# ESTABLISHING METROLOGICAL TRACEABILITY OF MEASUREMENT RESULTS OF URANIUM CONCENTRATION AND ISOTOPE AMOUNT RATIO

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**Abstract**

Uranium is one the most important chemical elements in the nuclear fuel cycle and its concentration and isotope composition must be accurately known for economic and nuclear safeguards reasons. The nuclear safeguards system relies on the comparison of measurement results provided by both the nuclear facility operator and the safeguards inspectorate. This comparison can only be meaningful if these results are traceable to the same reference. This work describes how the metrological traceability of measurement results of uranium concentration and isotope amount ratio was established in practice in a nuclear analytical laboratory.

***Keywords:*** metrological traceability, uranium concentration, isotope amount ratios.

## 1. INTRODUCTION

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

The political concerns associated with the military use of the nuclear energy led to the establishment of a nuclear safeguards system under the responsibility of the United Nations Organization (UNO) and managed by the International Atomic Energy Agency (IAEA) [3]. This system requires the measurement of nuclear materials properties (usually mass, concentration and isotopic composition) in all stages of the nuclear fuel cycle.

This internationally agreed system relies mainly on the comparison of the measurement results provided by facilities' operators and the safeguards authority (IAEA). This comparison can only be scientifically meaningful provided these measurement results are traceable to the same reference.

It is therefore very important to establish and demonstrate the metrological traceability of measurement results of uranium concentration and isotope ratio to the SI to guarantee the consistency within the nuclear safeguards system.

## 2. OBJECTIVE

The objective of this paper is to show how the metrological traceability for uranium concentration and isotope amount ratio measurement results was established in practice in a nuclear analytical laboratory.

## 3. METHODS AND MATERIALS

### *3.1. Measurement of 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 [4]. However, the procedure actually used is the NBL Modified Davies and Gray [5].

The principle of the method is the following: uranium in concentrated phosphoric acid medium is reduced to U(IV) with ferrous sulphate; the excess Fe (II) ions are 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 analytical procedure is the element uranium, despite the fact the entity actually measured is U(IV).

The potentiometric titratior used is the Titrino 719 S ( Metrohm, Herisau, Switzerland), as shown at figure 1.

**Figure 1. Uranium potenciometric titration device**

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 provided by the New Brunswick Laboratory (NBL) [6]. Its properties are presented at table 1.

| | |
|---|---|
| Uranium assay (%) | 99.975 ± 0.006 |
| Relative atomic mass | 238.0289 |

**Table 1. Properties of the NBL CRM 112-A**

### *32. Isotope ratio measurements*

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 at our laboratory, thermal ionization mass spectrometry (TIMS) was chosen for this specific work.

The mass spectrometer in use is the THQ, instrument manufactured by Finnigan MAT (Bremen, Germany) as shown at figure 2. 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).


**Figure 2. Thermal ionization mass spectrometer (THQ Finnigan MAT)**

In the TIMS technique, samples usually come in the form of pellets of uranium dioxide ($UO_2$), uranium trioxide ($UO_3$) or triuranium octaoxide ($U_3O_8$). They are dissolved with Suprapur nitric acid (Merck, Darmstadt, Germany) and the resulting uranyl nitrate solutions are adjusted to the concentration of 1.0 mgU/mL.

The rhenium filaments are 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 is deposited onto each filament, which is later dried at 2.0 A for 5 min. These filaments are assembled in the magazine. Each analysis comprises 10 blocks of 10 scans with integration time of 16 s.

The metrological traceability to the SI is established through the use of the NBL CRM U005, U010 and U030-A [6]. The properties CRM 030-A is presented in table 2.

| | $^{234}U$ | $^{235}U$ | $^{236}U$ | $^{238}U$ |
|---|---|---|---|---|
| Atom percent | 0.02778 ± 0.00006 | 3.0404 ± 0.0016 | 0.000599 ± 0.000005 | 96.9312 ± 0.0016 |
| Weight percent | 0.02732 | 3.0032 | 0.000594 | 96.9689 |

**Table 2. Properties of the NBL CRM U030-A**

Filaments having CRMs or samples are always processed using the same operational parameters. The measurement sequence starts analyzing one CIRM, followed by 3 samples maximum. The mass discrimination effect is corrected using the external calibration. In this approach, the mean mass discrimination correction factor obtained by the measurements of the isotope ratios in the CRMs is used to correct the observed isotope ratio for all samples [7].

## 4. RESULTS AND DISCUSSION

The participation in international interlaboratory comparison programs is regarded as an independent confirmation of the expertise of analytical laboratories. Thus, the results obtained in the Safeguards Measurement Evaluation Program (SMEP), a very prestigious international interlaboratory program organized by the New Brunswick Laboratory (NBL), will be used to demonstrate the metrological traceability of the measurement results.

Uranium concentration measurement results for several participants' laboratories are presented in table 1 while isotope ratio measurement results are presented in table 2. Each laboratory has a specific code that unfortunately will not be disclosed in this paper. It is important to inform that laboratories whose results are within the dotted lines have achieved a very good performance.

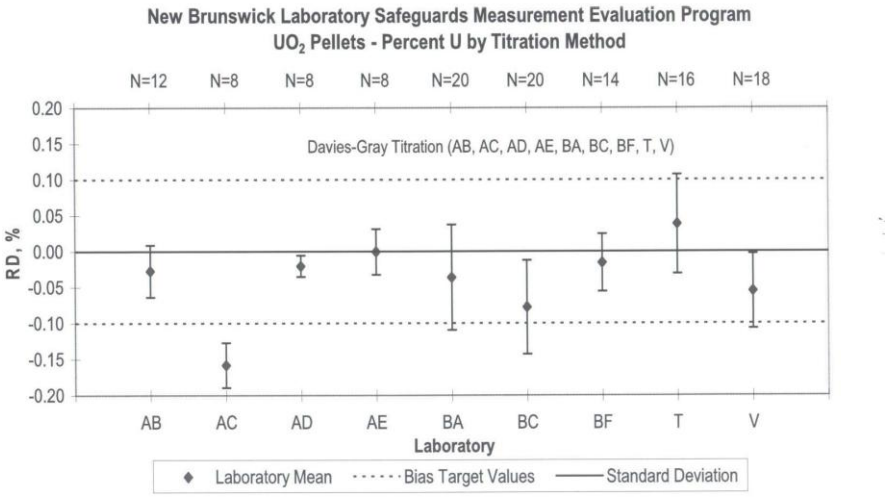


**Figure 3. Results of the participation in the SMEP program for uranium concentration**

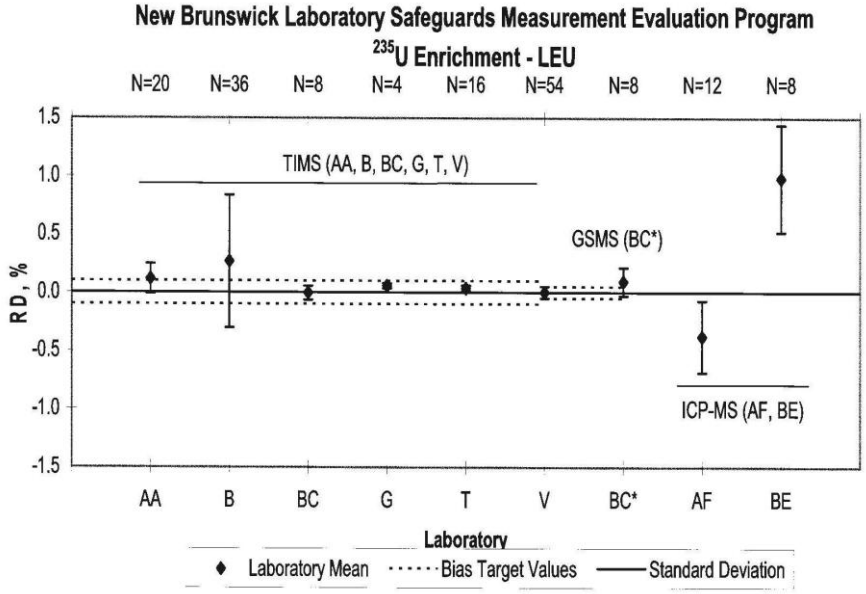


**Figure 4. Results of the participation in the SMEP program for uranium isotope amount ratio**

Figures 1 and 2 show that measurement bias and precision for our laboratory are lower than 0.1 %, maximum value allowed by the ITV 2000 [8], the reference document in judging the reliability of analytical techniques applied to fissile material. This means that all metrological requirements needed to provide reliable analytical results were actually employed.

## 5. CONCLUSIONS

The establishment of the metrological traceability to the SI through the use of NBL certified reference materials and the use of validated analytical procedures allowed the laboratory to obtain reliable measurement results for both uranium concentration and isotope amount ratios as demonstrated by the results of the participation in a independent external interlaboratory comparison program.

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