European Commission

Joint Research Centre

Executive Summary [1]

INS-CRM: Innovative nuclear certified reference materials (CRM) for EURATOM safeguards and industry

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The INS-CRM exploratory research (ER) project aimed at the application of unconventional methodologies, with limited prior knowledge to develop a new optimised process for the preparation, usage and longer-term stability of spike CRMs for a wide U/Pu ratio range.

Abstract

The European Commission (EC) is responsible for the control of all civil fissile nuclear material in the European Union. The Directorate General for Energy (DG ENER), relies on the EC - Joint Research Centre (JRC) to implement specific requirements in line with the EURATOM Treaty, the Commission Regulation on the application of EURATOM safeguards, and the Treaty on the Non-Proliferation of Nuclear Weapons. Particularly, EURATOM Safeguards entrusts the JRC, according to J.O. C 126 (1994), SEC (92) 515 and JRC BXL MOU 32924 - 2012 with the development of analytical and quality control methods, and with sample analysis. The JRC is a main provider of isotopic actinide certified reference materials (CRMs) in compliance with ISO/IEC 17034. Accurate measurement results with stated uncertainty and traceability play a crucial role in the accountancy and control of nuclear materials, performed by nuclear plant operators and for the verification of the correctness and completeness of activities and inventories declared by nuclear operators.

Isotope Dilution Thermal Ionisation Mass Spectrometry (ID-TIMS) is the most accurate analytical technique for determination of uranium/plutonium content in safeguards samples. It uses spike CRMs as a calibrant to measure accurately the uranium and plutonium amount content in nuclear safeguarding relevant materials. The IRMM-1027 series of LSD spikes are specifically designed U/Pu RMs certified for the mass of ^{235}U, ^{238}U and ^{239}Pu per unit and the uranium and plutonium isotope amount ratios [2]. They are a metrological quality tool for nuclear plant operator and safeguards laboratories to meet the existing requirements for reliable accountancy and verification measurements in compliance with the International Target Values 2010 (ITVs-2010) [3].

The IRMM-1027 LSD spikes series are prepared gravimetrically from certified high purity uranium and plutonium metals. After dissolution of the metals the mother solution is dispensed, weighed into individual vials and dried down. The spikes are covered with a thin layer of an organic substance to preserve integrity of the dried nitrates, but this layer tends to chip and flake after about three years of storage. Therefore, the organic matrix is a critical component for the quality and long-term stability of the spike CRM. To meet the customer needs for longer shelf life, research on the optimization of the organic layer with embedded uranyl- and plutonium nitrate as well as investigations on new types of coatings have been undertaken by the JRC. The first approach was therefore to apply knowledge about organic substances commonly used in food, textile or paper industry to the nuclear field. Subsequently it was aimed to develop and transform this knowledge further, to finally find an alternative to the current processing of dried spikes, which is prone to degradation during transportation and storage.

LSD spikes requirements:

- reliable certified values for U and Pu with sufficiently small uncertainties to achieve the ITVs-2010 under routine measurement conditions. [3]
- no interferences during column chromatographic separation
- no interferences during Isotope Dilution Mass Spectrometry (IDMS) measurements
- good adherence to glass
- quick and complete dissolution in nitric acid
- ease of preparation
- fairly good resistance to radiation

Apart from the main requirements listed above there are other laboratory, procedure or matrix specific requirements. While testing new materials as potential embedding matrixes to improve long term stability, all the requirements (main, laboratory, procedure and matrix specific) must be met to find the potential successor of the current coating. Therefore a thorough research was required on mechanical/chemical properties of these organic substances as well as the effects of the radiolysis of the nuclear components on the matrix.

Due to the changing nuclear landscape the ratio of U/Pu in CRMs for measurement of different types of safeguards/industrial/waste samples needs to be optimized to achieve measurement uncertainties below the ITVs-2010. Therefore, the large range of samples currently measured in the EURATOM on-site laboratories and also by operators could be improved with different U/Pu ratios spike CRMs.

Introduction

Three main approaches have been followed to address the goals of the project:

1. Improvement of the mechanical properties of the CAB film by using plasticizers [4], [5].
2. Reconditioning of CAB spikes by treatment with phosphoric acid (H_3PO_4).
3. Research on new types of dried U/Pu CRMs applying alternative organic substances to LSD spikes. In particular, the use of carboxymethyl cellulose sodium salt (CMC) foam as coating material [6], [7].

In order to test the coating capabilities of the proposed materials under real conditions and to check that they meet the requirements, several sets of spikes have been produced. These sets of samples have been exposed to elevated and low temperature and different resilience tests during simulated transport and irradiation conditions have been performed. Finally, in order to confirm the reliability of the spikes, several samples have been analysed for the isotopic composition and the uranium and plutonium content by TIMS and ID-TIMS. A set of spikes were prepared with the high energy alpha emitter ^{238}Pu to assess the influence of α radiation on the organic matrix. With its relatively short half-life of 87.7 years, ^{238}Pu is a good candidate to simulate the exposure to α radiation equivalent to the same amount of radiation of the longer lived ^{239}Pu in a shorter time exposure. Mechanical testing for tensile stress and tensile strain behaviour have also been applied to the CAB spikes.
Improving the coating capability for different types of samples requires theoretical and experimental research and understanding concerning the influence of the variation of the U/Pu ratio on the stability of the spike CRM embedded in the respective organic matrices. IRMM-1027 series LSD spikes have been used for these investigations [2]. In addition, various laboratory internal reference test samples have been produced and characterized. Six spike materials have been prepared for this purpose, four with mainly different uranium amounts (plutonium is maintained steady) and variable U/Pu ratios between 1 and 100 and two more spike materials with only plutonium and uranium, respectively.
Furthermore, several characterisation techniques such as X-ray Absorption Spectroscopy (XAS), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS) and Transmission Electron Microscopy (TEM) were applied with the aim to perform in depth research to better understand the binding mechanism and distribution of the uranium and plutonium in nitric systems.

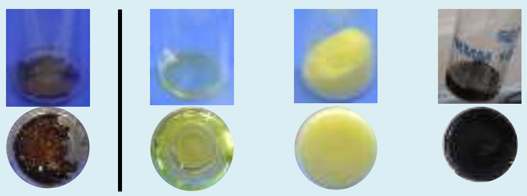

Figure 1. Flaked, unreliable LSD spikes (left) and different pathways that lead to improved integrity and stability (right – CAB + DOP, CMC, H_3PO_4)

1. Improvement of current coating - CAB

For almost two decades CAB (Figure 2) was used as embedding matrix of the dried uranyl and plutonium nitrate, but CAB on its own cannot meet the requirements on longer shelf-life for safeguards and industry.

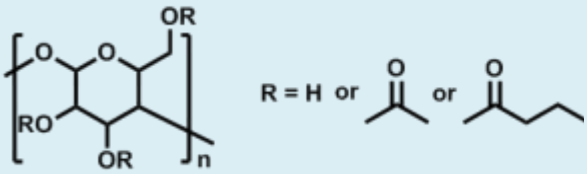

Figure 2. CAB is built up from repeating anhydroglucose units. Certain percentage of the –OH groups are converted to acetyl or butyryl groups.

<u>Properties</u>:
- good adherence to the glass (initially)
- easy to dispense
- dissolves within hours in hot HNO_3
- shelf life: limited (< 3 years)

<u>Attempts to improve</u>:
- use of plasticizer (DOP) to increase flexibility and durability

<u>Outcome</u>:

- flexibility greatly improved (Stress-Strain tests, Figure 3)
- crack formation slowed down (TEM analysis, Figure 4)

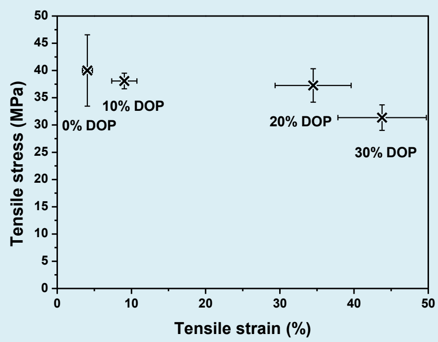

Figure 3. Stress-strain data of CAB films with different DOP content.

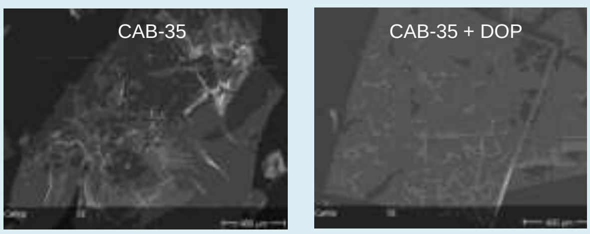

Figure 4. Different crack sizes formed in CAB films without and with DOP additive.

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2. Spike reconditioning – H_3PO_4

As some customers have stored over the years CAB based LSD spikes that are nowadays discoloured or cracked and where the certificate has expired, a method for reconditioning has been developed.

Properties:
- easy to prepare and non-lab specific
- dissolves quickly in hot HNO_3
- solid or very viscous liquid product
- no acid fumes
- two different protocols were developed (Figure 5 b,c)

Outcome:
- reconstructs homogeneity and integrity
- long-term stability under investigation

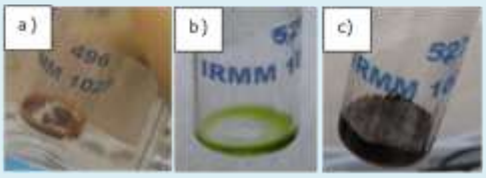

Figure 5. Appearance of CAB coated spike (a) before and (b,c) after reconditioning with H_3PO_4.

3. The most promising alternative – CMC

The applications of CMC in many areas, particularly in food industry, are well known, but there are not many studies on the interaction of CMC with nuclear materials. The material shows properties which makes this substance a very good candidate to be used as coating material for the LSD spikes. CMC in nitric acid solution, dispensed and dried in the spike vials builds foam which tends to remain fixed on the walls and at the bottom of the vials [5]. With time the foam might collapse and form a viscous gum which remains firmly attached to the glass ensuring the integrity of the spike material.

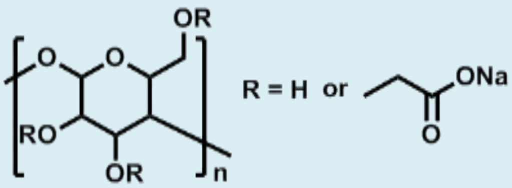

Figure 6. CMC is made of repeating anhydroglucose units, it contains carboxymethyl instead of acetyl or butyryl side groups.

Properties:
- good adherence to the glass
- easy to prepare and dispense but preparation is lab specific (and time consuming)
- homogeneous distribution of actinides (SEM-EDS)
- dissolves quickly in hot HNO_3
- no tendency towards crack formation and flaking
- high U/Pu complexation capacity (Figure 7)
- no significant self-irradiation and radiolysis susceptibility
- foam volume allows a better covering of the dried spike
- preserves spike's integrity under transport simulation tests

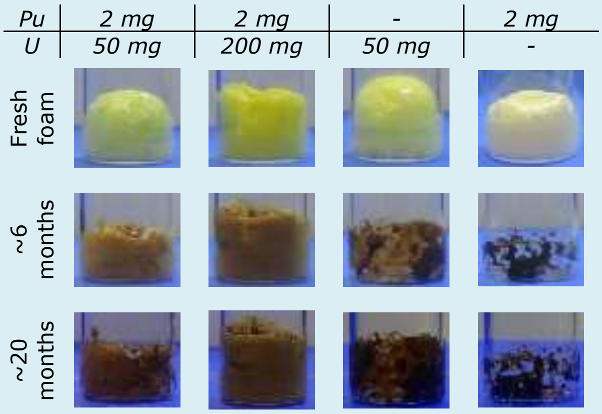

Figure 7. Ageing of CMC coated spikes.

Outcome:
- wide range of U/Pu ratios (also Pu spikes)
- excellent long-term stability expected

About 100 spikes have been prepared for long term stability evaluation – only 2 spikes covering the highest amount of nuclear material presented some loose particles after one year of production.

Outcome and dissemination

The outcome of the ER project teams' joined efforts shows promising results:

- Improvement of the mechanical properties of the CAB film by using plasticizer. With the use of 10-30 % dioctyl phthalate (DOP) plasticizer the CAB film shows greater flexibility that most probably leads to a delayed flaking of the spike material.
- The new production method replacing the CAB film with carboxymethyl cellulose sodium salt (CMC) foam that has no tendency to flake. With time the foam collapses and forms a viscous gum which remains firmly attached to the glass ensuring the integrity of the spike material. Its high U/Pu complexation capacity allows the production of spikes with a wide range of U/Pu ratios. Moreover, the spikes dissolve quickly in nitric acid.
- A process for reconditioning of CAB coated spikes by treatment with H_3PO_4. Flaked spikes can be transformed into a homogeneous amorphous material and via this process the validity of the CRM's certificate can be extended.
- Neither of these materials showed interference during actinides separation and mass spectrometry measurements. Long-term stability tests, including effects of temperature, resilience and irradiation, show promising results.

As outcome of this exploratory research project LSD spikes coated with CAB+DOP and coated with CMC show optimised properties conferring a longer shelf life. In addition faster dissolution, higher resistance when exposed to transport means, as well as the potential to allow producing other U/Pu ratios with the same properties is an asset. Consequently it is guaranteed that the production of spike CRMs, such as the LSD spikes, in large batches in compliance with ISO 17034 is possible. The findings of INS-CRM have already been (and will continue to be) published/presented at the European Safeguards Research & Development Association (ESARDA), the Actinides 2017 Conference, in technical meetings with DG JRC, EURATOM safeguards (DG ENER), the National Nuclear Laboratory (UK), Sellafield Site (UK), Japanese Nuclear Fuel Ltd (JNFL), the Japanese Atomic Energy Agency (JAEA) and the IAEA [4], [5], [6], [7]. The outcome of the project was disseminated at several international scientific conferences and meetings, including the INCC 2017, the ACTINIDES 2017, the AEMWC 2018, the Plutonium Futures 2018, and the CEA/CETAMA GT03 Meeting. The successful outcome of this ER project is of mutual benefit for CRM producers and CRM users within the nuclear community since it permits to prolong the validity of the reference material certificate and aims at reducing nuclear waste and cost of analyses. It will be a major step forward for enhanced robustness of safeguards analytical results and sets new benchmarks for state-of-the art characteristics of nuclear CRMs to be supplied, to EURATOM safeguards, IAEA and industry in the future.

Scientific importance, impact and added value

The rationale of this project was in compliance with the JRC key orientation 3.3.5 to further improve the analysis of safeguards samples, focusing on scientific innovation. The scientific novelty is that by applying materials such as CMC, which are used in food and textile industry but not in nuclear industry an alternative approach was pursued for embedding the U/Pu mixed spike material within an organic foam layer. Desired properties were high elasticity, good stability to impacts during transportation and high resistance to the otherwise damaging alpha radiation and not posing problems for the subsequent chemical analysis of the actinide material. This could enable in combination with long-term stability studies the future provision of a wide range of U/Pu ratios in those new spike CRMs, applicable for EURATOM, and international safeguards but also for the analysis of waste and decommissioning samples. The goal was to overcome the current limitations of LSD spikes having a fixed U/Pu ratio and a limited shelf-life of 3 years, aiming at a long term stability of ideally > 5 years. Furthermore, to develop a simple approach for reconditioning of old U/Pu spike CRMs that were already showing signs of degradation by treatment with phosphoric acid is in addition to organic coating of U/Pu spike CRMs of interest for the IAEA operating the on-site laboratory at the Rokkasho reprocessing plant in Japan and particularly also for industry.

Implementation

The successful outcome of INS-CRM was due to collaborative efforts of JRC internal and external researchers from the nuclear and non-nuclear fields and policy partners. This encouraged the INS-CRM project team to implement the investigated approaches in the JRC institutional work programme 2018. This ER project is an outstanding example of transdisciplinary, diverse JRC internal and JRC external team work supporting EC key policies while responding by strengthening JRC's research and knowledge production to the JRC2030 strategy [8].

Thus, the 2018 series of LSD spikes, IRMM-1027t, have been partially covered by CMC (for the EURATOM safeguards labs) and partially by CAB that contains DOP additive (for JNFL, Rokkasho, Japan).

Figure 8. IRMM-1027t LSD spikes coated with CMC and CAB-35 + DOP20.

Analytical techniques used for the characterization of the samples

- ID-TIMS for U/Pu amount content and isotopic composition
- Gel Permeation Chromatography (GPC) and Analytical UltraCentrifuge (AUC) for polymer molecular weight and polydispersity analysis
- Thermo Gravimetrical Analysis (TGA) and Differential Scanning Calorimetry (DSC) for thermal analysis
- Mechanical testing for tensile stress-strain behaviour
- Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX), Transmission Electron Microscopy TEM (imaging techniques, morphology, defects)
- Nuclear Magnetic Resonance spectroscopy (NMR) for chemical structure analysis
- X-ray diffraction (XRD) and X-ray Absorption Spectroscopy (XAS) for molecular structure determination
- Transport simulation

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