

JRC TECHNICAL REPORTS

Metrodecom: JRC-Geel Radionuclide Metrology Sector contribution to WP5 Task 2

Reference materials and standard sources for radiochemical analysis

Raf Van Ammel, Timotheos Altitzoglou, Guillaume Lutter, Maria Marouli, Heiko Stroh, Gerd Marissens, Mikael Hult, Stefaan Pommé

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Foreword

MetroDecom (ENV54), Metrology for decommissioning of nuclear facilities, is a European Metrology Research Programme (EMRP) project carried out by 15 partners to address the needs of the nuclear decommissioning process. This is done by developing and implementing new measurement techniques, instruments, standards and reference materials, and by ensuring knowledge transfer to stakeholders. The project is divided in five Work Packages (WP):

- WP1 Characterisation of waste materials present on decommissioning sites
- WP2 Measurement facility for waste segregation
- WP3 Implementation of free release measurement facility on decommissioning site
- WP4 Radioactive waste repositories monitoring
- WP5 Development of reference materials and standard sources

The Work Package 5, coordinated by the Physikalisch-Technische Bundesanstalt (PTB), consists of 4 different tasks.

- Task 1 Reference materials and standard sources for segregation of materials and for free release measurements (Lead by Cesky Metrologicky Institut (CMI))
- Task 2 Reference materials and standard sources for radiochemical analysis. (Lead by National Physics laboratory (NPL))
- Task 3 Gaseous reference materials (Lead by NPL)
- Task 4 Reference materials and standard sources for surface contamination monitors (Lead by Institut National de Cercetare Dezvoltare pentru Fizica si Inginerie Nucleara (IFIN))

The JRC-Geel Radionuclide Metrology Sector(RN) is involved in WP5 task 1 and task 2. This report summarises the work carried out in task 2 of WP5.

Abstract

JRC-Geel is a partner in the EMRP-project named Metrodecom, Metrology for decommissioning nuclear facilities. The project focusses on the different aspects of metrology applied in the field of decommissioning of nuclear facilities. The commitments of the Radionuclide Metrology Sector of JRC-Geel (RN) are part of the work to be carried out in WP 5 Development of reference materials and standard sources. In Task 1 reference materials and standard sources for segregation of materials and for free release measurements needed to be produced and characterised. Task 2 consisted in the production and characterisation of reference materials and standard sources for radiochemical analysis.

The first task of RN was to characterise blank graphite. This characterisation was done using the gamma-ray detectors located in our underground laboratory.

The second task was the standardisation of a ^{151}Sm and a ^{236}U solution in the primary standardisation laboratory.

1 Introduction

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The Radionuclide Metrology sector of JRC-Geel is involved in WP5 task 1 and task 2.

This report describes the work carried out in task 2:

- 1) The characterisation of blank graphite in our underground laboratory.
- 2) The calibration of a ^{151}Sm solution and a ^{236}U solution.

After this characterisation of the material and calibration the solutions, both will be used in WP1 of the project.

2 Characterisation of 5 NPL Graphite samples

2.1 Materials and Methods

2.1.1 Samples

Blank graphite was prepared by NPL and partitioned into aliquots. Five samples and an empty container (for background correction) were received by JRC-Geel for characterisation. Table 1 gives an overview of the 5 samples, Table 2 gives the properties of the empty container.

Table 1. Data and description of the 5 samples.

Name	JRC registration number	Mass sample + container (g)	Sample height (mm)	Sample density (g/cm ³)
Graphite 1	D04-SN3S-LLR-2015-02-06323	51.5	46.3	0.632
Graphite 2	D04-SN3S-LLR-2015-02-06324	50.5	49.0	0.561
Graphite 3	D04-SN3S-LLR-2015-02-06325	48.5	48.6	0.543
Graphite 4	D04-SN3S-LLR-2015-02-06326	48.2	53.7	0.489
Graphite 5	D04-SN3S-LLR-2015-02-06327	48.2	52.3	0.501

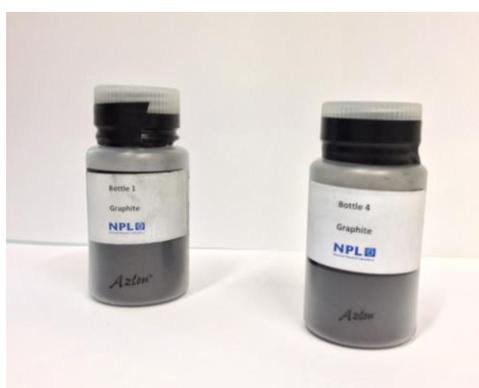


Figure 1 Two of the blank graphite samples.

Table 2. Data and description of the empty container as measured by RN.

JRC registration number	D04-SN3S-LLR-2015-02-006328
Material	Polypropylene
Outer diameter (mm)	51
Inner diameter (mm)	48.4
Outer height* (mm)	77.3
Inner height (mm)	54.4
Thickness (mm)	1.31
Mass (g)	23.8

* from bottom to neck

No specific sample treatment was performed except for wiping the outside of the containers with isopropanol.

The sample containers were not opened; the net sample masses were calculated by subtracting the mass of the empty container from the gross mass of sample containers.

2.1.2 Detectors and measurements

The samples were measured using ultra low-level gamma-ray spectrometry (ULGS) (see Ref 1 and Ref 2).

The detector Ge-8, located in the underground laboratory HADES, was employed for the measurements. Its main characteristics together with a description of the underground laboratory HADES are presented by Andreotti et al. (Ref 3).

Detector Ge-8 is a planar p-type detector so-called Broad Energy Germanium. It has a relative efficiency of 19% and a sub-micron dead layer at the top. The peak count rate of gamma lines from primordial radionuclides is below 1 count per day. There is no ^{137}Cs in the background ($< 0.1 \text{ d}^{-1}$).

For the measurements, the sample containers were placed directly on the end cap of the detector.

A measurement of the empty container was conducted to be sure that the container contained no radionuclides (which was confirmed by the measurement). The resulting spectrum was used as background in the analysis of the sample spectra. Table 3 gives an overview of start and the measurement time (t_m) of each sample.

Table 3. Overview of the measurements carried out on detector Ge-8.

Sample	Acquisition start	t_m (days)
Graphite 1	24/03/2015	13.7
Graphite 2	07/04/2015	6.8
Graphite 3	14/04/2015	2.9
Graphite 4	17/04/2015	3.9
Graphite 5	21/04/2015	2.9
Empty container	17/03/2015	6.9

2.1.3 Efficiency calculation models and programs

Full Energy Peak (FEP) efficiencies for the gamma-rays were calculated using the EGSnrc Monte Carlo program (I. Kawrakow and DWO Rogers, 2003, Ref 4) using data from:

- Measured dimensions of the sample
- Estimated composition of sample matrix
- Manufacturer's information on measurable dimensions of the Ge-detector
- Values of Ge dead layer and crystal position when cooled derived from (i) radiographs of the detectors followed by (ii) experimental calibration measurements of the efficiency curve vs. energy using standardized point sources from PTB

The simulations assume that the gamma-ray emissions are isotropic and uncorrelated.

Summing coincidences were calculated using EGSnrc for all identified radionuclides.

The FEP efficiency calculations were validated through participation in proficiency testing schemes organized by NPL.

All calculations assume that the radionuclides are homogeneously distributed in the sample and that the sample material is homogeneously distributed in the sample container.

2.1.4 Calculations

First a qualitative analysis of the gamma-ray spectra was done. The identified radionuclides are listed in Table 4.

Table 4. List of identified radionuclides.

Detected Radionuclide	Assumed to be in secular equilibrium with
In the ^{238}U decay chain	
^{234}Th	^{238}U
$^{226}\text{Ra}^*$	^{226}Ra
^{214}Pb	^{226}Ra
^{214}Bi	^{226}Ra
^{210}Pb	
In the ^{232}Th decay chain	
^{228}Ac	^{228}Ra
^{224}Ra	^{228}Th
^{212}Pb	^{228}Th
^{212}Bi	^{228}Th
^{208}Tl	^{228}Th
In the ^{235}U decay chain	
^{235}U	n.a.
Primordial radionuclides	
^{40}K	n.a.

*After interference correction of the 186 keV gamma-ray of ^{235}U .

The activity of the nuclides was calculated based on individual gamma-rays using the following formula:

$$A = \frac{C_{TOT} - C_{Peak}^{Bkg} - C_{Continuum}}{\varepsilon \cdot P_{\gamma}} \cdot e^{\lambda t_d} \cdot \frac{\lambda}{1 - e^{-\lambda t_m}} \cdot K_1 \cdot K_2 \cdot K_3$$

Where C is the number of counts in the peak in the sample spectrum (*TOT*), in the background spectrum (*Bkg*) and in the continuum under the peak in the sample spectrum (*Continuum*), λ is the decay constant, P_{γ} the gamma-ray emission probability, ε the full energy peak efficiency calculated using Monte Carlo simulation, t_d the decay time, K_1 the coincidence summing correction factor, K_2 the branching correction factor, K_3 the equilibrium correction factor. The massic activity was obtained by dividing the activity by the mass of the sample. The FEP efficiencies are traceable to PTB via point source calibrations.

For each radionuclide with multiple gamma-rays, a weighted mean of the activity from the different gamma-rays was calculated.

For ^{226}Ra a weighted mean of the activity was calculated based on its decay products (see Table 4).

The nuclear decay data was taken from the Decay Data Evaluation Project (DDEP) website http://www.nucleide.org/DDEP_WG/DDEPdata_by_Z.htm

The 186 keV peak is a doublet with contributions from ^{235}U and ^{226}Ra . The number of counts from ^{226}Ra in that peak was calculated using the activities from the radon decay product ^{214}Pb and ^{214}Bi .

2.2 Results

The activities (Bq/g) are given at the reference date of 24/03/2015.

The reported uncertainties are the combined standard uncertainties ($k=1$). When combining the uncertainties, the correlated quantities (like detection efficiencies) were combined separately.

2.2.1 Equilibrium in decay chains

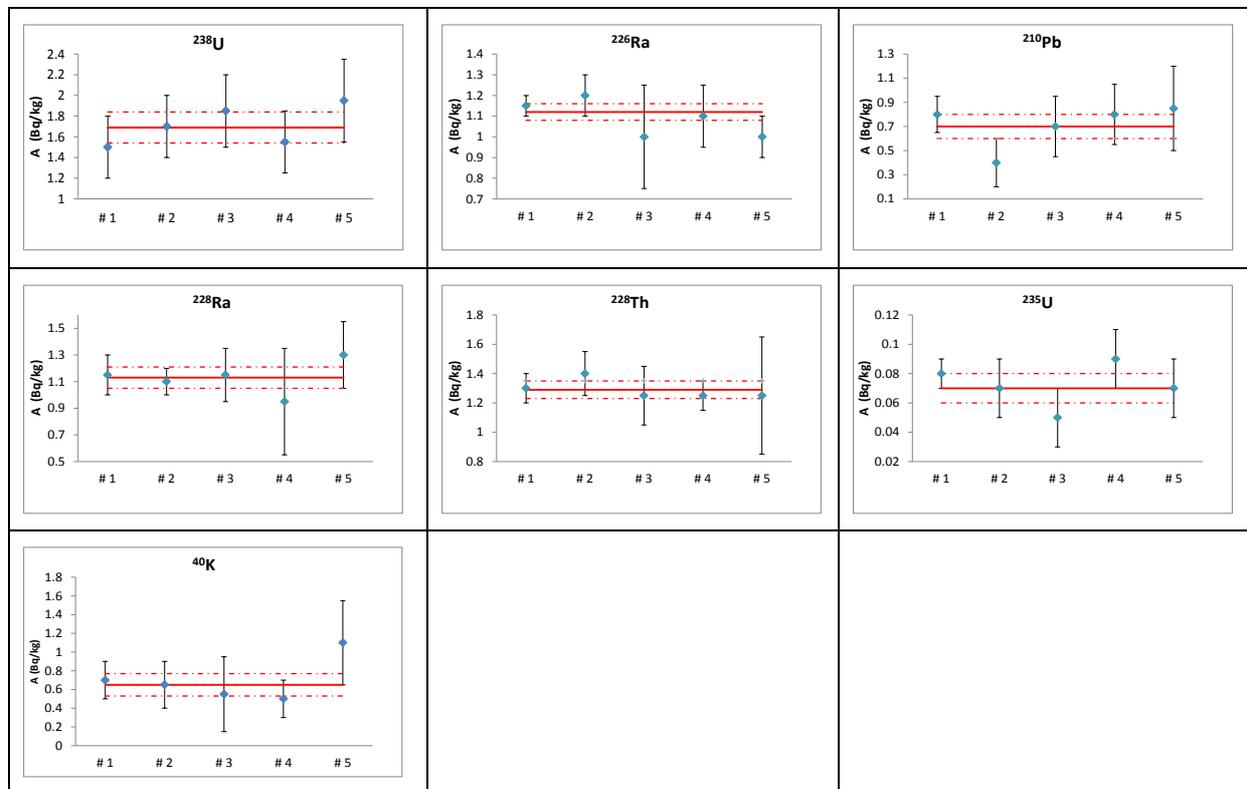
The sample containers were not opened and secular equilibrium has been assumed between the long-lived radionuclides ^{226}Ra , ^{228}Ra , ^{228}Th , ^{238}U and their short-lived decay products.

2.2.2 Results

The activities (Bq/g) for each radionuclide and graphite sample are presented in Table 5. The measurement of the empty container resulted in no peaks above background levels. Hence no radionuclide was detected in the empty container.

Table 5. Massic activities and combined standard uncertainties (k=1) of the 5 graphite samples at reference date 24/03/2015.

Radio-nuclide	Detected radionuclide	Massic activity (Bq/kg)					Power Moderated Mean
		Graphite1	Graphite2	Graphite3	Graphite4	Graphite5	
^{238}U	^{234}Th	1.50 ± 0.30	1.70 ± 0.30	1.85 ± 0.35	1.55 ± 0.30	1.95 ± 0.40	1.69 ± 0.15
^{226}Ra	$^{214}\text{Pb} + ^{214}\text{Bi}$	1.15 ± 0.05	1.20 ± 0.10	1.00 ± 0.25	1.10 ± 0.15	1.00 ± 0.10	1.12 ± 0.04
^{210}Pb	^{210}Pb	0.80 ± 0.15	0.40 ± 0.20	0.70 ± 0.25	0.80 ± 0.25	0.85 ± 0.35	0.70 ± 0.10
^{228}Ra	^{228}Ac	1.15 ± 0.15	1.10 ± 0.10	1.15 ± 0.20	0.95 ± 0.40	1.30 ± 0.25	1.13 ± 0.08
^{228}Th	$^{224}\text{Ra} + ^{212}\text{Pb} + ^{212}\text{Bi} + ^{208}\text{Tl}$	1.30 ± 0.10	1.40 ± 0.15	1.25 ± 0.20	1.25 ± 0.10	1.25 ± 0.40	1.29 ± 0.06
^{235}U	^{235}U	0.08 ± 0.01	0.07 ± 0.02	0.05 ± 0.02	0.09 ± 0.02	0.07 ± 0.02	0.07 ± 0.01
^{40}K	^{40}K	0.70 ± 0.20	0.65 ± 0.25	0.55 ± 0.40	0.50 ± 0.20	1.10 ± 0.45	0.65 ± 0.12



3 Standardisation of a ^{151}Sm and ^{236}U solution

3.1 Samples and measurements

A solution of ^{151}Sm available at JRC-GEEL and a ^{236}U solution received from NPL were certified in the RN laboratories. The ^{151}Sm solution is 1M HCl solution, the ^{236}U is a 1M HNO_3 solution.

The ^{151}Sm solution was measured by Liquid Scintillation Counting (LSC) using the CIEMAT/NIST efficiency tracing and triple to double coincidence ratio counting methods. In addition the ampoule was measured prior to opening it on an HPGe detector. The activity concentrations of the impurities detected are listed in Table 6. The ampoule was opened and different aliquots were gravimetrically added to high performance liquid scintillation vials containing 15 mL of scintillation cocktails (either Ultima Gold or Insta-Gel Plus) using a microbalance. The aliquots had a mass between 9 and 49 mg corresponding to an activity from 800 to 3200 Bq. A Packard TRI-CARB 3100 TR and a Wallac 1220 Quantalus LSC were used to measure the samples for the CIEMAT/NIST method. LSC TDCR measurements were performed using an in-house built counter.

Table 6. Activity concentrations of the impurities determined by gamma spectrometry, on reference date 1 Jan 2016.

Nuclide	Activity conc. (Bq/g)
^{154}Eu	21.4 (13)
^{155}Eu	7.3 (5)

The ^{236}U solution was certified by alpha defined solid angle counting. Ten samples were made by dispensing gravimetrically aliquots on 34 mm diameter glass plates. A microbalance was used to weigh the aliquots having masses between 35 and 101 mg corresponding to an activity from 30 to 100 Bq. After dispensing, the samples were dried on a hot plate having a temperature of 150 °C and measured in two different alpha defined solid angle counters. The solid angle was calculated from the geometrical setup of the system. Corrections were applied for the inhomogeneous distribution of the activity over the glass plates by making autoradiographs of the sources. The solution provided is not a pure ^{236}U solution but other uranium isotopes were present. The exact composition was determined by mass spectrometric analysis and the relative activity fraction of the different uranium isotopes is listed in Table 7. Those activity fraction values are used for the calculation of the ^{236}U activity.

Table 7. Relative activity fraction of the different uranium isotopes in the solution, reference date 1 Jan 2016 determined by mass spectrometry (Ref 5).

Nuclide	Activity fraction
^{233}U	0.00164 (0.00003)
^{234}U	0.11384 (0.00036)
^{235}U	0.003073 (0.000008)
^{236}U	0.88138 (0.000037)
^{238}U	0.0000690 (0.0000002)

3.2 Results

The activity concentrations for the different solutions are given at the reference date of 01/01/2016. The uncertainties are the combined standard uncertainties ($k=1$).

The result of the ^{151}Sm is the mean value of the results obtained from the LSC CN method. The result is the average of the measurements of 12 different samples 6 ultima gold®(UG) samples and 6 instagel plus®(IG) samples. No difference between UG and IG samples was observed, although the latter were more stable resulting in a smaller standard deviation of the different results (0.10% for IG, 0.19% for UG). The results were corrected for impurities and adsorption. The activity concentration for the ^{151}Sm is **77.6 (4) KBq/g**. The major contributions to the uncertainty come from the decay scheme parameters, the standard quench parameter, the weighing and sample stability.

The activity concentration for the ^{236}U is calculated from the mean value of all measurements performed on the 10 sources on 2 different defined solid angle alpha counters. The results obtained from the measurements performed on both counters are in good agreement with each other (<0.2% difference). The ^{236}U activity concentration in the solution is **912 (4) Bq/g**. The main contributors to the total uncertainty are the counting statistics, the detection efficiency and the extrapolation of the spectra to zero energy.

4 Conclusion

In ENV54 Metrodecom work package 5 Task 2 the radionuclide metrology sector of JRC-Geel had two tasks to carry out.

Five samples of a blank graphite containing very low levels of naturally occurring radionuclides were characterised. The samples were measured using a HPGe detector located in the underground laboratory HADES. The activities obtained from the five different samples are in good agreement within their uncertainties.

The activity concentration of two different solutions, a ^{151}Sm and ^{236}U solution, was determined using primary standardisation methods. The ^{151}Sm solution was standardised by liquid scintillation counting the ^{236}U solution by alpha defined solid angle counting.

The results of the characterisation of the blank graphite and the activity concentration determination of the ^{151}Sm and ^{236}U solution were reported on 31 of August 2015 to the task coordinator. The task coordinator will make the results and the materials available for use in WP1: Characterisation of waste materials present on decommissioning sites. For the work in this work package blank material can be mixed with a standardised solution to obtain a material spiked with a known amount of radioactive material.

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