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EVALUATING THE RELIABILITY OF URANIUM CONCENTRATION AND ISOTOPE RATIO MEASUREMENTS VIA AN INTERLABORATORY COMPARISON PROGRAM

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Abstract: The nuclear fuel cycle is a strategic area for the Brazilian development because it is associated with the generation of electricity needed to boost the country's economy. Uranium is one the key chemical elements in this cycle and its concentration and isotope composition must be accurately known. In this present work, the reliability of the uranium concentration and isotope ratio measurements carried out at the CTMSP analytical laboratories is evaluated by the results obtained in an international interlaboratory comparison program.

Keywords: potentiometric titration, mass spectrometry, interlaboratory comparison programs.

1. INTRODUCTION

The nuclear fuel cycle comprises the processes related to the production of nuclear energy, involving technical, economical, safety and environmental aspects [1].

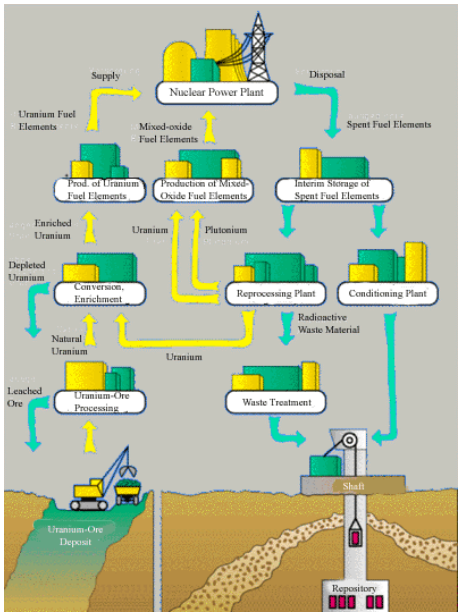

Figure 1. The nuclear fuel cycle

Its first stage is ore mining, followed by milling, uranium extraction, concentration, purification, conversion to uranium hexafluoride, isotope enrichment, conversion to uranium dioxide, fuel fabrication, nuclear fission, reprocessing, waste management, waste storage and decommissioning of installations that have processed nuclear materials [2].

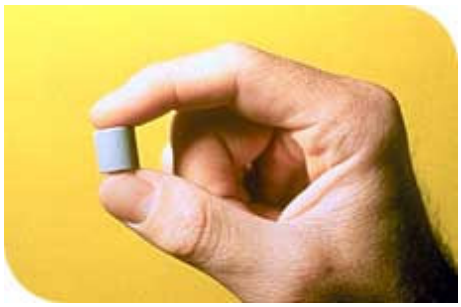

Figure 2. Uranium dioxide (UO2) pellet

The element uranium is therefore submitted to several chemical, physical and isotopic changes during the whole nuclear fuel cycle. These stages are so intricate and complex that about a twenty-year span is required from the initial mining to the final nuclear waste storage [3].

The uranium concentration and isotopic composition must be accurately known in each stage of the nuclear fuel cycle for economic but mainly for nuclear safeguards reasons [4]. The effectiveness of this system depends on the reliability of the measurements carried out by laboratories. Aiming to help the improvement of the measurement results, a document listing the most important nuclear materials, the analytical methods used to measure its concentration and isotopic composition and the target values for measurement uncertainties was set in force. The ITV 2000 has become the international reference in judging the reliability of analytical techniques applied to fissile material [5].

The technical requirements of the ITV 2000 are so demanding that it is necessary to apply the concepts and practices of metrology to comply with the target values for measurement uncertainty.

2. OBJECTIVES

The objectives of this paper are two-fold: first to present the measurement results of uranium concentration and isotope composition in a set of samples of the 2008 Safeguards Measurement Evaluation Program (SMEP), an international interlaboratory comparison program organized by the New Brunswick Laboratory (NBL) to monitor the measurement capability that exists in nuclear facilities worldwide [6].

Second, to compare the obtained values of measurement precision and bias with the requirements of the ITV 2000.

It is noteworthy that neither the SMEP nor the ITV 2000 document have completely adopted the modern concept of measurement uncertainty, which includes both the measurement bias and measurement precision, as defined in the BIPM-GUM guide [7] as well as in the newest VIM edition [8].

3. METHODS AND MATERIALS

3.1 Uranium concentration

The analytical method selected for measuring the uranium concentration was the potenciometric titration. This highly precise and accurate method was originally proposed by Davies and Gray [9]. However, the procedure actually used was the NBL Modified Davies and Gray [10]. The principle of the method is the following: uranium in concentrated phosphoric acid medium is reduced to U(IV) with ferrous sulfate; the excess Fe (II) ions is removed by molybdate-catalyzed oxidation with nitric acid. The nitrite formed in the above reaction is removed by sulfamic acid.

The critical step in this method is the titration, where the U(IV), in the presence of vanadyl ions, is titrated against a standard potassium dichromate. The end point of the titration is determined through the measurement of the electrode potential of the solution. The uranium content is calculated from the amount of dichromate used.

The mesurand in this procedure is the element uranium, despite the fact the entity actually measured is U(IV). The metrological traceability to the International System of Units (SI) is established via the amount of potassium dichromate used, which, by its turn, was standardized against the solution produced by the dissolution of certified reference material CRM NBL 112-A, uranium metal assay standard.

Figure 3. Uranium titration

3.2 Uranium isotope ratio

The analytical method selected for measuring the isotope amount ratios required for calculating the isotope composition of uranium samples was mass spectrometry. Among several different mass spectrometry techniques presently available, thermal ionization mass spectrometry (TIMS) was chosen because of its high reliability.

The mass spectrometer used was the THQ, instrument manufactured by Finnigan MAT (Bremen, Germany). It is equipped with a sample magazine for thirteen filaments, quadrupole analyzer and one Faraday collector. For small signals it also has a secondary electron multiplier (SEM).

Samples in this current program were in the form of pellets of uranium dioxide (UO_2), uranium trioxide (UO_3) or triuranium octaoxide (U_3O_8). They were dissolved with Suprapur nitric acid and the resulting uranyl nitrate solutions were adjusted to the concentration of 1.0 mgU/mL needed for isotope ratio measurements with TIMS.

The rhenium filaments were degassed at 5 A for 30 min in a high vacuum bake-out unit manufactured by Finnigan MAT. A sample drop of 1.0 µL containing 1.0 µg of uranium was deposited onto each filament, which was later dried at 2.0 A for 5 min. These filaments were assembled in the magazine. Each analysis comprised 10 blocks of 10 scans with an integration time of 16 s.

Filaments having CIRMs or samples were processed using the same operational parameters. The measurement sequence started analyzing one CIRM, followed by 3 samples maximum. The mass discrimination effect was corrected using the external calibration. In this approach, the mean mass discrimination correction factor obtained by the measurements of the isotope ratios in the CIRMs is used to correct the observed isotope ratio for all samples [11].

The metrological traceability to the SI was established through the use of the CRM NBL U005, U010 and U030.

Figure 4. THQ Finnigan MAT mass spectrometer

4. RESULTS AND DISCUSSIONS

The NBL sent four different samples to the laboratories in year 2008: two samples for the measurement of the uranium concentration and two for isotope composition.

In the SMEP, laboratories can select the analytical method and procedures of their choice. They must carry on the measurements and report the results according to certain specified rules and before a fixed deadline.

The pellets devised for uranium concentration had an amount of uranium in the range of 5mg to about 10g.

The measurement results of the uranium concentration are presented in table 1.

Table 1. Measured values of uranium concentration

Analysis	Sample number	Measured value (%U)
1	EU 013	88.0174
2	EU 013	88.1168
3	EU 013	88.0930
4	EU 013	87.9957
5	EU 013	88.0484
6	EU 013	88.2233
7	EU 013	88.2732
8	EU 013	88.0819
9	EU 013	88.1342
10	EU 013	88.1503
11	EU 014	88.0449
12	EU 014	88.0079
13	EU 014	88.0401
14	EU 014	88.0174
15	EU 014	88.0820
16	EU 014	88.1260
17	EU 014	88.1907
18	EU 014	88.1479
19	EU 014	88.0940
20	EU 014	88.1355

The evaluation of the measurement results presented above is summarized in the table 2.

Table 2. Evaluation of results of uranium concentration and comparison to the requirements of the ITV 2000 document

	U concentration	ITV 2000
Measurements	20	
Outlier	None	
Certified value	88.1290	
Bias	-0.032	< 0.1
Standard deviation	0.085	< 0.1
95% C.L. of the mean	0.794	

In the SMEP framework, bias and standard deviations are the most important values to evaluate the measurement reliability. They are both below 0.1, the limit required by the ITV 2000 for the uranium concentration.

The pellets devised for uranium isotope composition had ^{235}U enrichment levels between 0.7 and 5 weight %.

The results of the uranium isotope composition, in terms of the ^{235}U weight percent are presented in table 3.

Table 3. Measured values of the isotope composition

Analysis	Sample number	Measured ^{235}U wt %
1	EU 013	4.0049
2	EU 013	4.0102
3	EU 013	4.0029
4	EU 013	4.0104
5	EU 014	4.0058
6	EU 014	4.0116
7	EU 014	4.0108
8	EU 014	4.0057

The evaluation of the measurement results provided by mass spectrometry is summarized in table 4.

Table 4. Evaluation of the isotope composition and comparison to the requirements of the ITV 2000 document

	U isotope composition	ITV 2000
Measurements	8	
Outlier	None	
Certified value	4.0078	
Bias	-0.011	< 0.1
Standard deviation	0.083	< 0.1
95% C.L. of the mean	0.069	

The bias and standard deviations are also below 0.1, the limit required by the ITV 2000 for uranium isotope ratio measurements in low-enriched samples.

The results presented in tables 2 and 4 indicate the potentiometric titration and the isotope composition measurements for low-enriched uranium are being carried out with high repeatability and accuracy, within the limits required by the ITV 2000.

5. CONCLUSIONS

The measurements of uranium concentration and isotope composition carried out at the CTMSP analytical laboratories can be considered as reliable because they met the requirements of the ITV 2000 document.

This statement is based on the results of the participation in the 2008 NBL SMEP international interlaboratory comparison program.

The good results obtained in this year as well as in the last years were just achieved with the introduction of sound concepts and practices of metrology in chemical measurements.

The participation in external, independent, international quality control programs like NBL SMEP are essential to demonstrate the competence of analytical laboratories.

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