac{SS_R}{SS_r}$ | p =number of parameters in the model | | |
| Maximum % EXPLAINABLE variation | $Var_{expt} = \frac{SS_T - SS_{pe}}{SS_T}$ | n =total number of observations (replicates) m =number of distinct levels of the independent variables | | |

For more detailed comments, refer to [3].

2.1.2. Homogeneity

Homogeneity was evaluated using the one-way ANOVA table as shown in the Table 2. Calculations were performed in 2010 Microsoft Excel®. The ANOVA results presented are from an available 2010 Excel tool and were initially verified in comparison to step by step calculations also in Excel spreadsheet. Distinct population and sample size are declared as m and n , respectively [1]. As usual, the confidence interval adopted was 95 percent, nearly two times the standard deviation.

Even in the between or in the within approach, data are considered to be normally distributed, so the F test can be applied. This normality is based on the nature of generated data. In order to confirm this assumption, Shapiro-Wilk test was applied to the data collection. ICP-OES technique is based on measurements of signals produced by electronic transitions (emission) due to the existing quantities of entities such as atoms and ions. In the light of present discussion, this outer electrons phenomenon is regularly considered as dependent on such quantities and, if a constant source of energy is provided, and the ICP is considered as, the output is, statistically, a normally distributed response. If the response is suspected to be non-normal, other parameters have to be checked such as, sample introduction system, detector

behavior, electronic artifacts, and so on. This unique situation can, most of time, be realized during the regular daily tests.

For solution homogeneity, one of those 4 solubilized samples was randomly chosen and 3x1 mL aliquots were withdrawn (m=3) and measured 10 times (n=10).

Non-homogeneity or some artifacts will be evaluated by analysis of variance (One-way ANOVA). Dispersion (variance, standard deviation or uncertainties) of the results was analyzed as dilutions were applied.

Table 2: General equations for one-way ANOVA [4,5].

| Source of variation | Sum of Squares | df | Mean Square | F | F critical |
|---------------------|--|--------|----------------------------|-------------------------|------------|
| Between | $SS_b = n \sum_{i=1}^m (X_i - \bar{X}_i)^2$ | $m-1$ | $MS_b = \frac{SS_b}{m-1}$ | $F = \frac{MS_b}{MS_w}$ | 95 percent |
| Within | $SS_w = \sum_{i=1}^m \sum_{j=1}^n (X_{ij} - \bar{X}_{ij})^2$ | $nm-m$ | $MS_w = \frac{SS_w}{nm-m}$ | | |
| Sum | $SS = SS_b + SS_w$ | $nm-1$ | | | |

For more detailed comments, refer to [4,5].

The homogeneity uncertainty was calculated using one of the following equations, [2]:

$$u_h = \sqrt{\frac{MS_b - MS_w}{n}} \quad (1)$$

or

$$u_h = \sqrt{\frac{MS_w}{n}} \cdot \sqrt{\frac{2}{df_w}} \quad (2)$$

where,

u_h = homogeneity uncertainty
 MS_b = mean square between bottle
 MS_b = mean square between bottle
 MS_w = mean square within bottle
 MS_w = mean square within bottle
 n = number of replicates
 df_w = degree of freedom within bottle

One uses the equation (1) when MS_b is higher than MS_w and uses equation (2) when MS_b is lower than MS_w .

In this work, the uncertainty of the analytical components will not be presented. If considered, the total combined uncertainty would be obtained using equation (3), as follow [6]:

$$u = \sqrt{u_c^2 + u_h^2} \quad (3)$$

where,

$u_c =$ *uncertainty of the analytical components*

3. RESULTS AND DISCUSSION

3.1. Calibration Curve

Three uranium emission lines were tested: 367.007, 385.958 and 409.014 nm. These wavelengths were selected as they are in different regions of the spectrum. For each line, calibration curves with 6 concentrations (10, 20, 30, 50, 70 and 100 $\mu\text{g}\cdot\text{mL}^{-1}$ nominal values) were evaluated. This concentration range was used in accordance to the expected uranium concentration after two dilutions and instrument response (for instance, detector sensitivity and reading capacity and liquid sample viscosity).

The 385.958 nm and the 409.014 nm emission lines behavior curves are showed in Figure 1 and the ANOVA study in Tables 3, 4 and 5 for the 3 lines. Normality has previously been checked as required for ANOVA and F test. Homoscedasticity was checked using Cochran test [7] for 95% confidence level. This test was chosen as sample size was the same for each concentration. Cochran test deals with variances of the data collection considering each suite of concentration. The slope and intercept tests were applied only to the two aforementioned lines and, statistically, no statistical difference was found between the curves. These tests are also based on the curve equation coefficients (a and b) and on the data dispersion (variance and standard deviation). This means that, for the two spectral regions, the lines behaviors are similar within the concentration range and both can be used unless specific needs or physico-chemical features. No significant performance difference is expected in the sensitivity.

Among these lines, 385.958 nm line presented better indicators (percentage of explained variation), Table 4. The maximum explainable variation for the experimental data was 99.99%. One can consider this value as a sequence of data pairs with a linear behavior in this concentrations interval. The explained variation obtained for this curve fitting was 99.96%, meaning that residues between the original data and the predicted values by the proposed model were very small. When curve fitting coefficients are estimated by linear least square approach, this information is given by the R^2 value (coefficient of determination) expressed in the range of 0 to 1 (99.96% is equivalent to an R^2 of 0.9996 and for value 1 the fitted model is perfect). The F test indicates a good curve fitting (regression), say $F_{\text{calc}} > 10 \times F_{\text{critical}}$ (ten times the critical F value), and no lack-of-fit was evidenced. For the present experimental conditions, the F_{critical} is 4.53.

In this study, confidence or prediction intervals were not calculated for the calibration curve range being considered for the near future.

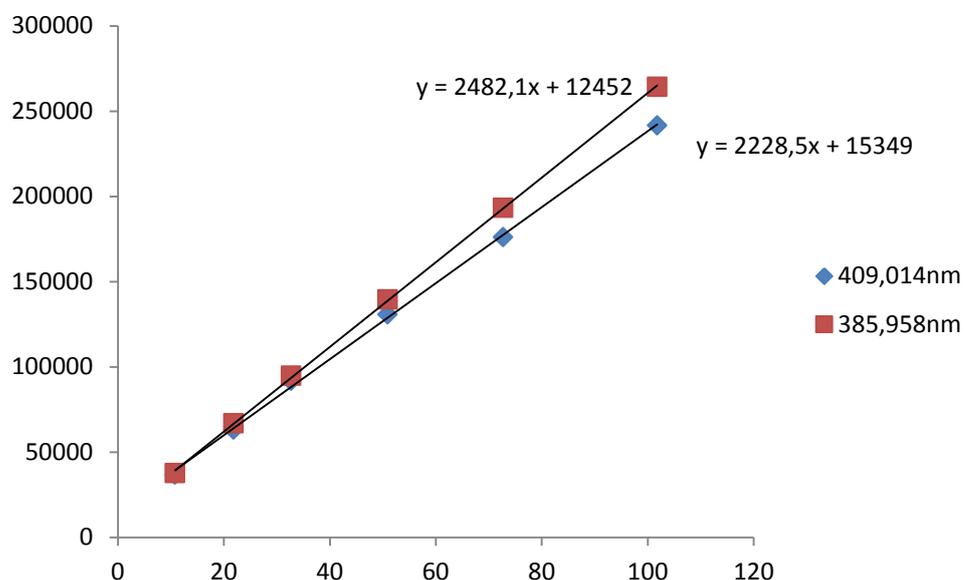


Figure 1: Calibration curves for 385.958nm and 409.014nm uranium emission lines.

Table 3: ANOVA table for curve fitting using 367.007nm Uranium emission line.

| Source of Variation | Sum of Square | df | Mean Square | F test |
|---------------------------------|---------------|----|-------------|--------|
| Regression | 27646778141 | 1 | 27646778141 | 4326 |
| Residual | 63906497 | 10 | 6390650 | 6.62 |
| Lack of Fit | 52105901 | 4 | 13026475 | |
| Pure Error | 11800596 | 6 | 1966766 | |
| Total | 27710684638 | 11 | | |
| % EXPLAINED variation | 99.8 | | | |
| Maximum % EXPLAINABLE variation | 99.96 | | | |

Table 4: ANOVA table for curve fitting using 385.958nm Uranium emission line.

| Source of Variation | Sum of Square | df | Mean Square | F test |
|---------------------------------|---------------|----|-------------|--------|
| Regression | 70748128727 | 1 | 27646778141 | 23142 |
| Residual | 30571844 | 10 | 6390650 | 4.24 |
| Lack of Fit | 22580725 | 4 | 5645181 | |
| Pure Error | 7991119 | 6 | 1331853 | |
| Total | 70778700571 | 11 | | |
| % EXPLAINED variation | 99.96 | | | |
| Maximum % EXPLAINABLE variation | 99.99 | | | |

Table 5: ANOVA table for curve fitting using 409.014nm Uranium emission line.

| Source of Variation | Sum of Square | df | Mean Square | F test |
|------------------------------------|---------------|----|-------------|--------|
| Regression | 58470594216 | 1 | 58470594216 | 9060 |
| Residual | 64539094 | 10 | 6453909 | 4,00 |
| Lack of Fit | 46946668 | 4 | 11736667 | |
| Pure Error | 17592426 | 6 | 2932071 | |
| Total | 58535133310 | 11 | | |
| % EXPLAINED variation | 99.9 | | | |
| Maximum % EXPLAINABLE variation | 99.97 | | | |

3.2. Solubilized Sample Homogeneity

Very diluted or highly concentrated solutions are difficult to measure. Care has to be taken to avoid dispersion due to inhomogeneity and false negative results in the first case and dispersion detector saturation or some physicochemical artifacts in the second case. The direct reading of a 100 mg U-Al alloy solution is prohibitive with normal dilutions. Then, 2 sequential dilutions were applied in order to make a final solution of tens of $\mu\text{g.mL}^{-1}$, within the working range of ICP-OES reading. The solution homogeneity test is presented in Tables 6 and 7. For both lines, the F test confirms that even with high concentrations, performing a proper homogenization, solutions can be measured with low dispersion.

Table 6: ANOVA table for solubilized sample using the 385.958 nm line.

| Source of variation | Sum of Squares | df | Mean Square | F | F critical |
|---------------------|----------------|----|-------------|------|------------|
| Between | 0,000502 | 2 | 0,000251 | 1.99 | 3.35 |
| Within | 0,003406 | 27 | 0,000126 | | |
| Sum | 0,003908 | 29 | | | |

Table 7: ANOVA table for solubilized sample using the 409.014 nm line.

| Source of variation | Sum of Squares | df | Mean Square | F | F critical |
|---------------------|----------------|----|-------------|------|------------|
| Between | 0,000873 | 2 | 0,000437 | 1.26 | 3.35 |
| Within | 0,009387 | 27 | 0,000348 | | |
| Sum | 0,01026 | 29 | | | |

3.3. Uranium Concentration

Using the 409.014 nm line, the uranium concentration obtained for the three solutions were: 0.80 ± 0.01 , 0.80 ± 0.01 and $0.79 \pm 0.03 \mu\text{g.g}^{-1}$. As can be seen, results are all closed to an

average value of $0.80 \mu\text{g}\cdot\text{g}^{-1}$ which is within the expected range of an UAl_2 predominant alloy. Unfortunately, there is no information of UAl_x distribution for that sample.

3.4. Uncertainty of Sample Solution Homogeneity, u_h

The uncertainty (equation 1) for sample solution homogeneity using the 385.958 nm line was $0.006 \mu\text{g}\cdot\text{g}^{-1}$ and $0.005 \mu\text{g}\cdot\text{g}^{-1}$ for the 408.014 nm line. There is no significant difference between these values considering the obtained uranium concentration ($0.80 \mu\text{g}\cdot\text{g}^{-1}$). Although uncertainty estimate is closely related to dispersion, high values for uncertainties cannot be attributed only to non-homogeneity sample condition. The limit between non-homogeneity and uncertainty is not easy to define and has primarily to be stated by the customer.

One of the next issues of this project will be the homogeneity study of the as received sample powder. If using much lesser sample mass, inhomogeneity can eventually be compromised. Grain size distribution also can bias the test. Large grain size and heterogeneous size distributions associated to improper sample mass withdrawn invariably change the results. Then, the customer has to provide the laboratory with all necessary information about the sample. Laboratory has to ask customer if previous treatment has to be carried out before initializing the analytical procedure.

4. CONCLUSIONS

This simple procedure can be used to quantify uranium concentration in UAl_x powder samples. Solubilisation was not a major issue and HNO_3/HCl can be used producing a clear solution if using the experimental conditions of this work. No aluminum precipitation was found. ICP-OES has proven to be an excellent instrumental technique when addressed to such conditions, spending less sample mass than volumetric techniques. This is particularly interesting when dealing with enriched uranium compounds.

The initial concern about measuring high uranium concentration was not confirmed. Eventually, higher uranium concentrations can be measured with no or minimal changes in this procedure.

With respect to solution homogeneity, no significant difference was found between the replicates using these uranium lines.

Although chemical analyses can be carried out in sample as received, laboratories have to be aware about some physicochemical features of the sample that can determine the bulk homogeneity or heterogeneity. The *as received* condition has to be clearly defined between the laboratory and the customer before the service is accepted or additional homogenization care established when preparing the sample. In the case considered in this work, sample solution homogeneity was confirmed and no additional artifact was found out.

Future studies are to be carried out, mainly exploring the application of statistics to improve some analytical chemical procedures.

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REFERENCES

1. Q.S.H. Chui, C.O. Iamashita, J.M.A. Bispo. “Estudo de homogeneidade de lote de material silício metálico candidato a material de referência”. *Quim. Nova*, **Vol. 28**, n. 3, pp.497-501 (2005).
2. BRASIL. Instituto Nacional de Metrologia, Normalização e Qualidade Industrial, INMETRO. “*Ensaio de proficiência em cachaça. Relatório final – 2a rodada*”. Coord. P.R.F. Santos, D.S. Santos, V. Souza, M.H.C. la Cruz. Duque de Caxias, RJ, Brasil, 2006.
3. R.E. Bruns, I.S. Scarminio, B. de Barros Neto. “*Data Handling in Science and Technology*”, 25. Statistical Design – Chemometrics. Elsevier, Amsterdam, The Netherlands, 2006
4. R.P.J. Lisinger, J. Pauwels, A.M.H. van de Veen, H. Schimmel, A. Lamberty. “Homogeneity and stability of reference materials”. *Accred. Qual. Assur.* 2001, 6:20-25.
5. S.M. Ross. “Introduction to probability and statistics for engineers and scientists”. Elsevier Academic Press, San Diego, CA, USA, 2009.
6. A.M.H. van der Veen, T.P.J. Lisinger, H. Schimmel, A. Lamberty, J. Pauwels. “Uncertainty calculations in the certification of reference materials 4. Characterisation and certification”. *Accred. Qual. Assur.* **Vol. 6**, pp. 290-294 (2001).
7. P.L.O. Costa Neto. “*Estatística*”. Edgard Blücher, São Paulo, 1977.