CETAMA contribution to safeguards and nuclear forensic analysis based on nuclear reference materials

D. Roudil\textsuperscript{a}\textsuperscript{*}, C. Rigaux\textsuperscript{a}, C. Rivier\textsuperscript{a}, J.C. Hubinois\textsuperscript{b}, L. Aufore\textsuperscript{c}

\textsuperscript{a}CEA/DEN/DRCP, Centre de Marcoule, BP 17171, 30207 Bagnols-sur-Ceze cedex, France
\textsuperscript{b}CEA/DAM/DMA, Centre de Valduc, 21120 Is sur Tille, France
\textsuperscript{c}CEA/DEN/DEC centre de Cadarache, 13108 Saint Paul lez Durance, France

Abstract

Measurement quality is crucial for the safety of nuclear facilities: nuclear reference materials (CRM) and interlaboratory programs (ILC), beyond the assessment of analytical measurement quality, play an important role. In the nuclear field, the CETAMA proposes suitable scientific and technical developments, in particular the preparation and certification of CRM used either as analytical standards or as reference samples for ILCs. The growing emphasis on nuclear forensic measurements will require some re-certification of old CRMs. But the future analytical challenges of meeting nuclear fuel cycle needs and of ensuring safeguard performance improvements will also concern the future CRMs.

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1. Introduction

The accuracy and comparability of analytical results can only be achieved if metrological traceability schemes are well established.

* Corresponding author. Tel.: +33-4-66796329; fax: +33-4-66796989.
E-mail address: danielle.roudil@cea.fr.
The three main tools to assess the quality of analytical measurement are first, the certified reference materials, second, the Proficiency Test Scheme (PTS), and finally the use of standardized methods.

CETAMA, the Commission for Establishment of Analytical Methods of France’s Alternative Energies and Atomic Energy Commission, has been playing an important role in the establishment of these traceability schemes since 1961, date of its creation, by providing certified reference materials (CRMs), interlaboratory comparisons (ILCs) and by participating in the standardization of analytical methods. The methodology and tools developed are incorporated into its quality system. They are based on the national and international standards in force and take into account the recommendations of CIPM and its CCQM commissions.

The role and involvement of the CETAMA’s laboratory network thus contributing to the quality assessment of analytical results and their comparability, is shown in Fig. 1.

The CETAMA catalog of nuclear certified reference material was initiated nearly 40 years ago. It now contains aging samples, often due for renewal for stability issues, but potentially rich in new information related to forensics and safeguards.

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**Nomenclature**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>CRM</td>
<td>Certified Reference Material</td>
</tr>
<tr>
<td>DA</td>
<td>Destructive Analysis</td>
</tr>
<tr>
<td>NDA</td>
<td>Non Destructive Analysis</td>
</tr>
<tr>
<td>CIPM</td>
<td>Comité International des Poids et Mesures (International Weights and Measurements Committee)</td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization, Geneva</td>
</tr>
<tr>
<td>GUM</td>
<td>Guide to the expression of Uncertainty in Measurements</td>
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</table>
2. Present CETAMA positioning for the assessment of quality results in nuclear analysis

In nuclear industrial and research applications, and particularly in the nuclear fuel cycle, the accuracy of any analytical results for uranium and plutonium is extremely important:

- to obtain accurate fissile material balances
- to enable reliable monitoring for nuclear material accountancy and for environmental control
- to ensure flow accounting of fissile materials and thus ensure the absence of loss or misappropriation.

For laboratories, reproducibility may be determined by "internal" measurements, but the determination of accuracy is mainly based on:

- The use of independent methods based on different principles, implemented by different operators,
- Participation in interlaboratory round robin tests,
- And especially for quality control analysis using reference materials, matrices as close as possible to the samples analyzed.

Global comparability of chemical measurements is also essential in order to comply with regulations. Long term credible comparability can be established by making all measurements metrologically traceable to the same long-term stable references. High purity CRMs are essential as the base, transfer and calibration standards to establish metrological traceability.

Laboratories need reference materials as representative as possible, both in nature and chemical composition, of the matrix they have to analyze.


In the case of actinides or actinide compounds, the high level of purity and the existence of validated and possibly independent methods allow the certification of reference materials with known metrological quality. Our catalog proposes these kinds of reference materials, divided into four main categories:

- 11 standards certified in the major elements, U, Np and Pu
- 15 standards certified in impurities, metallic or anionic
- 6 standards certified in isotopic composition, U and Pu
- 1 standard certified in specific surface area, UO2.

For the fuel cycle, such specific necessary reference materials have a limited shelf life, depending on their radionuclides and their half-life. Renewal or recertification is carried out regularly to ensure their availability and overcome the stability problems. Fig. 2 gives an overview of all the standards proposed in our catalog, linked with analytical fuel cycle processes.

![Fig. 2: Nuclear fuel cycle and nuclear CETAMA CRMs for analytical processes](image-url)
The most recent standard available from the CETAMA is an isotopic standard, a $^{242}$Pu nitric solution manufactured by the LAMMAN laboratory. This laboratory is part of the Atalante facility on the CEA Marcoule site, and has the use of analytical equipment in glove boxes and hot cells with well-validated methods for the realization and checking of these operations.

The certification round robin test was conducted in 2011 for Pu isotopic composition. The element concentration is given as an indicative value. The full statistical treatment is described in [3].

Two new projects are underway:
- The renewal of the high purity Pu metal standard for mass balance analysis (project MP4 - see Fig. 2),
- Certification of sintered pellets of Pu dioxide for calibration of X-ray elementary analyses, including electron microprobes ($\text{PuO}_2$ in Fig. 2)

The availability of raw materials and safety and security constraints in laboratories now lead to international collaborations among CRM producers and to agreements to propose complementary new offers. The future standards proposed by CETAMA will be unique in the world.

The Pu metal reference material has to be renewed regularly (10-15 years) because of the high accuracy level of the Pu mass concentration expected. To take into account shipping constraints, the mass of each sample will be reduced to less than 39 mg. The CRM renewal project, called MP4, will begin in 2012.

The plutonium dioxide dense sintered pellets, fabricated in the LEFCA laboratory of CEA Cadarache, will be certified as the only Pu standard for quantitative X-ray analysis. In the past, CETAMOX certified pellets were developed for DA and NDA analysis of MOX fuels in industrial control laboratories. They are now also used in the Seibersdorf safeguard analysis laboratory of the IAEA in Vienna.

Meanwhile as part of its mission, the CETAMA has established a program called EQRAIN "Quality Assessment of Analytical Results in the Nuclear Industry", which focuses on the analysis of uranium or plutonium solutions, and on the analysis of trace impurities, mainly metal, in an aqueous matrix. Interlaboratory comparisons, such as the EQRAIN proficiency test schemes (PTS) program, have considerable significance in carrying out external quality control of measurement quality, for nuclear fuel cycle materials accountancy.

The manufacturing and packaging of U and Pu samples, as well as the determination of reference values, were assigned to the LAMMAN laboratory. Mass concentrations are certified with a relative uncertainty of 0.1%, by gravimetric method.

These inter-comparisons provide laboratories with the opportunity to evaluate their performance in terms of accuracy and reproducibility in relation to their objectives and to the requirements of their quality systems, and to verify the absence of bias. Since 1987, the EQRAIN program has lead to the regular organization of interlaboratory tests: a total of thirteen U EQRAIN, twelve Pu EQRAIN and seventeen EQRAIN traces tests have been carried out to date.

The traceability of analytical techniques used by laboratories, with associated uncertainties determination, possibly based on the GUM[4] approach, has been established [5] and is consistent with the syntheses published by the IAEA concerning International Target Values [6].

### 3. Possible Applications in Safeguarding Nuclear Materials and Forensics

The nuclear fuel cycle is also the focus of attention for safeguards, and here the analysis of actinides (mainly uranium and plutonium) is a key element, as nuclear material accountancy requires the best possible level of analytical performances.

In the safeguards field, analytical measurements are also particularly important during the reprocessing of spent nuclear fuel, in facilities where considerable amounts of fissile material are separated each year.

Nuclear forensics focuses on detecting illicit trafficking of nuclear and radioactive material. Seized material has to be analyzed in order to obtain clues as to its origin and intended use, and to prevent any diversion of nuclear
material from the same source in the future. Nuclear forensic analysis enables the recognition of important features of the material, present either in bulk form or as micro-particles, e.g. its nature (weapons-grade), its date of production, its isotopic composition (enrichment), the microstructure (production path) and trace element content (geo-location).

The detection of a diversion of declared nuclear material and the verification of the absence of undeclared activity depend partly on the evaluation of analytical results from samples collected for safeguards purposes. Nuclear reference materials play an important role in ensuring that sample processing is under control, by establishing correct instrument calibrations, and in verifying that measurements are carried out within specified limits. In many cases, the nuclear certified reference materials now available were produced more than 30 years ago. They are certified either in terms of impurity content or isotopic composition.

3.1. Impurity certified nuclear materials

Trace levels of metallic elements in nuclear samples may be used for source attribution and facility identification. But in most cases, the concentration of the metallic impurities in the uranium matrix is not certified in available CRMs, thus leading to new fabrications or certification round robin tests.

Based on the PTS EQRAIN, a specific interlaboratory round robin test on trace analysis in a uranium matrix was organized by the CETAMA during 2010-2011. All the analytical results, generally obtained by ICP-MS with a good level of performance, are presented in this ATALANTE 2012 conference and synthesized in [7]. To meet IAEA needs, CETAMA now proposes a re-certification program applied to two old ores, certified 30 years ago, based on ammonium and sodium uranate matrices [8]. This re-certification, managed through our Working Group n°2, will profit from the increased accuracy of today’s analytical techniques, and a widening to include some new metallic impurities. The selected elements of interest will be U, Mo, V, Zr, Ti, and Th, with uncertainty levels as low as possible and 8 rare earth elements for pattern identification. The impurity contents must meet the ASTM standard specifications for uranium ore concentrates [9] and may reflect both the origin of the uranium ore and processes involved, particularly during concentration. The specific REE signature represents a powerful tool to characterize the geochemical conditions of the mining deposit, and can be used as an origin tracer [10].

After an initial step of homogeneous reconditioning of the existing available samples, to anticipate running out of the stock and to be consistent with current analysis techniques needs, the CETAMA interlaboratory comparison will assess both certification and proficiency test:

- For the analysis of impurities in this type of matrix
- In identification of rare earth patterns.

3.2. Isotopic composition of certified nuclear materials

Nuclear forensics focuses on the origin and the history of the seized material. Elemental and isotopic compositions give information on the production process and intended use of the material. The knowledge of the material’s age helps in identifying the facilities where the material has possibly been elaborated. Assuming that the initial separation process has been complete, and that all the radionuclide daughters have been removed, the age of the material can be evaluated from the ratio of daughter and mother radio nuclides, e.g. in case of plutonium samples $^{241}\text{Pu}/^{241}\text{Am}$, $^{239}\text{Pu}/^{235}\text{U}$, and possibly $^{242}\text{Pu}/^{238}\text{U}$.

Some of the old CETAMA catalog standards may be proposed within this framework, including:

- MIRF 02, CETAMIR CETAMIR 1 and 2 for uranium isotopic certified ratios (minor U isotopes),
- MP2 and MIRF 01 for plutonium isotopic certified ratios. [11]
The different specific U minor isotope standards are shown in Table 1. U930, Muse1 and Muse2 are HEU uranium oxide samples (U$_3$O$_8$).

**Table 1. Atomic isotopic ratio in U oxide samples**

<table>
<thead>
<tr>
<th>Ref CRM</th>
<th>CETAMIR1</th>
<th>CETAMIR2</th>
<th>MIRF</th>
<th>U930 (NBS)</th>
<th>MUSE1</th>
<th>MUSE2</th>
</tr>
</thead>
<tbody>
<tr>
<td>U233/U236</td>
<td>-</td>
<td>-</td>
<td>9.68E-1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>U234/U238</td>
<td>2.88E-4</td>
<td>1.04E-3</td>
<td>-</td>
<td>1.81E-1</td>
<td>4.79E-1</td>
<td>2.01E-1</td>
</tr>
<tr>
<td>U236/U238</td>
<td>4.10E-3</td>
<td>1.26E-2</td>
<td>-</td>
<td>-</td>
<td>5.27E-3</td>
<td>3.77E-2</td>
</tr>
</tbody>
</table>

The MP2 Pu isotopic standard currently, and in the future, gives access to suitable samples for dating as shown in fig. 3, with a slow decrease of isotopic ratios. The total mass concentration of Pu decreases due to alpha decay and renewal is planned. Nevertheless the relative ratio $^{239\text{Pu}}/\text{Pu}_{\text{total}}$ is quite stable (slight increase, due to the loss of shorter half-life Pu isotopes, such as 238 and 241).

4. Conclusions and perspective for CETAMA Laboratory Network

The standards used today in nuclear laboratories contain much information not currently used in the framework of fuel cycle analysis, but of high interest for safeguards and forensics.

Two approaches are examined in parallel in this field of reference material development:
- Extended re-characterization/re-certification of old standards to optimize their possible applications,
- Renewal and manufacture of new standards better adapted to the issues of current and future fuel cycles, certification being based on an upstream reflection regarding the wider needs brought about the safeguards or forensic aspects.
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References