D5: Document describing two radioactive reference materials, developed and shipped to participants for their radioactive content characterisation

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21GRD09 MetroPOEM

D5: Document describing two radioactive reference materials, developed and shipped to participants for their radioactive content characterisation

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Deliverable Cover Sheet

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Glossary

CEA	Commissariat à l’énergie atomique et aux énergies alternatives
CMI	Czech metrology institute
ICPMS	Inductively coupled plasma mass spectrometry
ILC	InterLaboratory Comparison
NPL	National physical laboratory (UK)
PE	PolyEthylene
RM	Reference Material
TIMS	Thermal ionisation mass spectrometry
ID	Isotopic dilution

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Summary

In order to have comparable data in time and space, the aim of the work package 3 of the MetroPOEM project is to produce two candidate reference materials, comprising common radioactive pollutants found in environmental samples (^{241}Am, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{234}U, ^{235}U, ^{236}U and ^{238}U). Two matrices were chosen, one liquid and one solid. These materials will be used in an interlaboratory comparison, where partners will use radiometric and/or mass spectrometry measurements to determine the concentrations and isotopic ratios of the radionuclides.

The synthesis of the candidate reference materials will be described in a publication in 2025. Indeed, this work was selected for an oral communication at the ICRM 2025 conference in May 2025 and the authors plan to submit a paper associated with the talk. The paper must be submitted by 18th April 2025.

The first part of gives the general strategy for the development of the two reference materials (RM): the method of spiking, the number of samples chosen for homogeneity and stability studies, the total amount of materials to produce and the sampling plan. The next two parts describe in more details the preparation and characterisation of the two reference materials.

1 The development of the two reference materials (RMs)

To ensure the traceability of the RMs to be developed, it was decided to keep the possibility to characterise their property values based on mass or volume of ingredients used in the preparation of the RM. This is one of the five approaches presented in ISO 17034 standard [1]. In addition, the characterisation of both final materials was performed by two competent metrology laboratories (CEA and NPL). The initial radioactive content in the sterilised and acidified seawater was assessed by several laboratories before spiking.

The quantity of material required for the production of a RM is determined by a number of factors, including the number of units of the RM required for distribution over its anticipated lifetime, the number of units required for the homogeneity study, the number of units required for the short-term stability study, the number of units required for characterising the candidate RM, and the number of units needed to monitor stability over its anticipated lifetime.

The homogeneity of all RMs must be assessed, which includes both within- and between-unit homogeneity. Within-unit homogeneity is required when subsamples can be taken for measurement by the users, whereas between-unit homogeneity is important to ensure that each RM unit contains the same value for each property.

Reference materials should be reliable enough for the purpose for which they are designed, allowing the end user to rely on the given value at any time within the validity period of the certificate. Usually, it is crucial to take stability into account when considering long-term storage, transit, and, if necessary, storage conditions at the laboratory of the RM user. If reuse is allowed, stability after opening must also be taken into consideration.

The reference document on the homogeneity, stability and characterisation of reference materials is the ISO 33405 standard [2]. The following preparation procedures follow its guidance.

1.1 Strategy for the production of the two RM

On one hand, the liquid RM was selected to be as close as possible to a real environmental sample. Sea water was chosen as the matrix, in common with WP4. The solid material was chosen to be synthetic, to reduce the uncertainties due to homogeneity and stability. The material selected was silica, which can be ground to mimic a sand-like material and is easily synthesised through a sol-gel process.

1.1.1 Spiking procedure

The radioactivity of both materials was added by spiking with known starting solutions. A 2-step spiking procedure was selected to allow a precise measurement of the spiking mixture. Indeed, some of the monoelemental spiking solutions contain at least one of the other radioisotopes as an impurity level. The measurement of the spiking mixtures should allow to check the compatibility of the initial measurements together with the dilution factors. Some of these mixtures were retained to be sent to CEA and NPL for characterisation and the remaining material used to spike the seawater or silica precursors mix.

The liquid RM was obtained by mixing the 4 radionuclide spiking mixture with raw seawater, while the solid RM was obtained by mixing a different 4 radionuclide spiking mixture with liquid silica precursors, which later solidified (Figure 1).

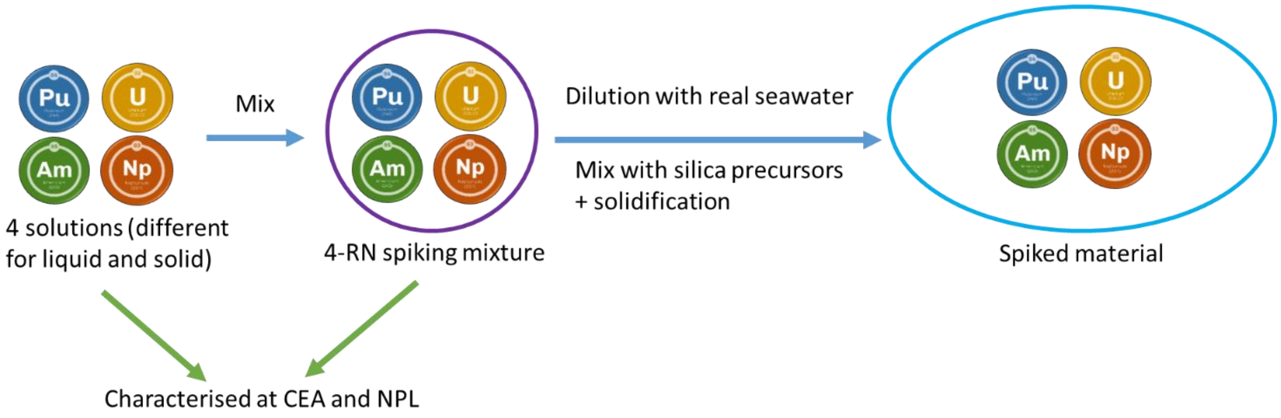


Figure 1: Illustration of the 2-step spiking procedure selected to prepare the candidate liquid RM.

1.1.2 Origin and characterisation of the spiking solutions

Both the liquid and the solid reference materials were spiked with four starting solutions: ^{241}Am, ^{237}Np, ^{239}Pu, ^{240}Pu and natural or slightly enriched U. The ^{241}Am and Pu solutions were supplied by CEA, as well as the U solution for the solid RM. NPL supplied both ^{237}Np solutions and the U solution for the liquid RM (Table 1).

Table 1. Summary of the origin of the starting solutions used to spike the liquid and solid RM.

Radionuclides	^{241}Am	^{237}Np	^{239}Pu + ^{240}Pu	Natural or enriched U
Liquid candidate RM	CEA	NPL	CEA	NPL
Techniques used for characterisation	ID TIMS, ionisation chamber	Calibration curve by Quadrupole ICPMS	TIMS and ID TIMS (Pu purification)	ID TIMS
Solid candidate RM	CEA	NPL	CEA	CEA
Techniques used for characterisation	ID TIMS, ionisation chamber	Calibration curve by Quadrupole ICPMS	TIMS and ID TIMS (Pu purification)	ID TIMS

All four solutions were analysed by mass spectrometry and/or by secondary or primary radiometric techniques at CEA and NPL to lower the uncertainty on their characterisation.

1.2 Homogeneity assessment plan for the two RMs

During the kick-off meeting, the amount of liquid and solid RM per bottle was discussed with the participants in the interlaboratory comparison. The values of 0.5 L for the liquid RM and 100 g for the solid RM were chosen, and the minimal sample intakes of 20 mL for the liquid and 0.5 g for the solid were selected. The minimal sample intake for the liquid reference material was later lowered to 5 mL

Knowing that at most 20 laboratories could take part in the interlaboratory comparison, it follows that the production batch is small, as defined in ISO 33405 [2] section 7.4.1.3. Following this standard, at least three units or 10 % of all the samples produced should be used for the homogeneity assessment. The standard suggests random sample selection but it was informative to select some samples regularly during the filling of the bottles, to identify possible bias. For this study, five bottles were chosen for the homogeneity assessment, for each RM.

The homogeneity sampling plan proposed is the one described in ISO 33405 [2], as the more appropriate to use when sub-sampling is possible. It allows differentiating between within-unit homogeneity and between-unit homogeneity and ensures that the variations due to sub-sampling and sample preparation are included in the within-units variance and not the between-units variance. The number of sub-samples was set to five and the number of repetitions on each sub-sample was set to three (Figure 2).

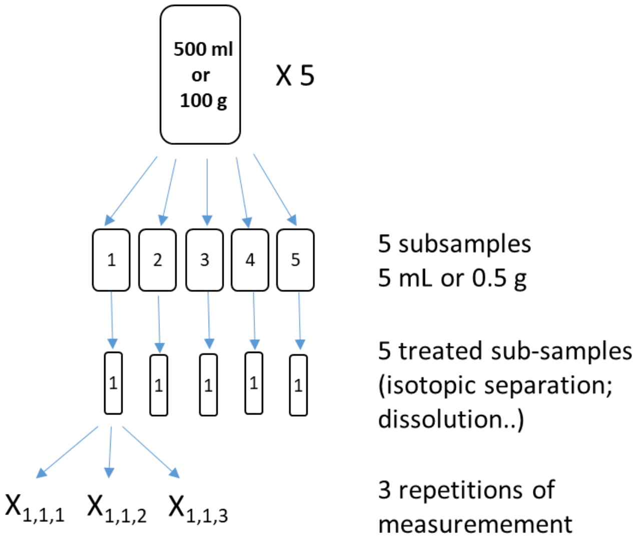


Figure 2: Sampling plan described in ISO 33405 to estimate in-between unit variance and within-unit variance

To estimate the within-units homogeneity, the within-units variance will be compared with a reliable estimate of the repeatability of the measurement technique, using a F-test or a χ^2 test.

All the homogeneity samples can be measured in a single run. The order of measurement of the samples can be randomised to identify any trend due to the measurement system.

1.3 Stability assessment plan for the two RM

The intended duration between the preparation of the two RM and the end of the interlaboratory comparison is one year. Furthermore, the RM samples will be shipped to participants. It is therefore necessary to perform measurements to assess the stability of both RM under transport conditions (short-term stability) and in the long term. According to ISO 33405 [2], stability studies can be classical or isochronous, meaning that the stability measurements can be done over time, or grouped in one run, with the samples being stored in reference conditions before measurement. A classical approach eliminates the risk of instability even at the reference conditions. In the isochronous approach, since all measurements are done at the same time, they are under repeatability conditions, and it facilitates the measurement. In this study, both approaches could be valid.

1.3.1 Short-term stability

The aim of the short-term stability study was to detect significant changes in the samples that can occur during transport. This study is relevant for both RMs, even though a sterilisation step was performed prior to spiking, in the case of the liquid RM. At most, transport should take about 1 week, and the temperature during transport can go above 30 °C or below 5 °C. Three temperatures were chosen: 4 °C, 20 °C and 40°C, and measurements will be performed at a given initial time and at least 1 week later, so a maximum of six samples are needed per characterising laboratory (NPL and CEA). The concentration of at least one radionuclide will be measured.

Three sub-samples (5 mL for the liquid RM and 0.5 g for the solid RM) will be prepared and analysed for each bottle, and only one repetition per sub-sample will be performed. The results will be compared with those of the homogeneity study using an analysis of variance.

The short-term stability measurements, based on ISO 33405 [2], are presented in Figure 3.

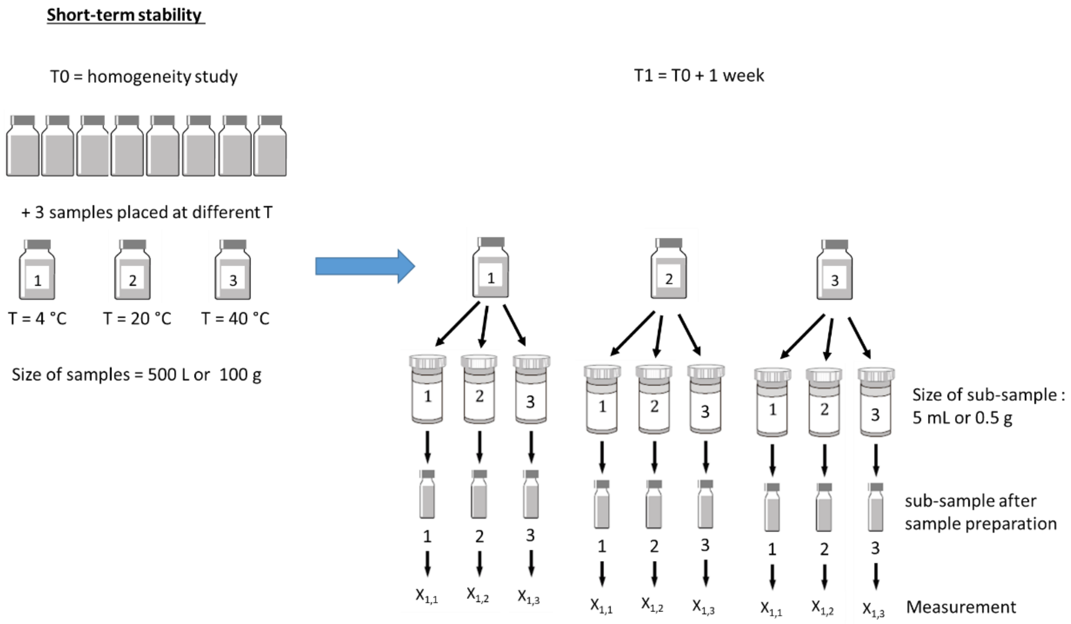


Figure 3: Short-term stability assessment for the liquid and solid RM

1.3.2 Long-term stability

The stability of the material during the period of validity of the RM will be assessed, under specified storage conditions. Here, the expected validity of the RM is 12 months, and the storage temperature could be either 4 °C or 20 °C for the liquid RM, and 20 °C for the solid RM. For the solid RM, a lower storage temperature might increase shelf life, however the humidity that will condense on the sample after repeated cycles between a low storage temperature and a usage temperature is likely to increase the mass bias due to the hygroscopic nature of the material.

Measurements will be performed every four months, and both temperatures will be tested for the liquid RM, while only room temperature will be tested for the solid RM. The initial measurement point can be the homogeneity study, and therefore six bottles of liquid RM and three bottles of solid RM are needed for each characterising laboratory. The concentration of at least one radionuclide will be measured.

The long-term stability assessment is described in Figure 4.

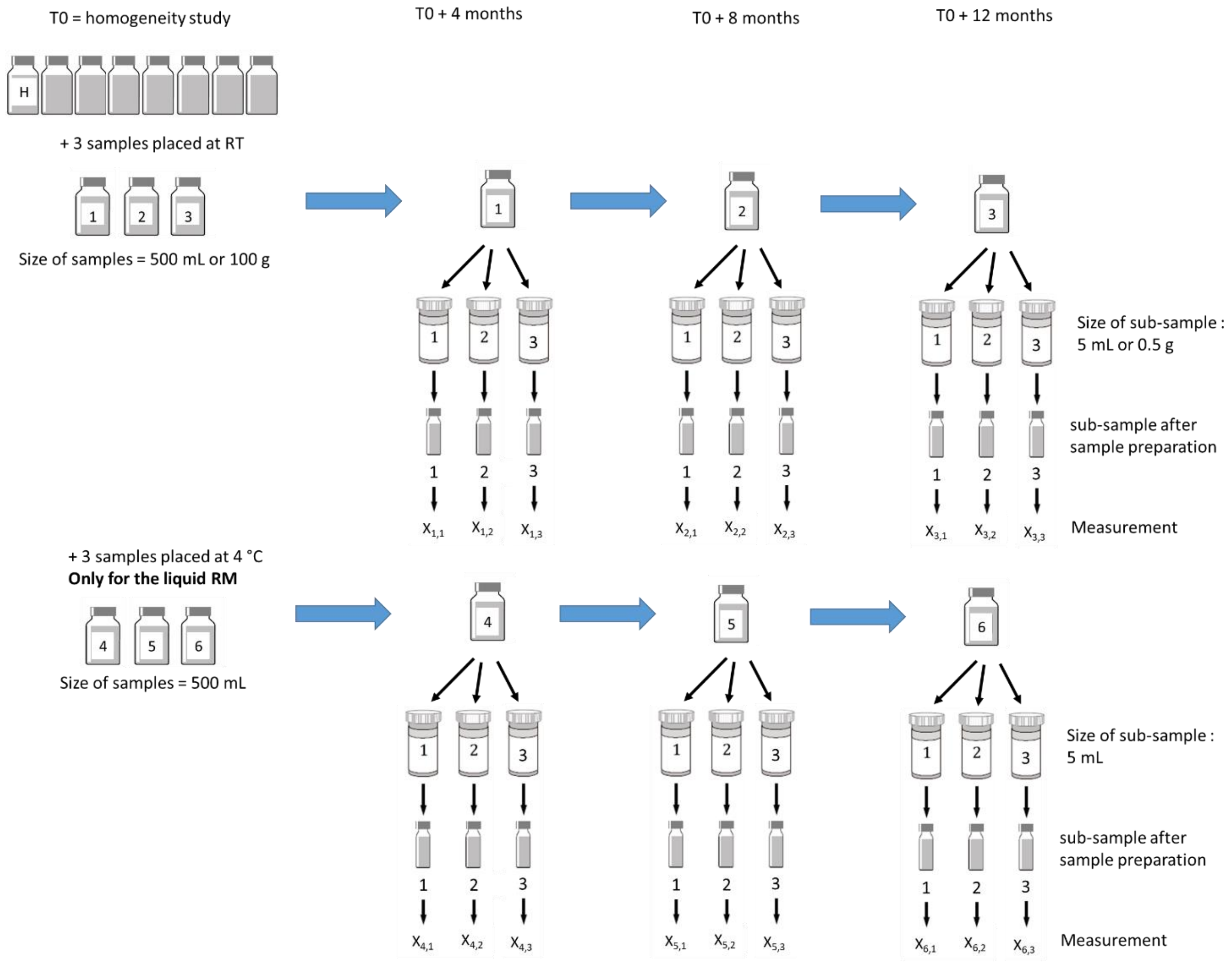


Figure 4: Long-term stability assessment for the liquid and solid RM

1.4 Total amount of RM to be produced

The sample size is 0.5 L, and to perform homogeneity and stability tests, the minimal amount to be produced was 24 L (Table 2), and the total amount of seawater spiked was 40 L (2×20 L carboys). Another 20 L carboy was dedicated to the initial characterisation of the material.

Table 2. Amount of liquid RM to be produced.

	Number of samples	Number of laboratories	Total amount (L)
Homogeneity after spiking and characterisation	5	2 (CEA and NPL)	5
Short term stability after spiking	3	2 (CEA and NPL)	3
For distribution (ILC)	1	20 participants	10
Long term stability	6	2 (CEA and NPL)	6
		Total (L)	24

For the solid sample, at least 5.2 kg of material should be produced (Table 3). It was decided to synthesise about 9 kg of spiked silicate material as some loss was expected during several production steps (transfer steps while the mixture is still liquid, drying of the material, grinding, filling of the bottles).

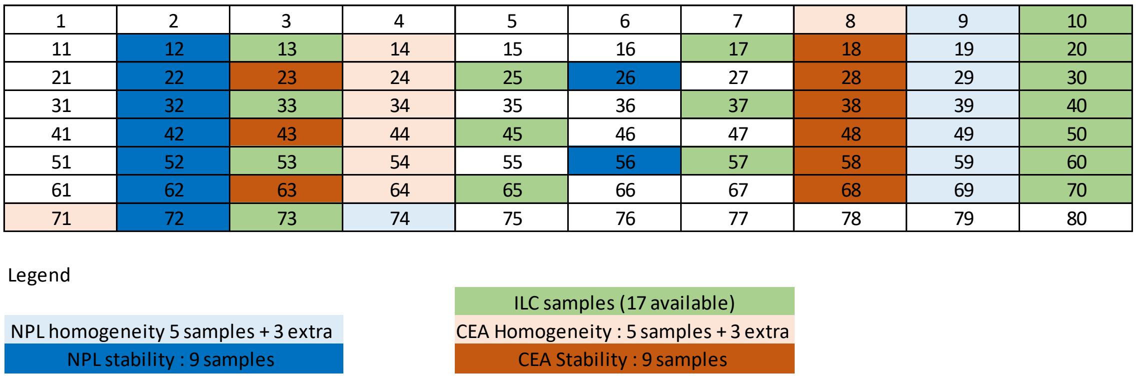
Table 3. Amount of solid RM to be produced.

	Number of samples	Number of laboratories	Total amount (kg)
Homogeneity after spiking	5	2 (CEA and NPL)	1.0
Short term stability after spiking	3	2 (CEA and NPL)	0.6
For distribution (ILC)	1	Up to 30 participants	3.0
Long term stability	3	2 (CEA and NPL)	0.6
		Total	5.2

1.5 Sampling plan for the two RM

CEA used a stratified sampling (not completely random): most of the whole amount synthesised (40 L for the liquid RM and 9 kg for the solid RM) was used to fill 80 bottles of 0.5 L liquid RM and 82 bottles of 0.1 kg of candidate solid RM. Then, seventeen bottles were sent to each of the certification laboratories. Only five are intended to be measured for the characterisation and homogeneity assessment, and nine are intended to be measured for the stability studies. The extra three are shipped in case of any problem during transport, or during measurement.

Sample number 1 is the first to be filled, and so on. The selection of samples for ILC, homogeneity, short-term stability and long-term stability studies in the two characterisation laboratories (NPL and CEA) is presented in Figure 5.



1	2	3	4	5	6	7	8	9	10
11	12	13	14	15	16	17	18	19	20
21	22	23	24	25	26	27	28	29	30
31	32	33	34	35	36	37	38	39	40
41	42	43	44	45	46	47	48	49	50
51	52	53	54	55	56	57	58	59	60
61	62	63	64	65	66	67	68	69	70
71	72	73	74	75	76	77	78	79	80

Legend

NPL homogeneity 5 samples + 3 extra
NPL stability : 9 samples
ILC samples (17 available)
CEA Homogeneity : 5 samples + 3 extra
CEA Stability : 9 samples

Figure 5: Selection of samples for homogeneity, short-term stability and long-term stability studies, for the liquid and solid RM

2 Preparation of the liquid radioactive candidate reference material

In order to produce a reference material close to a real environmental sample, sea water was used as a matrix. The targeted radionuclides (^{241}Am, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{234}U, ^{235}U, ^{236}U and ^{238}U) were added gravimetrically to obtain a spiked RM.

Relevant concentration (activity and concentration levels) were chosen in order to produce a suitable material that is representative of environmental radioactive pollutants.

2.1 Acquisition of starting material

HEREON sampled about 300 L of seawater in the North Sea from mid-May 2023. The seawater was transported in pre cleaned 20 L PE Carboys, which means that different aliquots needed to be mixed to obtain the individual final volume at CMI. About 60 L of pre-treated seawater (3 PE tanks) were requested for the liquid RM production.

2.2 Processing of the material

The seawater was filtered directly on-board during the sampling using cleaned PALL Acropak filters according to the Geotraces Cookbook [3]. Afterwards the seawater was stabilised with the necessary amount of acid. The prefilter pore diameter was 0.8 µm for a final filtering diameter of 0.2 µm.

The acidification of the matrix was performed on board using purified acids (sub-boiled twice in HEREON's clean rooms). The target pH chosen during the kick-off meeting was 0.1 M HNO_3, which is slightly more acidic than what is commonly chosen (pH 1.6 wrt HCl, ie 0,025 M). From each Carboy, HEREON took one sample for total analysis using SeaFast ICP-MS/MS.

During the kick-off meeting, a sterilisation step using ionising radiation was proposed, to enhance the stability of the material. Both WP3 and WP4 sterilised the seawater samples by delivering a dose of 25 kGy using a ^{60}Co irradiator.

Thanks to the sterilisation step, it was decided that the samples did not need to be stored at low temperature (4 °C). Nevertheless, the effect of the temperature storage is being studied as a short-term stability parameter over at least one week which corresponds to the transportation time to reach each lab.

Before being filled, the plastic bottles were cleaned from possible contaminants by a 24 h treatment in sub-boiled 1 % HNO_3, followed by a rinsing step with deionised water

Twenty-two samples were sent to participants for the initial radionuclide characterisation of the raw seawater (see Figure 6). The uranium content was expected to be measurable, around 3 µg.L^{-1}.

Figure 6: Picture of the 0.5 L bottles of the unspiked seawater

The raw seawater was analysed by several participants (CEA, DTU, ETHZ, HZDR, NPL, PTB, VINS) by mass spectrometry or by radiometric techniques. The lower detection limits offered by Accelerator Mass Spectrometry allowed measuring very precisely the initial amount of U in the seawater as well as its isotopic composition. This value is necessary to compare the final amount of U measured with the theoretical value after spiking.

2.3 2-step spiking procedure of the material

After spiking with the 4 radionuclide spiking mixture, the 40-L seawater was left to homogenise for two weeks, using a rod stirrer, and shaking the container (Figure 7).

Figure 7: Left: Picture of the four stock solutions used to spike the seawater at CMI, Right: canister filled with 40 L of spiked seawater.

Following the homogenisation, 80 bottles of 0.5 L were filled (Figure 8).

Figure 8: Picture of the 80 bottles of liquid candidate RM produced at CMI in October 2024.

To facilitate the shipment of both the spiking mixture and the 0.5 L sample of spiked seawater, their radionuclide content was kept below the exemption threshold.

2.4 Homogeneity assessment and characterisation of the liquid RM

The homogeneity of the amount of the different radionuclides present in the liquid RM will be analysed with different techniques. First, five 15 mL aliquots will be sampled from each bottle, and analysed by gamma spectrometry, to assess the relative variation of the ^{241}Am content. Then, four 5 mL and one 100 mL aliquots will be sampled from each bottle, to measure the relative variation of U, Pu and Np concentration, by Quadrupole ICPMS.

The concentration of radionuclides will be measured using three different measurements, on the five bottles selected for the homogeneity assessment. Gamma spectrometry will be performed on one 50 mL aliquot per bottle, to quantify the activity of ^{241}Am. Additionally, the U and Pu isotopic composition will be measured on one 100 mL aliquot per bottle, by MC ICPMS after chemical separation. Lastly, the concentration of U, Pu, Am will be measured by isotopic dilution (using independent tracers) and ^{237}Np by Q ICPMS on a 50 mL aliquot per bottle.

The homogeneity sampling plan and measurement methods chosen are summarised in Figure 9.

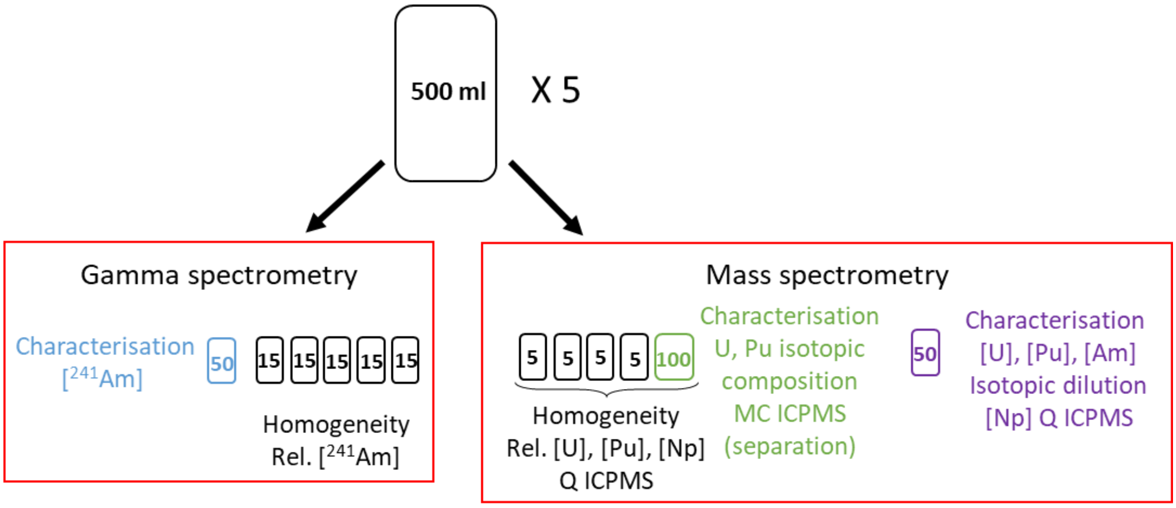


Figure 9. Characterisation and homogeneity assessment of the liquid RM

2.5 Liquid RM candidate: sample dispatch schedule

At the end of February 2025, most of the liquid RM samples have been shipped to participants. The remaining sample will be shipped in March.

Table 4. Liquid RM sample dispatch schedule.

Institute	Status	Sample reception date
CEA	Characterisation	07/02/2025
DTU	ILC participant	08/04/2025
ETH	ILC participant	13/02/2025
HZDR	ILC participant	02/12/2024
JSI	ILC participant	Dec 2024
NMBU	ILC participant	11/02/2025
NPL	Characterisation	03/2025
LUH	ILC participant	29/11/2024
PTB	ILC participant	10/12/2024
STUK	ILC participant	10/12/2024
UH	ILC participant	09/12/2024
VINS	ILC participant	21/02/2025
Agilent	Extra ILC participant	15/04/2025
AGES	Extra ILC participant	10/03/2025
NIST	Extra ILC participant	15/04/2025
BAM	Unable to participate (part of the lab' under decommissioning)	/
IFIN-HH	Unable to participate (concern with reception licence)	/
LNE	Unable to participate (concern with reception licence)	/

3 Preparation of the solid radioactive candidate reference material

The production of a synthetic solid RM matrix through the synthesis of a silicate material, spiked with radionuclides was chosen (^{237}Np, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu and ^{241}Am). The advantages are to provide a tunable radionuclide composition, to improve the traceability of the material by spiking it with a known amount of radioactivity, to obtain a reasonable homogeneity level, to measure the raw matrix to study its influence on mass bias affect and to achieve a reasonable shelf stability.

Relevant concentrations (activity and concentration levels) were chosen to produce a suitable material that is representative of environmental radioactive pollutants.

3.1 Acquisition of the starting materials

The approach from Harms and Gilligan [4] was chosen as a starting point to produce a homogeneous material. The sol-gel process (Figure 10) enables to mix the reagents and the radionuclides together in a liquid phase to ensure the homogeneity before the formation of the solid. The solid is formed after the hydrolysis (Equation 1 in Figure 10) and the condensation steps (Equation 2 in Figure 10).

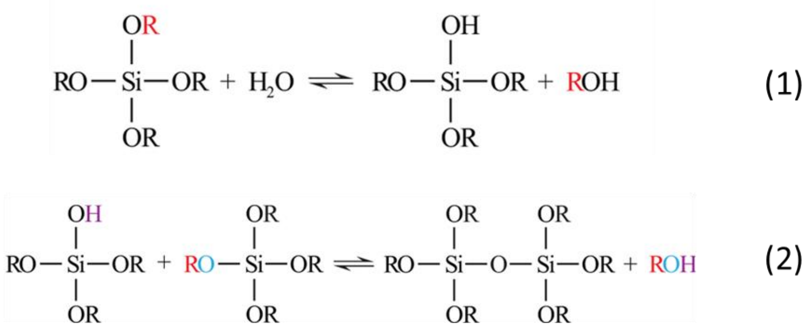


Figure 10. Hydrolysis (1) and condensation (2) reactions of the sol-gel process

The liquid silica precursor, tetraethyl orthosilicate (TEOS, Figure 11), is mixed with ethanol at acidic pH because of the radionuclides added. In [4] the radionuclides were in 1 M HCl whereas for the MetroPOEM solid RM, the medium chosen is 3 M HNO_3, to guarantee the stability of the radionuclides chosen.

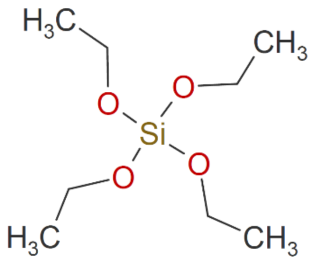


Figure 11: TEOS chemical structure

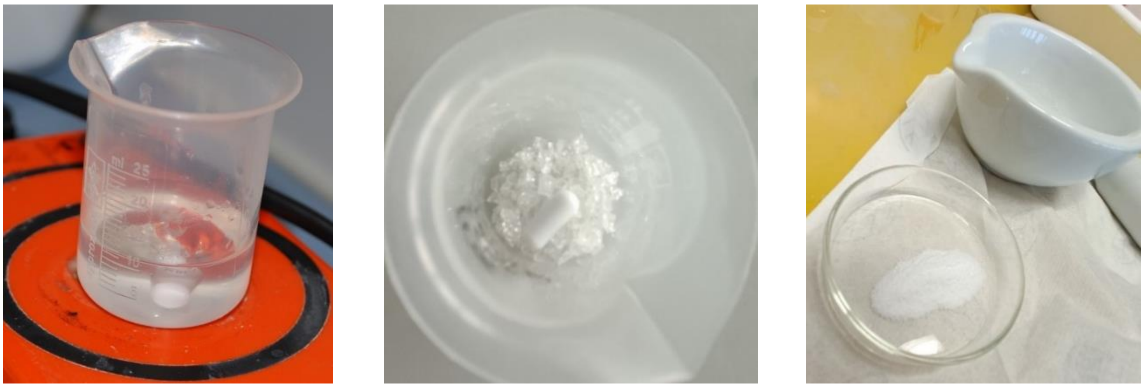
The heat generated by the reaction causes the evaporation of ethanol. The gel is formed and it solidifies in about a week when HCl is used.

In the publication from Harms and Gilligan [4], a standard uncertainty of 2.5% was chosen to account for the moisture content. To limit the moisture uptake, CEA decided to modify the reaction precursors to lower the moisture uptake of the resulting silicate matrix.

3.2 Feasibility studies

3.2.1 Small-scale

Several small-scale experiments, consisting in the synthesis of a few grams of material, were performed at CEA to test the sol-gel reaction with TEOS, ethanol and 3 M HNO_3. Pictures of the reaction and the following steps are shown in Figure 12.



(a) (b) (c)

Figure 12: Silica precursor (TEOS) mixed with EtOH and 3 M HNO_3 (a), after 24 h of reaction (b) and after grinding (c)

3.2.2 Use of more hydrophobic precursors to lower the moisture uptake

The moisture content of the material was measured after several drying steps at 105 °C until a constant mass was obtained. The resulting moisture content was (7.8 ± 1.0) %. To lower the final moisture content, three other silica precursors were tested to limit the water content of the resulting material (Figure 13).

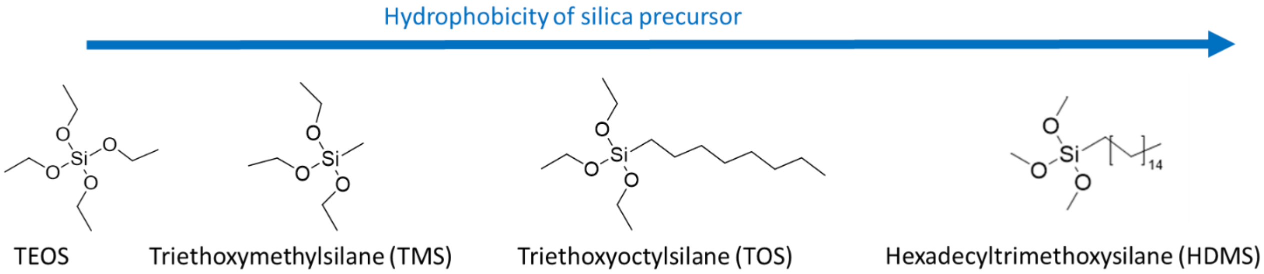


Figure 13: Chemical structure and increasing hydrophobicity of the silica precursors chosen

Using only HDMS and TMS as silica precursors, instead of TEOS, yielded materials which moisture uptake was greatly reduced. However, both materials obtained were not usable as a sand-like reference material. The 100 % HDMS solid melted at temperatures around 100 °C, and the 100 % TMS solid was impossible to grind, because the amount of organic matter was too important (Table 5).

Table 5. Moisture content measured with two new silicate precursors.

Precursors (mol %)	100 % HDMS	100 % TMS
Moisture content (wt %)	~ 0.1 %	~0.1 %
Notes	Quick solidification (a few minutes), once dried the solid becomes liquid at 100 °C	Hard to grind

Following the previous results, several mixture compositions were tested to try to keep the moisture uptake low, while retaining the sand-like character of pure silica.

Table 6. Moisture content measured with mixed silicate precursors (the uncertainties are estimated as the standard deviation between 4 measurements).

Precursors (mol %)	50 % TEOS+ 50 % HDMS	75 % TEOS+ 25 % HDMS	50 % TEOS + 50 % TOS	75 % TEOS + 25 % TOS	50 % TEOS+ 50 % TMS	75 % TEOS+ 25 % HDMS
Moisture content (wt %)	~ 1 %	(1.4 ± 0.6) %	Not measured	(2.9 ± 0.4) %	(5.0 ± 0.6) %	(8.8 ± 1.2) %
Notes	Quick solidification (a few minutes), sticky solid	Quick solidification (a few minutes)	sticky solid			

The HDMS silica precursor yielded solids with the lowest moisture content. However, this reagent reacts faster than the other silica precursors, probably because of the higher reactivity of the methoxysilanes over the ethoxysilanes. Using this precursor would not allow the homogenisation of the radionuclides with the other reactants; therefore, it did not seem appropriate for this study.

The solid produced with 50 % TOS and 50 % TEOS was not satisfactory because it could not be reduced into a powder and remained sticky even after drying.

Using 25 % of TOS resulted in a solid with a moisture content of 3 %, which was an improvement over the 8 % uptaken by a solid prepared with 100 % TEOS.

Using half TMS, half TEOS as precursors yielded a solid with a moisture content of 5 %, which was an improvement over the 8 % moisture content shown by a solid prepared with 100 % TEOS. Lowering the TMS content to 25 % yielded around 8 % of moisture uptake, which was not different from the original TEOS material.

Overall, the material obtained by mixing 75 % of TEOS and 25 % of TOS was the most promising, reducing the water uptake to around 3 %, while keeping the ability to be ground.

Next, the speed at which the original 100 % TEOS material and the modified 25 % TOS material uptake moisture from just sitting on a bench after being dehydrated was studied. For the 25 % TOS material, the maximum moisture content was reached after about 1 h, while it kept increasing after several hours for the 100 % TEOS material (Figure 14). Having a material which moisture content is stable is beneficial, because it would decrease possible errors in weighing if the material is not used right after drying.

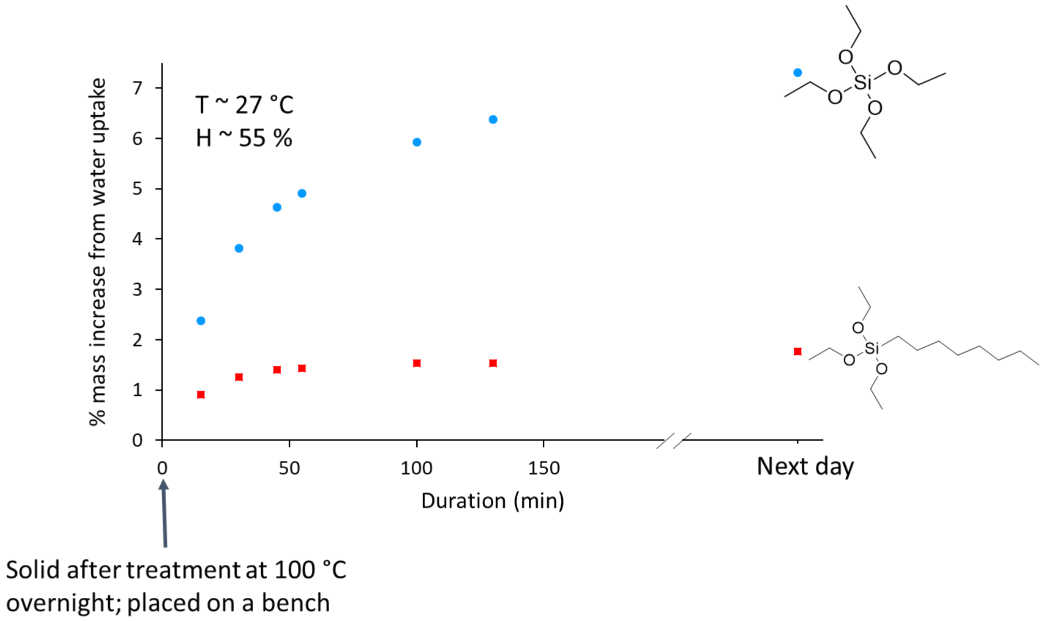


Figure 14. Rate of moisture uptake by a 100 % TEOS material (blue dots) and a 75 % TEOS, 25 % TOS material (red squares)

Following the feasibility studies, the silica material will be prepared with 25 % TOS and 75 % TEOS. The recommended use of the material will include a step to evaluate the moisture content, before the analysis.

3.2.3 Medium scale experiment (inactive)

The aim of this medium scale experiment was to produce about 2.5 kg of inactive silicate material and to monitor the duration of each step to extrapolate for the real scale experiment (possibly up to ten times more solid produced at once). The chosen molar ratio of 25 % TOS and 75 % TEOS was used, and the exact quantities of the reagents are presented in Table 7. To facilitate transfer the large amount of TEOS to the reaction vessel, a hand-pump was used.

Table 7. Quantities of reactants used for the medium scale experiment

Reactant	EtOH	TEOS	TOS	HNO_3
Mass (g)	1 580	4 500	1 990	1 150

This medium scale experiment showed that it took significantly longer to obtain the solid compared to the very small-scale experiment (Figure 15). The solidification took significantly longer, about 10 days instead of a few hours for the very small scale, and the solid obtained needed to be dried at a higher temperature (70 °C).

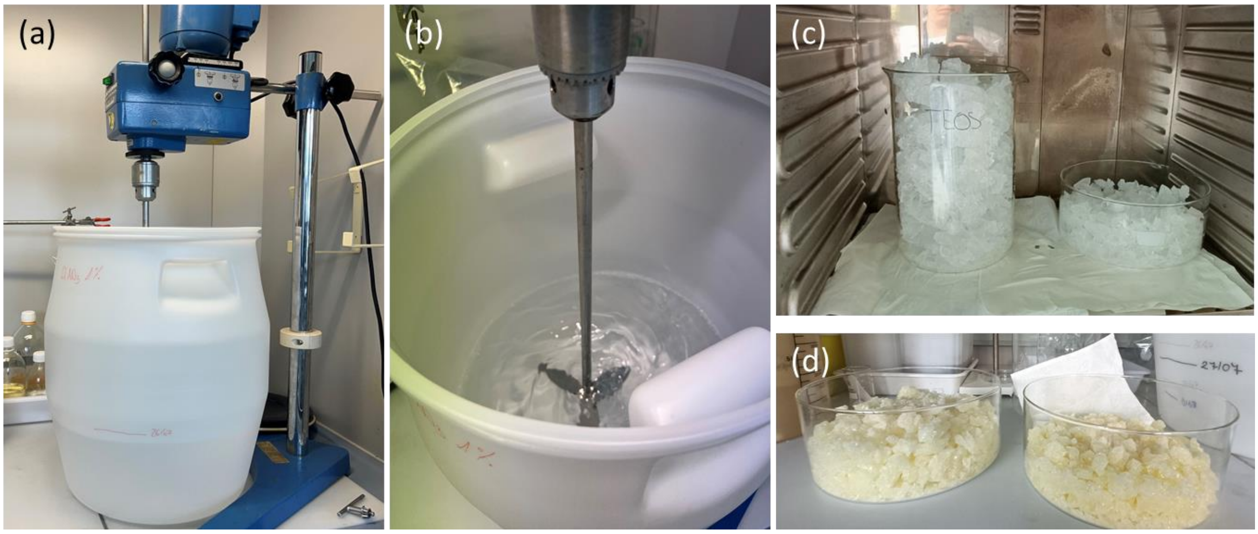


Figure 15: Medium scale experiment to produce 2.5 kg of silica (a) and (b), after mixing the ~9 kg of precursors, (c) wet solid obtained after 10 days and (d) solid obtained after 4 days of drying at 70 °C

3.3 Real scale synthesis of inactive material

3.3.1 Synthesis

To produce the inactive material that will be distributed to the participants, an inactive synthesis of the total amount needed for the solid RM, was prepared. The goal was to practice handling the reactants and the total amount of solid material, to practice for the experiment with activity. Additionally, the inactive material should be used as a ‘blank’, to assess matrix effects on the measurement. It is therefore important that this blank is as close as possible to the spiked solid.

Around 9 kg of the material was prepared, using the chosen molar ratio of 25 % TOS and 75 %TEOS. The exact quantities used are presented in Table 8.

Table 8. Quantities of reactants used for the real scale synthesis of the inactive material.

Reactant	EtOH	TEOS	TOS	HNO_3
Mass (g)	4 800	15 000	6 800	3 900
Mol	Excess			Excess

The solidification lasted for 11 days, which is not very different from the medium scale. However, it took a much longer time for the solid to completely dry from the ethanol (Figure 16). Drying took 5 weeks instead of 4 days for the medium scale, and the temperature was increased to 100 °C for the last week. The drying process was also not homogeneous, the top of the reaction vessel being dried first while the bottom was still wet. This could be detrimental to the homogeneity of the samples, because the radionuclides might migrate through the material during drying.

It could be beneficial to separate the reaction mixture into smaller containers, after sufficient homogenisation, but before solidification, to decrease the drying time, and produce a more uniform drying.

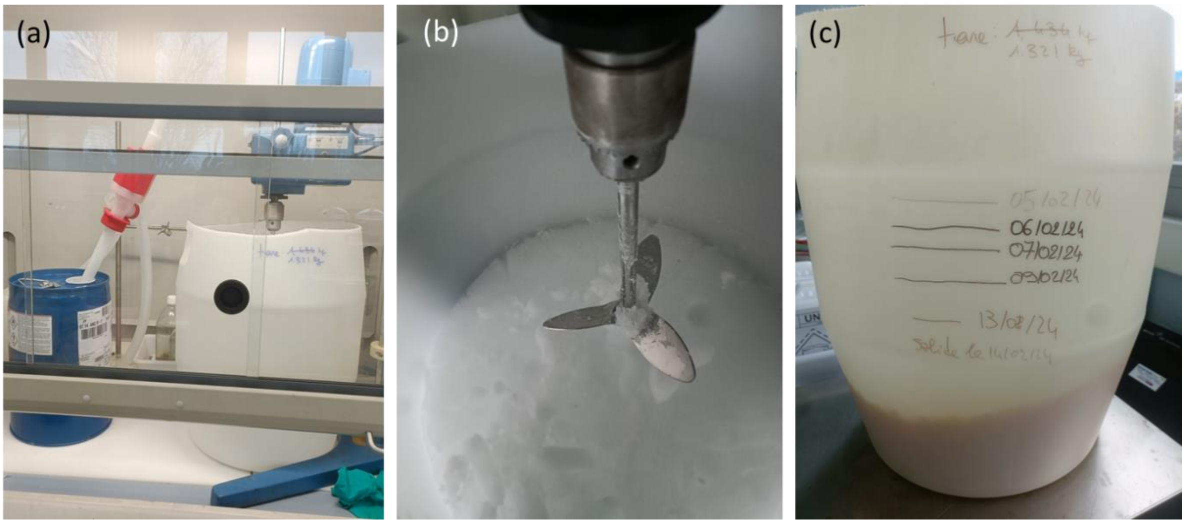


Figure 16. (a) the TEOS reactant being added with a hand pump, (b) the mixture is solid after 11 days, (c) the solid is dry after 5 weeks.

The resulting solid was milled using a jar miller (Figure 17.a). The 8 L jar was filled with around 7 kg of alumina beads, and around 3 kg of solid (Figure 17.b and c). The milling lasted 7 hours at 100 rpm. The resulting material comprised of particles below 250 µm (measured with vibrating sieves).

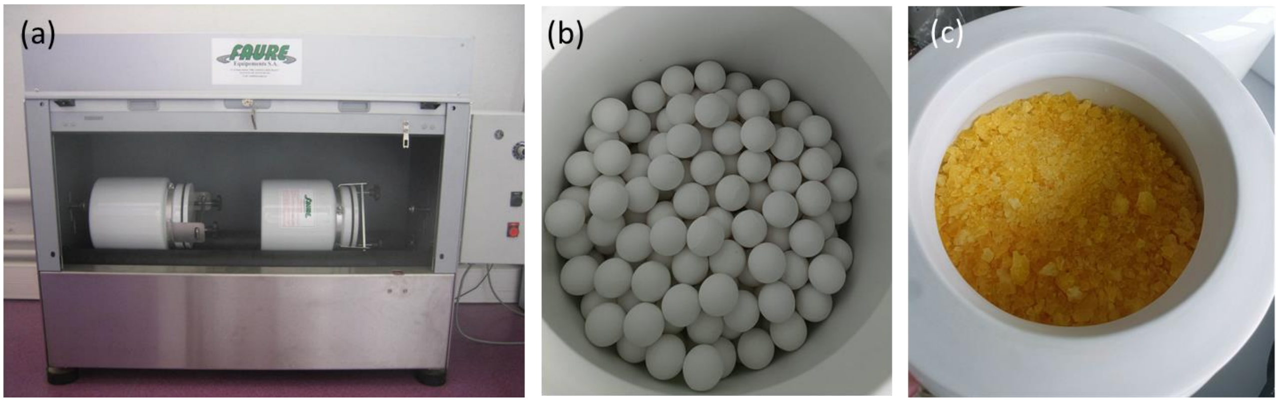


Figure 17. Pictures of (a) the jar miller, (b) a jar filled with alumina beads and (c) the jar filled with the solid to mill.

The jars were emptied and individual bottles were filled inside a disposable glove box, to prevent breathing potentially contaminated dust (Figure 18).

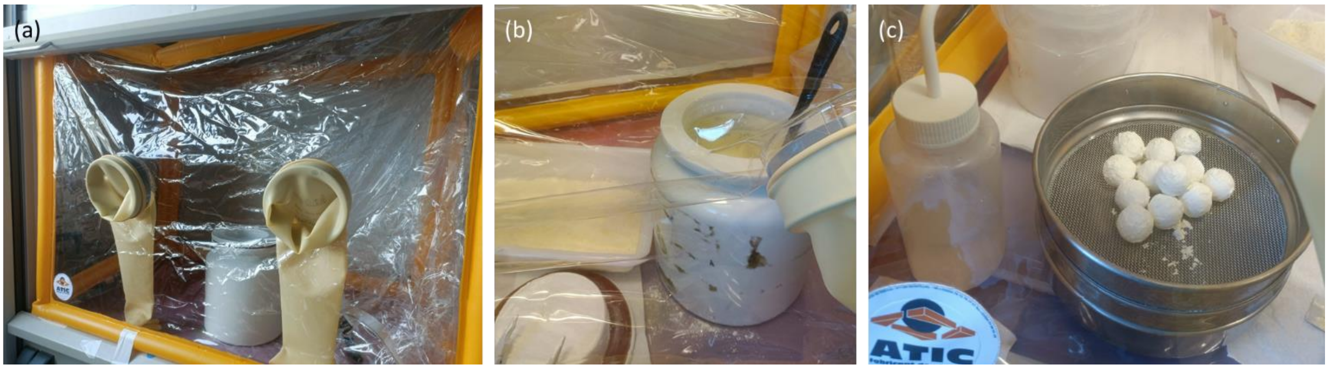


Figure 18; Pictures of (a) the disposable glove box, (b) a jar being emptied, (c) the beads being separated from the powder material.

Six kg of the inactive material were milled, and 50 bottles were filled (Figure 19). In May 2024, fifteen bottles of the inactive material were sent to the partners that will take part in the ILC of the solid RM.

Figure 19. Picture of inactive solid samples.

Scanning electron microscopy images of the inactive sample were taken at Gottfried Wilhelm Leibniz Universitaet Hannover (Figure 20). The solid material comprised polydisperse particles, ranging from a few µm to around 100 µm.

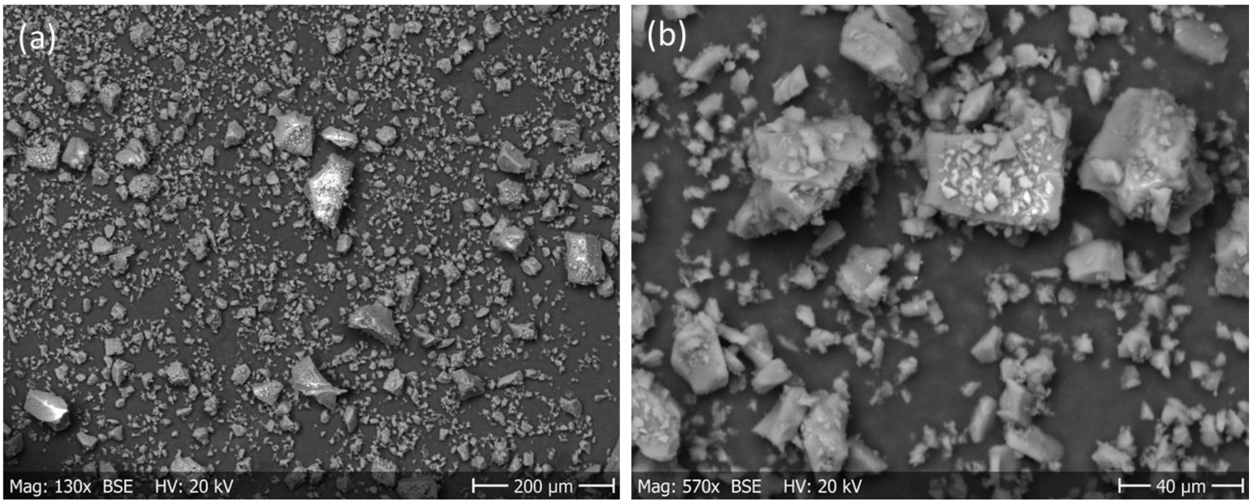


Figure 20. SEM images of the inactive solid material (Credits : Aaron Lenhert, Gottfried Wilhelm Leibniz Universitaet Hannover).

3.3.2 Dissolution procedures

Several partners that received a sample of the inactive material tested their usual dissolution procedures. They are summarised in Table 9.

Table 9. Experimental procedures tested by partners that lead to the dissolution of the inactive material.

Partner	Sample mass (g)	Calcination or pre-oxidation	Technique	Microwave	Temperature / Duration
CEA	0.5	Calcination	HF/HNO_3	No	150 °C / 30 min
NPL	0.5	No	Alkaline fusion	No	
NMBU	5	Pre-oxidation	HF/HNO_3	Yes (140 bar)	260 °C
ETH	0.5	No	$HF/HNO_3/HCl$	No	200 °C
STUK	0.5	No	HF/HNO_3	Yes	165 °C and 190 °C
PTB	0.5	No	$HF/HNO_3/H_2O_2$	Yes	210 °C

Most partners used HF and microwave digestion to dissolve the silica sample. HF reacts with silica through the reaction : $SiO_2 + 4HF \rightarrow SiF_4^{\uparrow} + 2H_2O$. The microwave digestion allows to dissolve the silica and evaporate the harmful HF in a safe way. Furthermore, it also oxidises the organic part of the solid material, added using the TOS precursor.

However, several labs do not have access to microwave digestion, CEA included. In this case, a calcination pre-step was recommended, to remove the organic matter, before dissolution with HF and HNO_3.

The partners agreed that HF dissolution would be used on the active solid RM, with use of microwave digestion if possible.

3.4 Preparation of the active solid RM

The quantities of reagents were similar to the inactive large-scale test. The 4 radionuclide spiking mixture was added at the same time as the HNO_3. The mixture was stirred for five days, then it was separated into nine trays, using a hand pump. The weight of the liquid transferred was measured. The trays were left at room temperature for 8 days, before solidification. Then, they were placed in an oven at 70 °C for five days, and the temperature was increased to 100 °C for four days (Figure 21).

Using trays allowed the solid to dry faster and in a more homogeneous way.

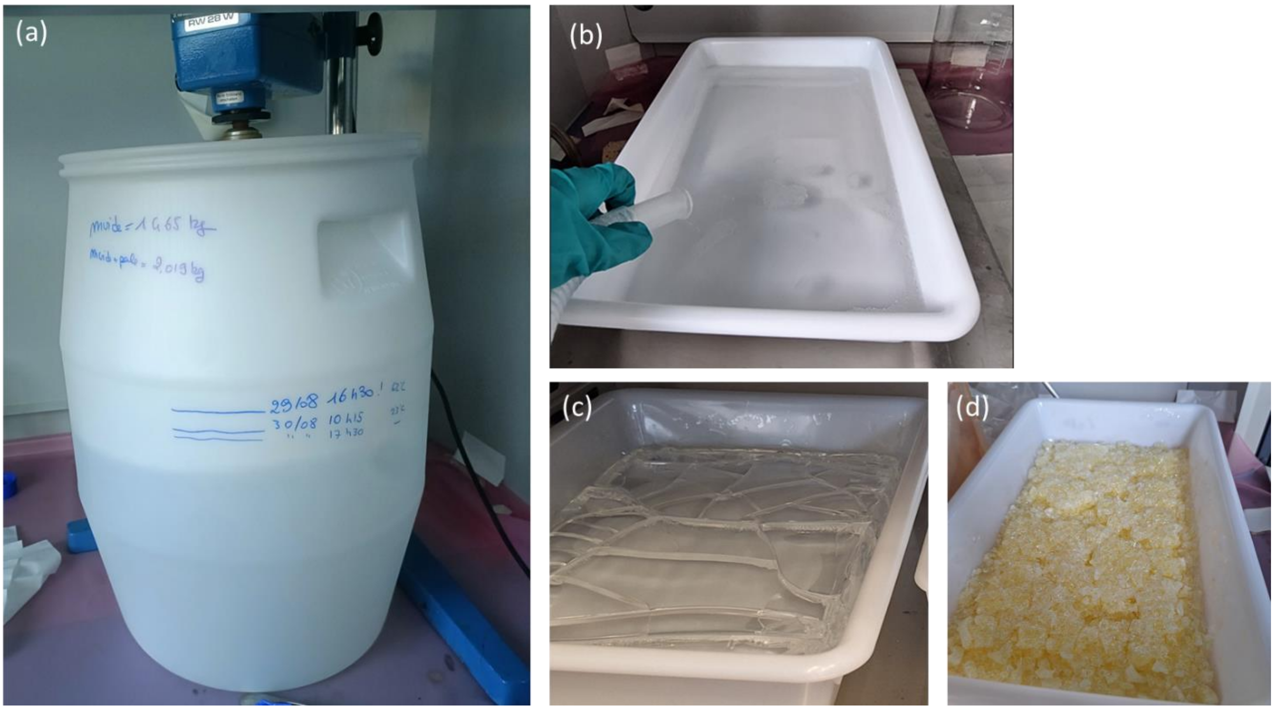


Figure 21. Pictures of (a) the reaction vessel, (b) a tray being filled after 5 days, (c) the mixture being solidified after 13 days, and (d) the dried solid after 22 days.

The solid was then milled and placed into 100 g bottles, in a similar way as the inactive sample. A total of four jars were used to mill the 9 kg of solid. 82 bottles of solid RM were produced (Figure 22).

Figure 22. Samples of solid RM.

3.5 Homogeneity assessment and characterisation of the solid RM

For the final homogeneity assessment, it was decided to use two main measurement techniques to assess the homogeneity of the batch and of the samples: first a non-destructive technique, gamma spectrometry, only possible on ^{241}Am, then mass spectrometry mostly on the minimum sample intake amount of material (0.5 g).

One homogeneity sample contains about 100 g of solid candidate reference material. A homogeneity sample analysed at CEA will undergo the following measurements presented in in Figure 23.

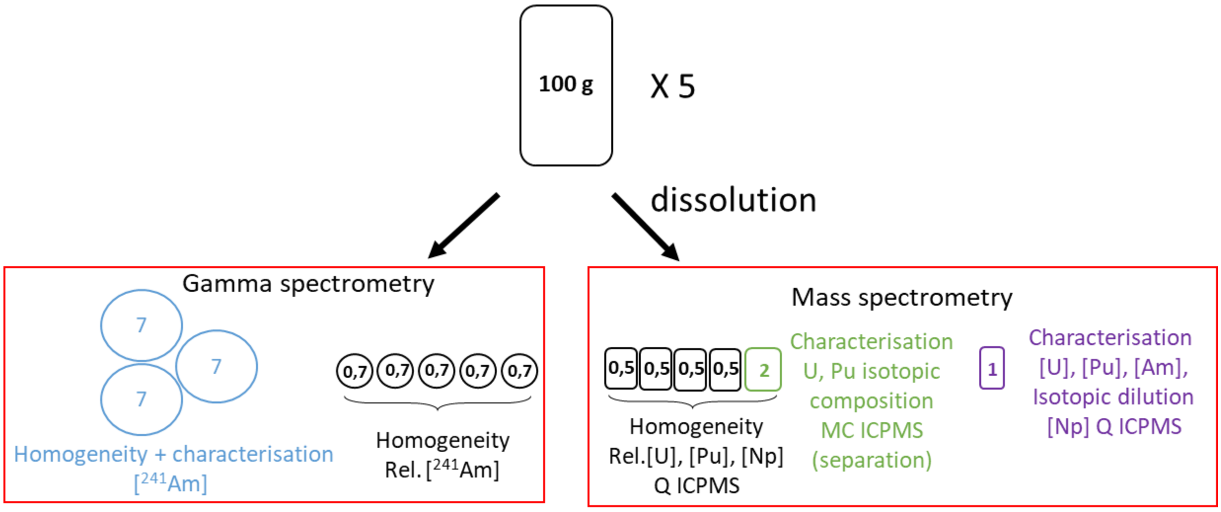


Figure 23: Homogeneity study on the solid candidate reference material using two techniques: non-destructive gamma spectrometry on ^{241}Am at CEA/LNHB and mass spectrometry at CEA/LANIE

In details :

- (non-destructive) gamma spectrometry measurements on ^{241}Am using:
  - Three 7 g cylindrical boxes (Figure 24.a). This will be performed in case the 0.5 g samples are not homogeneous enough and thus do not confirm the minimum sample intake value of 0.5 g.
  - Five 0.7 g cylindrical boxes (Figure 24.b), to assess the homogeneity at the level of the minimum sample intake targeted for mass spectrometry. The advantage here is that no destructive sample preparation step is needed so the variability could be lower than in the case of homogeneity measurements from mass spectrometry measurements.
- (destructive) mass spectrometry measurements:
  - Quadrupole ICPMS on four 0.5 g subsamples and one 2 g subsample to derive the homogeneity distribution of U, Np and Pu through the standard deviation obtained on these measurements. It is worth noting that the 2 g sample will be used to check the isotopic ratios of U and Pu. Those samples underwent the dissolution procedure chosen at CEA (Figure 24.c)

The three extra samples for homogeneity will be kept and measured if necessary.

For the characterisation, gamma spectrometry and mass spectrometry will also be used.

- The activity of ^{241}Am will be measured on the three 7 g cylindrical boxes per bottle (Figure 24.a).

- IDMS using tracers will be performed on one 1 g subsamples to assess the mass concentration of U, Pu and Am after the addition of a suitable tracer for each radionuclide. For U, a tracer of ^{233}U will be used, for Pu it will be ^{242}Pu, for Am: ^{243}Am. For Np because no ^{236}Np is available at LANIE a measurement by Q ICPMS using a CETAMA tracer will be used. The U and Pu isotope ratios will be measured by MC ICPMS after separation on the 2 g sample also used for homogeneity.

Figure 24. Pictures of the homogeneity and characterisation sub-samples: (a) boxes containing around 7 g of solid, (b) boxes containing around 0.5 g of solid and (c) crucibles and beakers used for the calcination and dissolution of the solid RM.

3.6 Solid RM candidate: sample dispatch schedule

The participants received a solid RM sample between November 2024 and February 2025. As of March 2025, only the samples for NPL were awaiting shipment.

Table 10. Solid RM sample dispatch schedule

Institute	Status	Sample reception date
CEA	Characterisation	Available from Nov. 4th 2024
DTU	ILC participant	13/02/2025
ETH	ILC participant	20/11/2024
FTMC	ILC participant	27/11/2024
HZDR	ILC participant	27/11/2024
JSI	ILC participant	21/11/2024
NMBU	ILC participant	21/11/2024
NPL	Characterisation	March 2025
PTB	ILC participant	20/11/2024
Spiez Lab	ILC participant	22/11/2024
STUK	ILC participant	20/11/2024
UH	ILC participant	25/11/2024
VINS	ILC participant	23/01/2025
Agilent	Extra ILC participant	23/12/2024
AGES	Extra ILC participant	12/12/2024
BAM	Unable to participate (part of the laboratory under decommissioning)	/
IFIN-HH	Unable to participate (concern with reception licence)	/

References

[1] ISO, General requirements for the competence of reference materials producers. International standard NF EN ISO 17034-2016, International Standardization Organisation, Geneva, Switzerland, (2016)

[2] ISO, Reference materials – Guidance for characterization and assessment of homogeneity and stability, NF ISO 33405, International Standardization Organisation, Geneva, Switzerland, (2024)

[3] Geotraces Cookbook version 3.0, August 2017

[4] A. Harms, C. Gilligan, Development of synthetic environmental radioactivity reference materials, Applied Radiation and Isotopes, Volume 70, Issue 9 (2012)