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EVALUATION OF THE PERFORMANCE OF A METRHOM TITRATOR TITRANDO-836 IN POTENTIOMETRIC ANALYSIS OF URANIUM FOR SAFEGUARDS PURPOSES

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ABSTRACT

To achieve the requirements of the Brazilian State System of Accounting for and Control of Nuclear Materials – SSAC the Safeguards Laboratory of Brazilian Nuclear Energy Commission, LASAL, has been applying the "Davies & Gray/NBL" method for Potentiometric determination of total uranium concentration in several forms of nuclear materials since 1984. To improve the accuracy and the repeatability the method uses as titrant, standard reference potassium dichromate NIST SRM 136e and the results are also corrected for bias with NBL CRM 112A uranium metal assay standard. This work describes the assays performed for validation of a Metrohm 836 potentiometric titrator acquired by LASAL in order to improve the analytical methodology of the laboratory. The titrator is attached to a Pt:Rh (90:10) as indicator electrode and a mercurous sulfate as the reference electrode. The evaluation of accuracy and repeatability were made by comparison the results provided by the titrator with the certified value of standards and also by the participation in round robin program sponsored by New Brunswick Laboratory – NBL. The validation was done by a comparison of the performance between the Metrohm 836 and a Mettler –DL67 titrator which has currently been used by the laboratory. It included evaluation of the results of both equipment, the repeatability of the measurement, any systematic contributions and its uncertainties.

1. INTRODUCTION

Independent verification of nuclear materials by non-destructive and destructive analysis is an important activity conducted by the Brazilian SSAC, in order to verify operators' declarations as well as their measurement systems. For destructive analysis, LASAL uses Davies & Gray/NBL method [1,2,3] for determination of total uranium concentration. To obtain accurate and precise results of total uranium content in nuclear materials LASAL has been acquiring new instruments and equipment. In addition, LASAL has also been participating in international intercomparison programs [3,4,5,6,7], sponsored by the several international organizations such as "Agência Brasileiro-Argentina de Contabilidade e Controle de Materiais Nucleares - ABACC" and "New Brunswick Laboratory – NBL/US-DOE".

Despite of having a Mettler DL-67 [8] titrator proving good results for uranium analysis, a new titrator Metrohm Titrando 836 [11] has been bought in 2008. This equipment uses software that permits to store the entire method parameters for analysis of uranium as well as other methods. After investigating all characteristics of the equipment, the Davies &

Gray/NBL method was loaded in the titrator by using recommended parameters. Several analyses of different uranium compounds were made to verify its performance.
In order to *study* the performance of the new titrator a set of analytical determinations were performed. Both titrators were use to analyze aliquots taken from the same solutions. Results obtained were compared with a reference value when standard solutions were analyzed.

2. DESCRIPTION OF THE METHOD

Potentiometric Davies & Gray/NBL method for determination of uranium is a selective method based on the reduction of U (VI) to U (IV) in a concentrated solution of phosphoric acid by excess of Fe (II) in sulfamic acid media. This excess of ferrous ions is oxidized with nitric acid in the presence of Mo (VI) and sulfamic acid. Then U (IV) is titrated with a standard solution of $K_2Cr_2O_7$ until a preset end point potential of 130 mV. This standard $K_2Cr_2O_7$ solution has its concentration in titer, that is, calculated in terms of the ratio of equivalent mass of uranium in mg by the mass of standard $K_2Cr_2O_7$ solution in g. To precise the potentiometric end-point, vanadyl sulfate is also added. In this method it is essential to avoid any reoxidation of U (IV) before the titration. Thus, all reactions times must be rigorously controlled and the time between the preparation of the aliquot and the titration. This time shall not be longer then 5 minutes. Besides, the presence of As (III), Sb (III), halides and organic material should also be avoided. Another important feature to assure the good performance of the method is the range of uranium concentration, which must be kept between 90 and 110 mgU/g of solution. A wire of Pt-Rh (90:10) was used as indicator electrode and the reference electrode was a mercurous one. This method may be applied for uranium analysis of oxides, nitrates, ADU, AUC of any physical form [5].

3.OPERATION OF METROHM TITRANDO 836

The Metrohm Titrando 836 is a microprocessor-controlled analytical titrator. One method can be loaded at a time. The operation of the titrator is controlled by means of a touch control device. It stores, for instance, titrant identification and the corresponding concentration. The minimum increment of the titrant that is dispensed just before to achieve the end-point is 2 μL. The construction and functional design of the dosing drive unit optimized uncontrolled release of air bubbles that may be formed within the system. Even if a small air bubble that has been formed and it stays there always present at the piston, this bubble is never ejected during dosing and it does not influence the dosing the precision in any way. Besides, it interrupts the titration after an equivalence point has been found, shows sample's data and results in the touch control's display. Titrant data and the type of electrodes used for indication and reference are stored in the same memory card wich is installed in the touch control.

Methods can be saved in the internal memory card or on cards. Either methods developed by Metrohm or any new one loaded in the memory or in a card can be used for analysis. New methods data are easily installed using the touch control. The equipment display shows details of a current determination, the calculated results and the raw data.

4. ANALYSIS AND RESULTS

Method Davies & Gray/NBL and its dynamic parameters as well as, the electrodes currently

used by the laboratory were succefully installed in a memory card of the titrator. Then, its performance was checked by the analysis of uranium solutions prepared from standard reference material metal uranium, NBL CRM 112-A. The results of this verification can seen in Table 1 which compares the amount of uranium present in 8 aliquots of a uranium metal standard solution and the one found by the titration of these aliquots. The table also shows the mean bias of 0.033% and the standard deviation of 0.017% for this determination. Considering that according ITV ESARDA [10], the relative bias and the standard deviation should be less or equal 0.14% and 0.1% respectively for this kind of analysis, it is possible to conclude that the titrator has performance adequate for safeguards purposes.

Table 1. Total uranium determination of a standard solution of a NBL CRM 112-A by "Davis & Gray/NBL" method using Metrohm Titrando 836.

Amount of uranium in the aliquot (mg)	Amount of uranium determined in the titration (mg)	Bias (%)
106,0102	106,0616	0,048
106,3551	106,3956	0,038
105,9483	105,9901	0,039
106,3728	106,3836	0,010
106,3020	106,3598	0,054
106,2667	106,3121	0,043
106,1517	106,1690	0,016
106,1075	106,1213	0,013
mean bias (% rel):		0,033
standard deviation (% rel):		0,017

To compare the performance of Metrohm Titrando 836 with Mettler DL-67 that has been used by LASAL until the purchase of this new equipment, both titrators were used to analyze three aliquots of the same sample, as it can be seen in table 2.

For these determinations a sample of UO_2 pellet was used. From this, three aliquots were taken and titrated by the Metrohm Titrando 836 titrator and three aliquots by the Mettler DL-67. In the Mettler titrator as well in the Metrohm it was also necessary to load instrument parameters such as: predispensing volume which is about 60% of the theoretical volume to be added to perform the titration; information about addition of volume increments just before the end-point; maximum dispensing volume which was pre-fixed in 40 ml; end-point (pre-fixed in 130 mV), etc. As mentioned in section 2, the sample solution concentration must be adjusted to be in the range recommended for this determination. Aliquots were taken, treated with H_2SO_4 1:1 to eliminate halides, nitric acid medium and possible organic interferents. In order to avoid any calibration error from volumetric flasks and pipettes, this method is performed in a weight basis. As a consequence, the burettes must be calibrated in a weight basis to convert the volume in milliliters of potassium dichromate dispensed into grams of titrant. The results were calculated by the equation 1 below:

$$C_{Ui}[\%] = \frac{100 \times T_D \times F_{bur}}{T_A} \times \frac{Vi}{m} \qquad (1)$$

where:
F_{bur} = Burette Factor [g/ml];

V_i = Volume of $K_2Cr_2O_7$ solution dispensed in the titration of aliquot "i" [mL];
m = Mass of aliquot [g];
T_D = Titer of $K_2Cr_2O_7$ standard solution [mg/g];
T_A = Titer of the Sample solution, which is a ratio of mass of the sample and the mass of adjusted solution [mg/g];
C_{Ui} = Uranium concentration of aliquot "i" [%].

Table 2. Results of uranium concentration obtained under the same conditions for aliquots from the same sample in both titrators

METTLER DL-67	METROHM 836
Results (% of U)	Results (% of U)
88.122	88.129
88.125	88.112
88.123	88.137
Mean: 88.123	Mean: 88.126
Standard deviation: 0.002	Standard deviation: 0.012
Coefficient of variation: 0.002%	Coefficient of variation: 0.015%
U (k=2; 95%)= 0.002	U (k=2; 95%)=0.014

To achieve the repeatability and accuracy adequate to this kind of analysis it was necessary to perform the calculations using concentration expressed as a titer (in mgU/g of solution) with five decimal places in an electronic calculator or by means of dedicated software because it affects the results performance in a significant manner.

5. DISCUSSIONS AND CONCLUSIONS

The results in tables 1 and 2 were obtained at the same analytical conditions including room humidity, temperature which is controlled using a meteorological station, analytical solutions and analytical balance. Outlier test of Grubbs was applied to the results of both equipments and no statistical outlier was obtained [9]. The reference value for this concentration is 88.129 % of uranium.

As it can be notice in table 2, despite of Mettler titrator has provided results with better repeatability than the Metrohm T-836 the mean result from the Metrohm T-836 is nearest to the reference value even considering the expanded uncertainty. On the other hand, since this first analysis the dynamic parameters of the Metrohm T-836 have been optimized and presently it is providing better repeatability.

The means and standard deviations of the results of the uranium solution analysis were statistically compared. The means were compared by use of a Student t-test and the standard deviations were compared by a F-test. The two tests were performed at 95%

probability level. Neither the means nor the standard deviations have presented significant statistical differences at this probability level. The relative error between the results should be less or equal to 0.14% relative. Results lying in these limits are accepted and reported. The uncertainty was calculated for both titrators taken into account repeatability of each titrator.

These values are according to the international target values for uncertainties associated to safeguards measurements. Considering all the results obtained and its evaluation, the Metrohm Titrando 836 titrator can be considered adequate for potentiometric analysis of uranium for safeguards purposes.

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