

Presentation of the Nuclear MATERIAL Metrology Laboratory (LAMMAN)

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Abstract – The EQRAIN Uranium or Plutonium programmes (Evaluation of the Quality of Analysis Results in the Nuclear Industry) have led to the creation of round-robins, which require reference solutions of uranyl nitrate or of plutonium nitrate to be made available.

The samples are fabricated and packaged, and their benchmark values determined, by the Nuclear Material Metrology Laboratory - Laboratoire de Métrologie des MATières Nucléaires in the Atalante facility. The French nuclear sector laboratories participating in the EQRAIN programs belong to the CEA and to the AREVA Group, with activities covering the entire fuel cycle. They have been joined by new participants from European, Japanese and South American laboratories.

INTRODUCTION

In the frame of the EQRAIN Uranium or Plutonium programmes, CETAMA (Commission for Establishing Analysis Methods - Commission d'ETAbblissement des Méthodes d'Analyses – of the CEA) organises regular inter-comparison circuits, enabling laboratories which so wish to test their analytical performances for the analysis of elements in solution. EQRAIN programmes require reference solutions of uranyl nitrate or of plutonium nitrate to be available. The samples requested are fabricated and packaged, and the benchmark values determined, by the Nuclear Material Metrology Laboratory - Laboratoire de Métrologie des MATières Nucléaires (LAMMAN – Fig. 1).



Fig. 1: View of the LAMMAN facility in Atalante

The LAMMAN, created in 1984 and now located in the Atalante complex at Marcoule, is

part of the LAMM (Analysis and Material Metrology Laboratory - Laboratoire d'Analyses et de Métrologie des MATières).

PREPARATION OF REFERENCE SOLUTIONS BY LAMMAN

At the LAMMAN, all the operations are carried out by highly precise weighing, including correction for air buoyancy. The procedure adopted consists in preparing pure solutions of uranyl nitrate or of plutonium nitrate, and in maintaining the same order of magnitude for the U and Pu concentrations from one round-robin to the next.

- from 4.5 to 6.5 g.Kg⁻¹ for plutonium solutions
- from 200 to 250 g.Kg⁻¹ for uranium solutions

In order to guarantee the reference samples' preservation, a laser-sealing apparatus is used to condition the final solutions in ampoules (Fig. 2 and 3).



Fig. 2: laser beam sealing apparatus

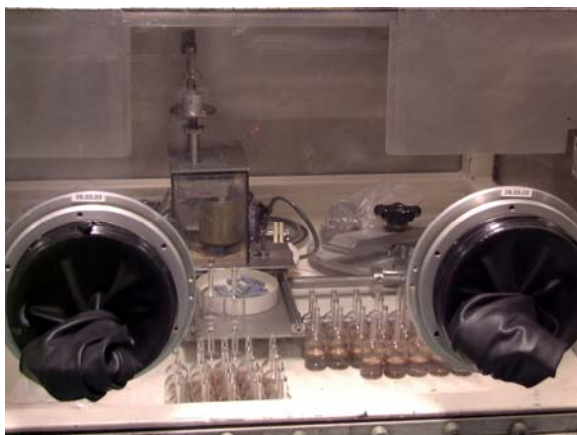


Fig.3: Ampoules of Plutonium nitrate solution in glove box

VERIFICATION OF REFERENCE SOLUTIONS

U and Pu reference solutions

Random tests to check the concentration of uranium or of plutonium are carried out in the laboratory on a certain number of the ampoules after the sealing step. The analyses are performed in a photogravimetric analysis line (in glove boxes for plutonium), based on the “titanium” potentiometric analysis method corresponding to internal reference No. 78 given in the CETAMA methods catalogue [1]. The method is based on ceric sulfate titration after reduction of U(VI) to U(IV) or Pu(IV) to Pu(III) using Ti(III). It has the advantage of being simple, reproducible and suitable for spectrophotometric detection of orthophenanthroline, for accurate determination of the equivalent point. This accuracy depends on knowing the concentration of the Ce(IV) titrant, which constitutes a secondary standard

solution. The concentration of this solution is determined with extreme care, using several reference materials that either reproduce an equivalent (U and Pu) redox system or constitute independent primary reference standards (As_2O_3 , Fe)

U reference solutions

The checks described above are supplemented by gravimetric determinations, weighing the U_3O_8 formed by calcining under specified conditions [2], [3].

Pu reference solutions

In the near future, controlled potential coulometry should contribute not only to the certification of plutonium materials, but also to guaranteeing the benchmark concentration value of EQRAIN Pu samples. The general procedure is first, to reduce the plutonium to plutonium (III) in an electrolysis cell (Fig 4), then to oxidize the plutonium (III) to plutonium (IV). The analysis cell contains a gold working electrode at which the couple plutonium (III)-plutonium (IV) is titrated.

The integrated current in the oxidation step is used to calculate the concentration of plutonium. Additional corrections are necessary to improve the determination accuracy, arising from two difficulties inherent to the method: ensuring a quantitative electrolytic reaction for the assayed element, and ensuring the complete selectivity of that reaction.

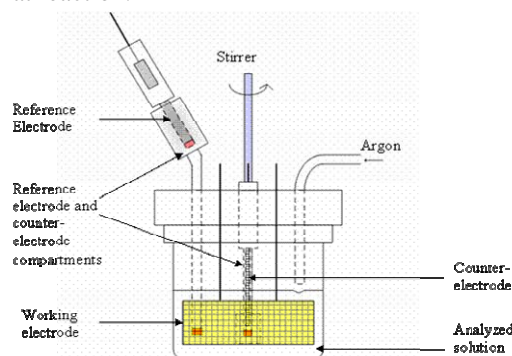


Figure 4: Coulometry cell

DISTRIBUTION OF REFERENCE SOLUTIONS

The ampoules are then packaged and shipped from Atalante to the participating laboratories on the basis of data provided by CETAMA, with the requirement that the participants comply with a specific operating protocol.

After receiving the results, CETAMA informs

the laboratory of the benchmark value.

INTERPRETING THE RESULTS (Fig 5)

At the conclusion of each round-robin, the overall results are presented to the working group members. CETAMA then drafts a summary report, or technical note. For each ampoule analyzed, the interpretation of the results is based on:

- the relative difference (%) between the mean value reported by the laboratory and the benchmark value,
- the relative confidence interval of the mean laboratory result for a 95% probability level.

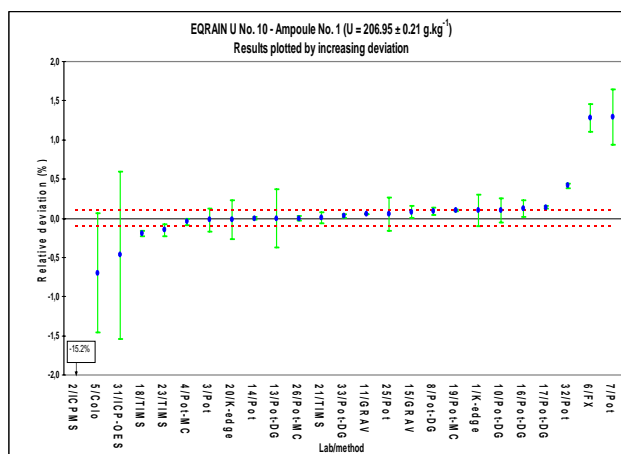


Fig.5: Inter-laboratory comparisons for U concentration measurements

OTHER LAMMAN ACTIVITIES

Apart from the preparation and checking of EQRAIN U and Pu solutions, the LAMMAN plays a major role in CETAMA activities, in particular contributing to:

- the certification of metal plutonium reference material (MP2 and future MP 3) by controlled potential coulometry,
- the certification of U mixed oxide, Pu O₂ (Cetamox pellet) by titriphotogravimetry and IDMS (Isotopic Dilution Mass Spectrometry),
- the preparation of uranium oxide material saturated with a certified quantity of impurities at different levels ("mushrooms" series: Bolet, Agaric, Chanterelle, Morille),
- the preparation of neptunium standard solution, from pure NpO₂

Parallel to these activities, the LAMMAN has undertaken a Quality approach, in order to obtain COFRAC EN 17025 certification in the medium term for the

preparation of EQRAIN U and Pu reference solutions.

REFERENCES

1. C.NICOL, J.F. WAGNER , *Proceedings of the 13th ESARDA Symposium on Safeguards and Nuclear Material Management Avignon* 171-173 (May 1991)
2. *Méthode CETAMA Tabou n°2*
3. ISO Standard 7476, Nuclear fuel technology – Determination of uranium in uranyl nitrate solutions of nuclear grade quality – Gravimetric method (2003)