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## 1 Executive Summary

### Introduction

The operation of nuclear facilities and their decommissioning (once their life cycle ends), must be done in a way to minimise environmental impacts. The project developed standardised and traceable measurement methods based on gamma-ray spectrometry, accurate decay data and radiochemistry and prototype mobile measuring equipment to support the organisations responsible for decommissioning.

### The Problem

The waste generated by nuclear facilities must be reliably separated into radioactive waste that needs to be stored in secure repositories and waste that can be released into the environment. For waste that can be released into the environment (referred to as 'free release'), the national regulators have specified very strict limits for the mass and surface activity of selected radionuclides contained in waste. In order to monitor the vicinity of the nuclear facility during decommissioning or during an accident in situ measurements are necessary. These measurements should be fast and flexible and there is a need for a rapid method of preparation and measurement of samples in the place of their origin. This requires the development of a standardised traceable method, to be used in mobile radiochemical laboratories. In addition, to protect workers in the repositories and also the general public against unexpected on-site as well as off-site irradiation, it is necessary to monitor gaseous radionuclides such as H-3, C-14 and Rn-222. Finally, the safe and optimised management of waste relies on a precise knowledge of the variation with time of artificial radionuclide concentrations.

### The Solution

Standardised traceable measurement methods based on gamma-ray spectrometry must be developed and used for free release and repository acceptance measurements that allow to identify radionuclides in wastes and determine their activities with sufficient accuracy. Rapid in-situ radiochemical analysis methods must be developed for indirectly measured radionuclides (pure alpha- and beta-radionuclides) occurring in wastes. A combination of the existing radiometric techniques (e.g. liquid scintillation counting) with the chemical species separation must be developed for the repositories. Decay data for long-lived radionuclides occurring in wastes must be improved.

### Impact

The development of equipment and standardised traceable method for free release and repository acceptance measurements will eventually lead to the reduction of repository costs. Recycle and reuse options provide a cost effective solution to waste management. Improved accuracy of free release measurements will eventually restrict the quantity of material incorrectly sentenced to repositories due to measurement inaccuracy and will thereby minimise disposal costs. The quantity of incorrectly released or stored material will be lowered and possible trade disputes will be less likely at national and international level. The development of an equipment and standardised traceable rapid method for in-situ radiochemical analysis will eventually reduce analysis costs for  $\alpha$ - and  $\beta$ -emitting radionuclide measurement by removing the need to transport samples to an external laboratory. The development of nuclide-specific gas-monitoring systems will ultimately provide a means of alerting workers in repositories of hazardous radioactive gases and will improve our understanding of waste degradation and therefore the dose implications for the population. The development of above mentioned equipment and methods will contribute to minimised contamination of the environment by radioactive material caused by inaccurate or incorrect measurement.

## 2 Project context, rationale and objectives

### 2.1 Context and rationale

The project supports and improves radiation protection and safe management of radioactive waste measurements. The needs and requirements are underlined by the following EC directives:

The directive 2013/59/EURATOM lays down basic safety standards for protection against the dangers arising from exposure to ionising radiation states in Article 30 the necessity of nuclide-specific measurement of waste materials released from regulatory control. Nuclide specific measurement is ensured by using spectrometric measurement method developed in the project.

The directive 2011/70/EURATOM, establishing a Community framework for the responsible and safe management of spent fuel and radioactive waste, provides binding legal force to the main internationally

endorsed principles and requirements in this field and states that radioactive waste shall be kept to the minimum by means of decommissioning practices, including the recycling and reuse of materials. Member states shall ensure that the national framework is improved where appropriate, taking into account operating experience and the development of relevant technology and research. The Commission shall encourage co-operation between the Member States in common areas of research and technological development. Minimisation of radioactive waste is ensured by accurate standardised traceable measurement methods developed in the project in cooperation of several EU states.

Commission Recommendation 2006/851/EURATOM on the management of financial resources for the decommissioning of nuclear installations, spent fuel and radioactive waste states that all nuclear installations should be decommissioned after permanent shutdown and the management of waste should be properly addressed. The project addresses this need by development of methods allowing accurate measurement of high amount of waste materials typical for decommissioning.

European Commission, COM(2005)666, A thematic strategy on the prevention and recycling of waste, states in Annex I, Article 4 Waste prevention that the potential for waste prevention depends on adopted best practice in reducing waste. Significant reduction of radioactive waste should be one of main project outcomes.

Following IAEA safety standards are addressed by the project:

IAEA Safety Standards Series No. WS-G-2.5, Predisposal management of low and intermediate level radioactive waste Safety Guide, 2009.

IAEA Safety Standards Series No. GSR Part 5, Predisposal management of radioactive waste, 2009.

IAEA Safety Standards Series No. GS-G-3.3, The management system for the processing, handling and storage of radioactive waste, 2008.

IAEA TECDOC-1537, Strategy and Methodology for Radioactive Waste Characterisation, 2007.

IAEA Safety Standards Series No. NS-G-2.7, Radiation protection and radiation waste management in the operation of nuclear power plants Safety Guide, 2002.

## 2.2 Objectives

In order to provide validated and traceable measurements/reference methods for radioactive waste management during nuclear decommissioning, the project addressed the following scientific and technical objectives:

- Development of standardised traceable measurement methods for solid radioactive waste free release (clearance levels verification) and for acceptance of solid radioactive wastes to repositories (acceptance criteria verification), according to international recommendations (EC and IAEA): as well as design of measurement facilities, software, calibration and testing methods.
- Development of novel instruments and methods for in-situ measurements: this includes improved on-site radiochemical analysis, rapid in-situ screening techniques for alpha, beta and gamma emitters and measurement of activity at varying depth.
- Development of gaseous effluent monitors and samplers for stored wastes. Rapid, sensitive methods are required to determine activity concentrations of key radionuclides (e.g. H-3 and C-14) in specific chemical forms (e.g. C-14 as CO<sub>2</sub>).
- Development of standards and 'spiked' or characterised 'real' reference materials for ensuring accurate, traceable radio-assays of materials from sites (concrete, steel, aluminium, cables, wood, insulator and others).
- Improvements to decay data for selected radionuclides present in nuclear wastes, focusing on half-life measurements of long-lived fission and activation products.

### 3 Research results

#### 3.1 Measurement of solid wastes generated in nuclear facilities

One of the main achievements of the project is measurement of solid wastes that are produced within the operation of nuclear facilities. Standardised traceable methods for free release measurement and repository acceptance measurement were developed, measurement facilities designs created and experimental Free Release Measurement Facility (FRMF) and Repository Acceptance Measurement Facility (RAMF) built, calibrated and tested.

Clearance levels and acceptance criteria specification is under the authority of national regulators. Although several international organisations like the IAEA and the EC have issued recommendations, the differences are still significant. That is why overviews of national regulations and also current measurement systems and their capabilities were performed prior to the research on the development of corresponding measurement methods and design of measurement facilities.

The main advantages of novel methods will be spectrometric detection, better resolution, sensitivity, measurement range, material throughput, traceability, accuracy (nuclear data revision, scale factors determination and implementation) together with corresponding software algorithms.

##### 3.1.1 Free release measurement of wastes released in the environment

Standardised traceable measurement method was developed to enable verification of compliance with legal clearance levels for free release according to EC and national legislation, international recommendations (IAEA, NEA) including the design of FRMF, software, calibration and testing. This method is based on gamma-ray spectrometry using four germanium detectors with high resolution enabling measurement of mixtures of radionuclides in waste packages and special low-background measurement chamber making very low detection limits for the measured radionuclides possible.

##### 3.1.1.1 Experimental Free Release Measurement Facility (FRMF) construction

Experimental free release measurement facility was constructed and built at the Czech company ENVINET a.s. The FRMF consists of the following main parts:

- low-background measuring chamber
- four coaxial mechanically cooled HPGe detectors
- conveyor
- ventilation

Shielded measuring chamber (Figure 1) is a dry construction, built from low-activity concrete blocks made of low-activity gravel, low-activity cement and water, with roof beams made of low-activity gravel and epoxy resin by a special technology. Concentration of natural radionuclides in the building materials is as follows:

$a(\text{Ra-226}) \approx 0.6 \text{ Bq/kg}$  ;  $a(\text{Th-228}) \approx 0.3 \text{ Bq/kg}$  ;  $a(\text{K-40}) \approx 6 \text{ Bq/kg}$ .

These mass activity values are about ten times lower than it is usual in the environment, which allows for significantly lower radiation background inside the chamber.

Slight overpressure is held inside the chamber using filtered the outside air to keep radon and its progeny from affecting the measurement.

HPGe detectors are additionally shielded by small lead collimators.

The internal dimensions of the measuring chamber are: height 1.5 m, width 1.5 m, length 3 m. Chamber walls thickness is 40 cm, floor thickness 60 cm, ceiling thickness 50 cm and door thickness 20 cm.





Figure 1: Experimental free release measurement facility

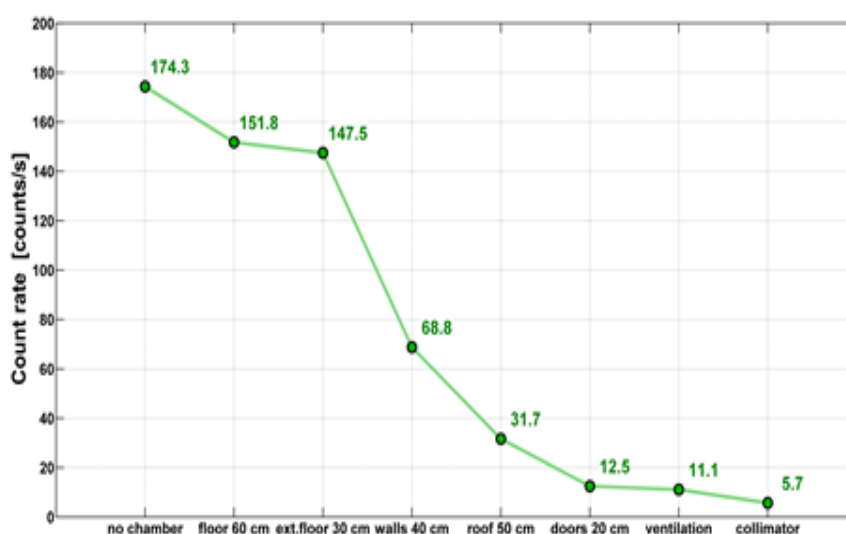


Figure 2 shows lowering of the inside background during the chamber construction measured by HPGe detector as a total count rate in the energy range from 20 keV to 2 MeV. The total background is about thirty times lower than the outside one without any shielding.

Background gamma-ray spectrum inside the chamber acquired using HPGe coaxial detector, with resolution FWHM = 1.8 keV and relative efficiency 50 % for Co-60 (1332 keV), is shown in Figure 3 compared to the spectrum outside the chamber (without shielding).

In the regions of interest of two key radionuclides occurring in wastes, i.e. Cs-137 (661 keV) as a representative of fission products and Co-60 (1332 keV) as a representative of corrosion products, the background for Cs-137 is reduced twenty-five times and for Co-60 fifty times. This leads to a significant decrease of minimum detectable activities to several Bq/kg for light waste materials.

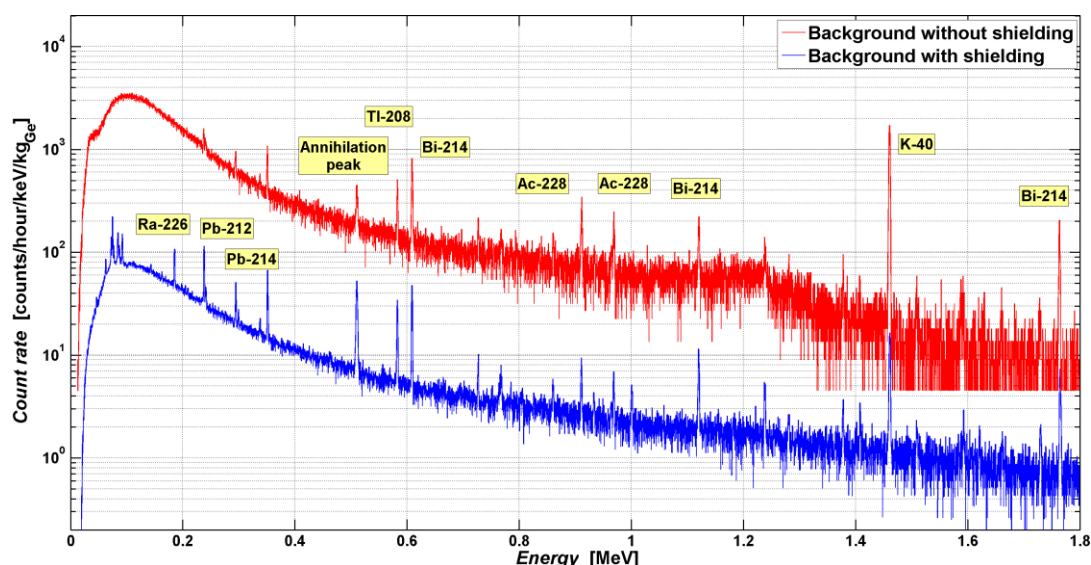


Figure 3: Comparison of gamma-ray spectra acquired outside and inside the measurement chamber

The experimental free release measurement facility was constructed and built in close cooperation with partnering institutes and a company producing ionising radiation measuring devices.

#### 3.1.1.2 HPGe detectors characterisation

Because the measured wastes contain different materials of different densities and shapes, determination of radionuclide activities depends significantly on self-absorption in the measured material. For accurate measurement, full-energy peak efficiency as a function of photon energy must be determined for tens of different types of materials. It is impossible to prepare special real reference materials for all types, therefore detection efficiencies were calculated with three Monte Carlo codes (MCNPX, PENELOPE, GEANT 3.21). For HPGe detectors used in the experimental facility, precise models were prepared and efficiencies calculated in the photon energy range from 59.5 keV to 2 MeV. For all three MC codes, the models were validated using real and spiked reference materials and standard sources developed within the project (see chapter 3.4.1).

Detector: p-type coaxial high-purity germanium crystal, diameter 85 mm, height 30 mm; aluminium cryostat; relative efficiency 50%, resolution FWHM 2.0 keV for Co-60.

For the model, the dimensions given by detector's producer were used, verified and refined using X-ray imaging (Figure 4).

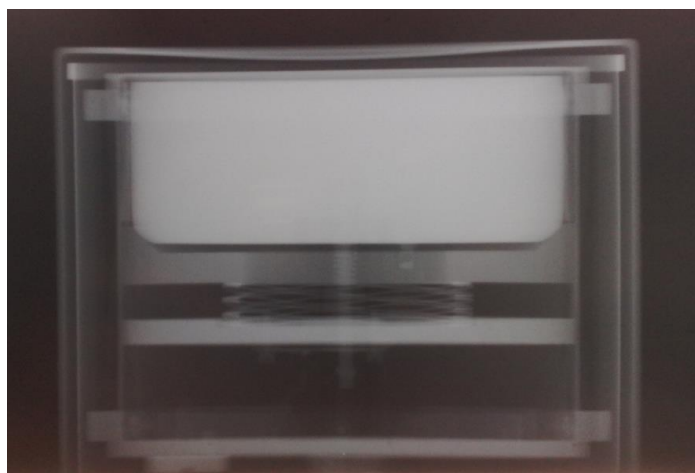


Figure 4: X-ray image of the detector

The Monte Carlo models of the IDM detector were created in three independent Monte Carlo codes based on the information obtained from the manufacturer and from an X-ray image of the detector. The models were validated and used for the optimisation of the parameters of the experimental facility. The models were created by three partnering institutes, which adds value to their credibility.

#### 3.1.1.3 Measuring geometry optimisation and validation

Monte Carlo calculations were used to optimise the thickness of the shielding chamber material, the dimensions of the container and the shape of detector collimators of the Free Release Measurement Facility. For the simulations, the validated model of the germanium detector was used.

A complex model of the FRMF was created in the Monte Carlo code MCNPX and the calculations were done. For optimisation of standard waste containers, a detector model created in the PENELOPE code was utilised. All calculations were performed to get a statistical uncertainty less than 3% ( $k = 1$ ).

Internal dimensions of the measuring chamber, floor thickness (60 cm) and thickness of the doors (20 cm) were predetermined by the dimensions of the detector modules, dimensions of measuring container and total weight of the doors. Optimisation was performed for the thickness of the walls and thickness of the ceiling. Calculations were performed concerning lead collimators usage.

As a result, the following decision was made:

- wall thickness 40 cm, ceiling thickness 50 cm
- pyramidal collimators of 5 cm thickness are convenient

Validation of the measuring geometry model was performed using reference materials and standard sources developed within the project (see chapter 3.4).

For all measurements, the difference between the calculated and measured activities was less than 10% and therefore the Monte Carlo model for detection efficiency calculation was validated.

Full-energy peak efficiency as a function of photon energy was calculated in the energy range from 59.5 keV to 2 MeV for four types of material (steel tubes, aluminium plates, plastics, building materials) and point sources simulating hot-spots. For the measurement of real waste materials, it is expected that the detection efficiency will be calculated for at least tens of material types.

#### 3.1.1.4 Software for free release measurement

For the entire system to function, the device has to be connected to a PC for measurement and analysis. The whole software system is divided into several modules.

*Measuring and communication module* is an autonomous system used for management and analysis of the whole process; it provides communication with the PLC and the MCA. This module also manages storing of measurement data in a relational database using web services made accessible by means of an application server.

*Client module* comprises a graphical user interface (GUI) for Windows OS. Communication between the client and the control system takes place via a TCP/IP-based protocol.

*Gamma spectrometric system* is used primarily for setting up and testing the spectrometric system; it is also utilised by the measuring module for communication with the acquisition of spectra and spectral analysis.

For experimental free release measurement facility, spectrometric software GAMWIN (developed by ENVINET a.s.) was used for spectra acquisition and evaluation, and for spectrometer performance control.

*Database system* allows access to the relational database (reading, writing) via the application server and its web services. The relational database may be, e.g., Oracle, Firebird, MS SQL Server, etc.

*Application server (web interface)* component of the web application is made as a set of so-called Java servlets, running as needed on the application server.



*Web client* component of the web application runs in an ordinary WWW browser (Internet, Explorer, Chrome, Firefox, etc.).

### 3.1.2 Repository acceptance measurement of radioactive wastes before repository

Standardised traceable measurement method was developed to enable acceptance of waste packages containing low and intermediate level radioactive waste into a repository according to EC and national legislation, international recommendations (IAEA, NEA) including design of RAMF, software, calibration and testing. This method is based on gamma-ray spectrometry using germanium detector with high resolution enabling measurement of mixtures of radionuclides in waste packages and special collimator enabling measurement in a wide dynamic range.

#### 3.1.2.1 Experimental Repository Acceptance Measurement Facility (RAMF) construction

Experimental repository acceptance measurement facility was constructed and built at the Czech company ENVINET a.s. The RAMF (Figure 5) consists of the following main parts:

- detection unit with electrically cooled shielded coaxial HPGe detector
- special automatic lead collimator
- assembly for positioning of drums with the measured wastes



Figure 5: Experimental repository acceptance measurement facility

#### 3.1.2.2 HPGe detector characterisation and validation

For the HPGe detector used in the experimental repository acceptance facility, a precise model was prepared and efficiencies calculated in the photon energy range 59.5 keV to 2 MeV. The model was then validated using real and spiked reference materials and standard sources developed within the project (see chapter 3.4.1).

Detector: p-type coaxial high-purity germanium crystal, diameter 55 mm, height 60 mm; aluminium cryostat; relative efficiency 28%, resolution FWHM 1.8 keV for Co-60.

The Monte Carlo model of the detector was created in the Monte Carlo code PENELOPE, based on information obtained from the manufacturer and from an X-ray image of the detector. The model was then used for calibration of the experimental repository acceptance measurement facility.

#### 3.1.2.3 Software for repository acceptance measurement

Software for repository acceptance measurement is based of the same modules and principles as described in the Chapter 3.1.1.4 for the free release measurement. The main difference is that the free release

measurement is aimed to low activities and detection limits, whereas repository acceptance measurement is aimed to high activities and wide dynamic measurement range.

### Summary of 3.1 results

Vast amounts of building waste at decommissioned nuclear power plants contain very low levels of radioactivity. Accurate on site monitoring is required to enable its consignment as 'free release' for land fill disposal or its designation as nuclear waste requiring long term storage in space limited nuclear waste repositories. Transportable waste measurement facilities which are easily moveable between nuclear sites undergoing decommissioning would assist this waste categorisation procedure.

An easily transportable automated prototype free release measurement facility has been designed and its HPGe gamma-ray radiation detection system's performance Monte Carlo modelled and experimentally validated using the reference materials developed in the project (objective 4). To prevent inaccurate measurements due to elevated ambient radiation backgrounds shielding is provided by novel lightweight and low background radioactivity bricks which can be easily re-assembled at another nuclear site undergoing decommissioning. A comprehensive system operation and measurement software package has been developed and tested to ensure that radionuclide quantification and identification by gamma-ray spectroscopy can be accurately and traceably determined using the on board nuclide library. This ensures legal free release clearance levels can be traceably measured and nuclear decommissioning waste can be safely and appropriately released or consigned to waste repositories.

In order to maintain an accurate long term inventory of the radioactive content in nuclear waste repositories it is essential to perform accurate acceptance measurements of incoming waste consignments. A waste repository acceptance measurement facility capable of meeting current industry requirements has been modelled and an operational design finalised. A prototype HPGe spectroscopy detection system incorporating a special collimator has been assembled for waste measurement and its performance validated using project manufactured reference materials. An appropriate nuclide library has been assembled and used to ensure the wide dynamic range of nuclides and activities likely in operational use can be accurately assayed.

## 3.2 *In-situ* radiochemical analysis

### 3.2.1 Technical Objectives

The technical objectives for *in-situ* radiochemical analysis were split into three main sections:

- initial sample processing
- development of analysis systems suitable for the use with sample processing and radionuclide measuring systems
- calibration and validation of radionuclide measuring systems

### 3.2.2 Initial sample processing

Current sample processing techniques are laboratory based, and involve forcing conditions for example, use of high temperatures, strong mineral acids (including hydrofluoric acid) that may not be appropriate to field deployment. Thus the work carried out here produced recommendations from work carried out in the laboratory in order to convert non-aqueous samples which potentially could have excess silica ( $\text{SiO}_2$ ), silicate ( $\text{SiO}_4^{4-}$ ) and phosphate ( $\text{PO}_4^{3-}$ ) prior to analysis into a form suitable for analysis by automated chemistry systems.



Figure 6: KATANAX K2 system.

A procedure for sample processing was produced as an outcome of this work, using:

- an automated sample fusion system (KATANAX) to destroy sample matrices, based on  $\text{LiBO}_2/\text{Li}_2\text{B}_2\text{O}_7/\text{LiBr}$  fusion to produce a melt that is soluble in dilute nitric acid.
- this melt is then dissolved in dilute nitric acid and excess silica removed by precipitation with poly ethylene glycol.
- the resulting solution was then prepared by evaporation with a small amount of HF to destroy the final traces of silica and resissolved in dilute nitric acid to produce a clear, stable solution for subsequent analysis

### 3.2.3 Development of analysis systems suitable for use with sample processing and radionuclide measuring systems

This part of the work assumes that a sample (as above) has been formed into a suitable matrix for radioactive samples to be chemically separated by an automated radiochemistry system. Once this has been carried out the sample is put through the radiochemical system for in-situ separations of Sr-90, Tc-99, uranium, plutonium and Am-241, using an Automated Radiochemistry system (ARS-IIe).

The delivery of this part was problematic in that the automated system (the NorthStar ARSIIe) was not capable of handling the samples presented to it.

Repeated interactions with the manufacturers were problematic, and this delayed work on this part of the work package. In the end, some success was achieved in that the analyses carried out by the ARSIIe worked on low solid content materials. Therefore bench procedures were generated, principally at PTB, that were capable of later migration to this, or an alternative automated system.

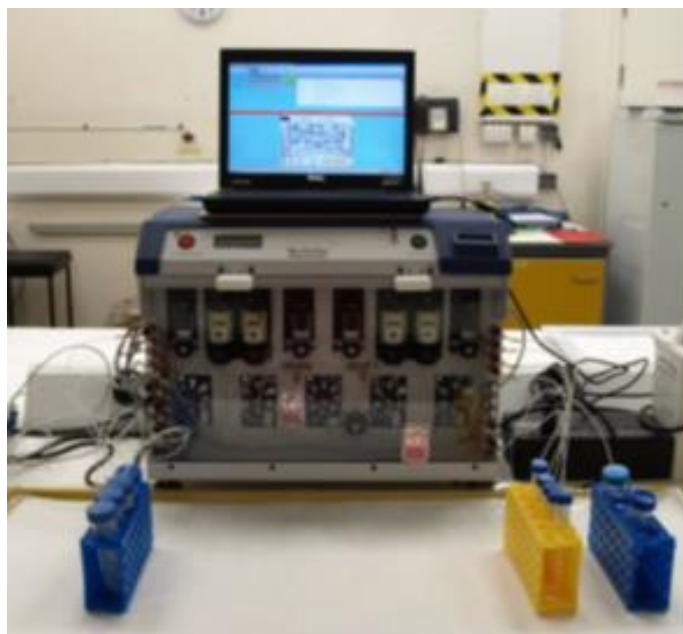


Figure 7: ARS-IIe with input and outputs connected to the respective vessels.

All in all the success of this part of the work package was entirely dependent on the performance of the ARSIIe and suffered as a result, but workable procedures have been developed and validated.

### 3.2.3 Calibration and validation of radionuclide measuring systems

Measurement systems employed for this part of the work package were based on liquid scintillation counting either primarily for  $\alpha$ -emitters, using the PERALS system:



Figure 8: Portable PERALS system

Alternatively, the measurement of  $\beta$ -emitters was carried out using the TriAthler detector:



Figure 9: Portable TriAthler system

PTB also did work on their own PERALS.

The calibration of these two counters was carried out for the project for the selected radionuclides – Sr-90, Tc-99, uranium  $\alpha$ -emitters, plutonium  $\alpha$ -emitters and Am-241.

#### 3.2.3.1 PERALS

This system is based on liquid scintillation counting, but with some signal discrimination to resolve events arising from  $\alpha$ ,  $\beta$  or  $\gamma$  detection. Thus, PERALS is designed specifically for  $\alpha$ -liquid scintillation spectrometry, although the successful achievement of such measurements is reliant on three factors: (i) the system electronics, (ii) optical integrity of the detector, and (iii) the chemistry of the sample preparation.

The last factor is wholly within the control of the user and the chemistry is based on solvent extraction, with three steps being required for successful source preparation. These are:

- to separate the radionuclide of interest from other radionuclides that may interfere with the identification and quantification
- to concentrate the nuclide into a small volume of an adequate solution media for increased analytical sensitivity, and
- to extract the nuclide into an appropriate scintillator (extractive scintillator) of constant, reproducible response to  $\alpha$  particles.

The PERALS systems are available either as NIM based units or as a portable version.

Counter linearity is excellent up to 50 kBq and as this exceeded the expected activity levels the detector is suitable for the purposes of this work. The benefits of  $\alpha$  spectrometry based on PERALS is that by the use of extractive scintillator it is possible to gain a quantitative extraction at phase ratios, as well as this the background attainable with the PERALS is very low because it is possible to reject virtually all of the ambient  $\gamma$  background. This is further shown by the measurements taken of U-232 from these spectra, where the peak in Figure 11 represents the top phase of the solution after it was dispensed into a separate vial. The resolution has improved and the tail has disappeared thus improving the FWHM max of the measurement.



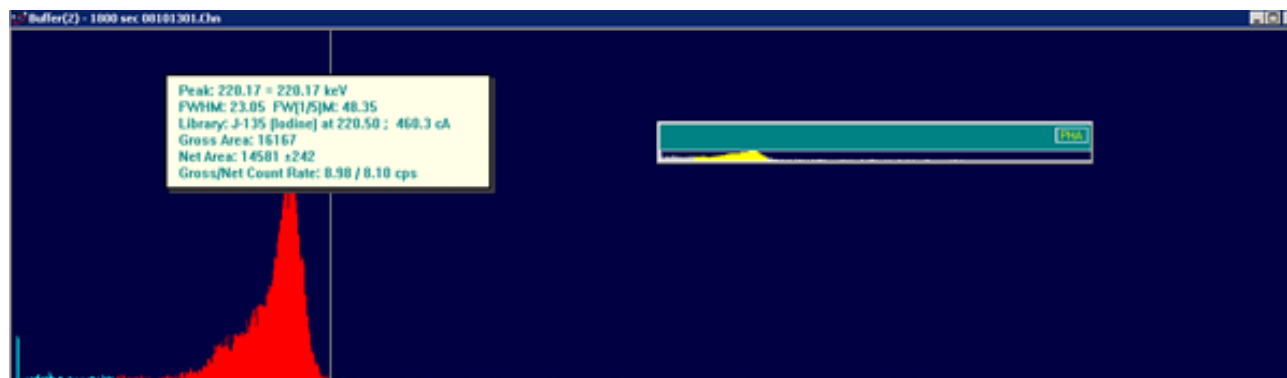


Figure 10: Spectra of U-232 taken from whole phase of solution before separation.

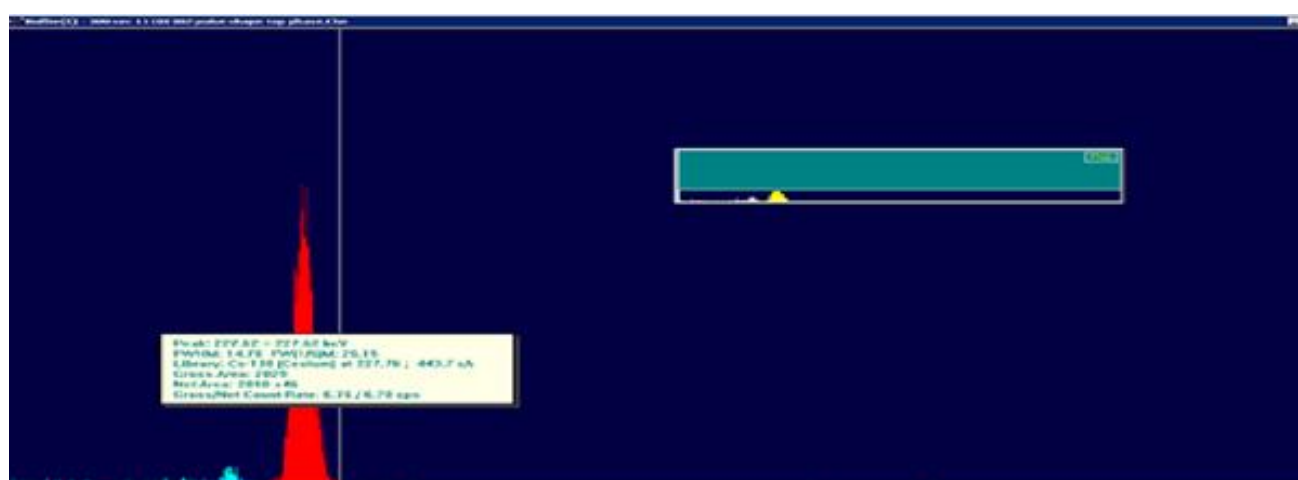


Figure 11: Spectra of U-232 taken from just the top phase of the separated solution in the extractive scintillant.

### 3.2.3.2 TriAthler

The TriAthler is based on 'conventional' liquid scintillation counting (as opposed to the pulse analysis employed by PERALS) based on single-photomultiplier detector, which can be applied to a wide variety of radionuclides – and is therefore somewhat more versatile than the Peralas. The detector is both portable and compact instrument that provides instant results for liquid scintillation counting and luminescence measurements. In liquid scintillation mode, the TriAthler has pre-set counting windows for various radionuclides and, for the project, was set up to count Sr-90/Y-90, with the option to include Tc-99.

Work therefore focused on the measurement of Sr-90 after radiochemical separation. This delivered Sr-90 in ~20 mL of 0.05 M HNO<sub>3</sub> with recovery measured using Sr-85 as a tracer.

For the optimisation of the measurement conditions, it was firstly evaluated whether 0.05 M could be directly mixed with the scintillation cocktail and the sample:cocktail ratio was optimised to a ratio of 7:13 was chosen for further work. A *BETA* protocol of the equipment was modified to be used as protocol for strontium measurements and vials containing Sr-90 and Sr-90 in 0.05 M HNO<sub>3</sub> were measured in order to evaluate and choose the regions of interest. No Y-90 separation was done at this point and the observed spectra are shown in Figure 12.

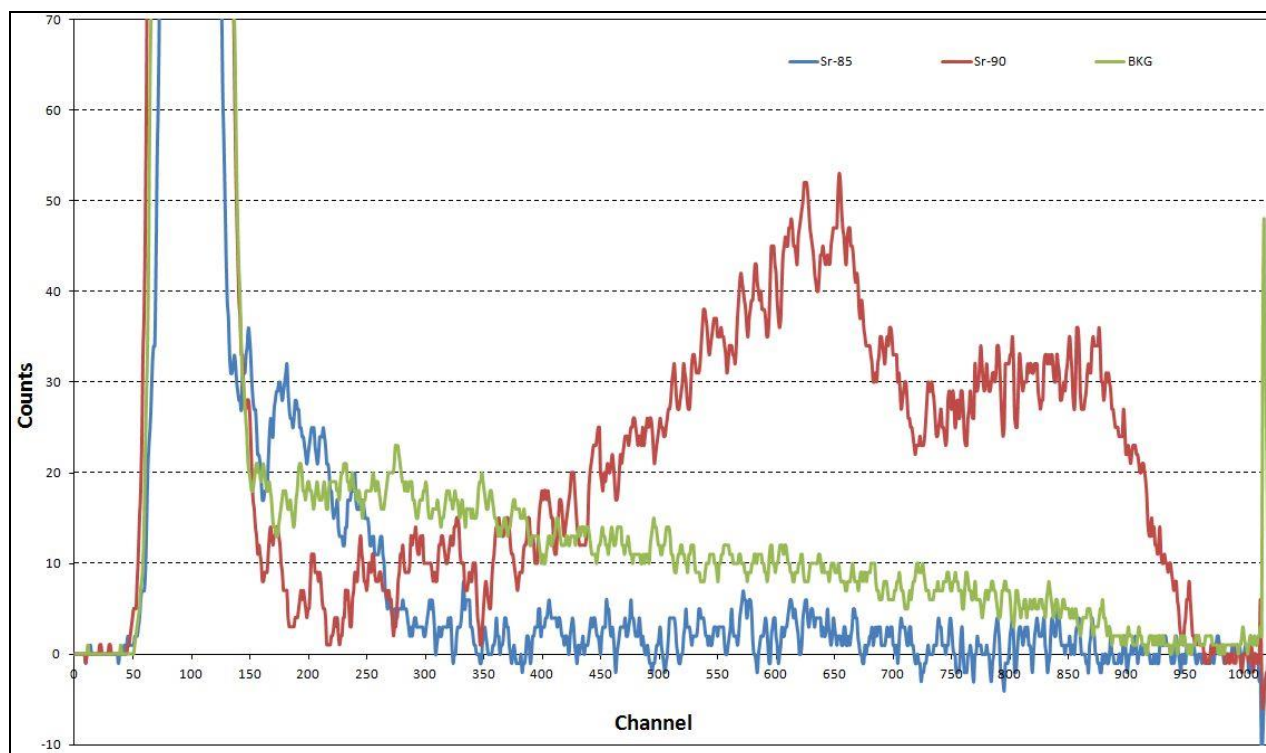


Figure 12: Spectra corresponding to background, Sr-90/Y-90 and Sr-85. In the case of active vials, background signal has been subtracted.

The spectrum of Sr-85 shows a signal at the lower region (channels 150-300), which signal does not interfere with that of Sr-90/Y-90 (channels 350-950) and this shows that the Sr-85 does not interfere with the measurement of Sr-90 and can therefore be used as tracer.

### 3.2.3.3 Mass spectrometry

Mass spectrometry may be employed in the determination of long-lived radionuclides ( $t_{1/2} > 10\,000$  years), or where detection is difficult. In this project, the measurement of  $^{41}\text{Ca}$  by ICP-MS was attempted with limited success. Calcium-41 is long lived ( $t_{1/2} \sim 10^5$  y) and is difficult to detect, decaying by electron capture with the emission of low energy X-rays. It was thus determined by an ICPMS (Agilent 7000) equipped with octopole reaction system (ORS). Calibration curves were prepared using a standard reference solution of  $\text{Ca}_{\text{nat}}$  with  $^{45}\text{Sc}$  as an internal standard.

Then, aliquots of mineralised sample solutions were spiked with known amounts of a standard Ca-41 solution and a calibration curve constructed for this nuclide. However, this met with limited success, due to the high abundance of  $\text{Ca}_{\text{nat}}$  in the samples and interference from the argon plasma.

### 3.2.4 Outcomes and overview

Overall much progress was made during the course of the project, future work will needed to further optimise the separation and measurement strategies.

Work on the reliable solubilisation of concrete samples was the most tangible outcome of this work package, and a successful, reliable and repeatable method to convert concrete samples to a clear and stable solution. Also, validation of the measurement systems was successful and extended the range of measurement options for such work to portable and thus field deployable systems.

Although the ARS-IIe was designed to carry out complex separation chemistry, practical experience shows that this is not always achieved and severe problems were encountered at both individual ARS-IIe units. These issues are detailed in the summary report for the project, but need solving if this system is to be used in future.

Greater success was achieved with the PERALS and the TriAthler with good performance being achieved and validation of both these systems being carried out.

The use of mass spectrometry conveys some advantages, particularly in analysis time, but is subject to matrix effects leading to signal loss and thus underestimation of sample analytes.

Overall, difficulties with the ARSIIe meant that although in practice the work has been carried out, the operational issues have resulted in a lack of coherent progress. In future projects such as MetroDecom that the ARSIIe will not be used and an alternative will be put into place.

Due to the success of the KATANAX, PERALS and TriAthler will be used in future experiments and protocols are currently being used to further the progress made with the equipment. The instruments and protocols made in the project are being now routinely used partnering laboratories and will be also used in the new project 'Metrology for decommissioning nuclear facilities'.

### Summary of 3.2 results

Some wastes require supplementary analysis using radiochemical techniques. Contaminated waste samples are currently sent to offsite radiochemistry laboratories where time consuming extraction techniques are used to produce aqueous solutions suitable for analysis. The use of portable compact rapid radiochemistry extraction and measurement methods at the point of waste generation is required to speed the waste consignment decision process and enable the timely and effective resolution of decontamination problems during decommissioning works.

One of the largest waste streams created during nuclear decommissioning is from the reactors concrete bio-shield. The extraction of radionuclides from concrete for accurate radioactivity measurement is particularly difficult. The project sought to assess the viability of commercial instruments for on-site radiochemical analysis. This involves: initial sample processing to extract radionuclide; radionuclide measuring systems; and the calibration and validation of such systems.

A number of commercial instruments were investigated. The KATANAX fusion system which uses a heated flux solvent to extract inorganic species from cements, ceramics, and refractory materials was found to give rapid and reproducible samples. A procedure enabling concrete preparation for wet chemistry devised that would be suitable for use in a basic radiochemistry laboratory on a nuclear site undergoing decommissioning. An automated wet chemistry radionuclide separation system (North Star ARSIIe), originally designed for the pharmaceutical industry, was found to be unsuitable for decommissioning applications and alternative validated lab based methods were developed for nuclide separation and activity measurements. The compact PERALS (Photon-Electron Rejection Alpha Liquid Scintillation) and TriAthler liquid scintillation counting systems were investigated and both were validated for potential use for radioactive concentration determination in a basic radiochemistry lab.

In conclusion, work on the reliable solubilisation of concrete samples was the most tangible outcome of this work, and a successful, reliable and repeatable method to convert concrete samples to a clear and stable solution was developed. Validation of the measurement systems was successful and showed that such measurements may be carried out in an on-site laboratory using commercially available instrumentation.

### 3.3 Measurement of gaseous effluents in radioactive waste repositories

An important aspect of the handling and long-term management of radioactive wastes is degradation of the wastes during storage or after repository emplacement and the release of gaseous radioactive species from the wastes into the container, the repository or the wider environment.

Substantial quantities of organic and metal wastes are present in LLW and ILW and will gradually evolve gases (e.g. hydrogen, methane, and other carbon species) over time. These bulk gases may include tritium and C-14 species which require measurement to (i) alert workers to high levels of airborne activity during the operational phase of the repository, and (ii) aid research into waste degradation mechanisms during the post-closure period. This may include monitoring of gases emanating from waste packages in storage, area monitoring of waste stores (e.g. disposal holes, tunnels, vaults and both sealed and unsealed silos), or gas

that has migrated through soil to the surface above the repository. A key aspect of these needs is that the activity of individual radioactive species (e.g.  $^{14}\text{CO}_2$ ) must be measured.

Four tasks have been undertaken to initially address these metrology needs: (i) the development of a time-integrated gas-in-air monitoring method for long-term measurements, (ii) the development of an ionisation-chamber based real-time gas-in-air monitoring method for short-term measurements, (iii) a study of ancillary methods for rapid sampling and assay of gases from individual containers, and (iv) the development of a mid-infrared spectroscope for carbon isotope analyses.

### 3.3.1 Time-integrated gas-in-air monitoring

Measurement of the specific activity of the gas at source (i.e. in the container itself) is a key parameter. This can be calculated by measuring simultaneously the activity concentration of the analyte concerned (say,  $^{14}\text{CO}_2$ ) in the repository air and the concentration of its bulk inactive analogue (in this case,  $\text{CO}_2$ ). The latter measurement can be carried out with existing bulk gas monitors, but the former is more difficult. Current practice for differentiating between different gaseous chemical forms of the same radionuclide (say, between  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$ ) is to use integrated gas-in-air monitoring ('bubbler') systems, followed by manual sampling of gas-trapping fluid and assay by liquid scintillation counting. However, an automated system is required in order to minimise required manpower, potential exposure to active gases and delays between sample collection and assay.

An automated integrated system incorporating two gas bubbler trains, a furnace, a fluid handling system, a portable liquid scintillation counter and a data analysis system capable of remote operation via a computer interface and data network has been designed, built and tested, and is designated the Automated Environmental Radioactive Gas Monitoring System (AERGMS – see Figure 13).

The response of the LSC2 to commercial standard scintillation sources of H-3 and C-14 was measured in order to determine an optimum operating voltage for the AERGMS; a voltage of 900 V was selected. For routine operation of the AERGMS, sodium hydroxide solution (1.5 M) was selected as the trapping fluid and Optiphase HiSafe 3 was chosen as the liquid scintillant. NPL standard solutions of H-3 and C-14 were combined with the trapping fluid and scintillant and counted.

Extensive tests were carried out on system functionality such as air sampling, bubbler train filling and draining, setting of liquid level sensors, fluid flow and mixing. Software for the AERGMS was written at NPL using LabView 2012 (National Instruments) and has been used for filling of bubbler trains to operator-specified set points, operation of the air intake pump and monitoring of air-flow during air sampling. Further functionality can be added later if required.

Finally, the AERGMS was tested with a sample of  $^{14}\text{CO}_2$  in 180 L of dry air to mimic potential conditions in a waste repository and to determine the  $\text{CO}_2$  trapping efficiency of the bubbler trains. The 'pre-furnace' bubbler train trapped around 37 % of the carbon dioxide from an air volume of the order of 180 litres and less than 1 % reached the post-furnace bubblers. The Limit of Detection for  $^{14}\text{CO}_2$  in ambient air using the AERGMS was estimated as being of the order of 1 - 10  $\text{kBq m}^{-3}$ , but this needs to be confirmed by further experiments. Regarding system decontamination, approximately 99 % of initially trapped activity in a bubbler train was found to be removed by rinsing the train twice. The AERGMS was exposed to a nominal atmosphere of  $^{222}\text{Rn}$  in air; the trapping efficiency of this nuclide and its decay products was found to be < 0.1 %.

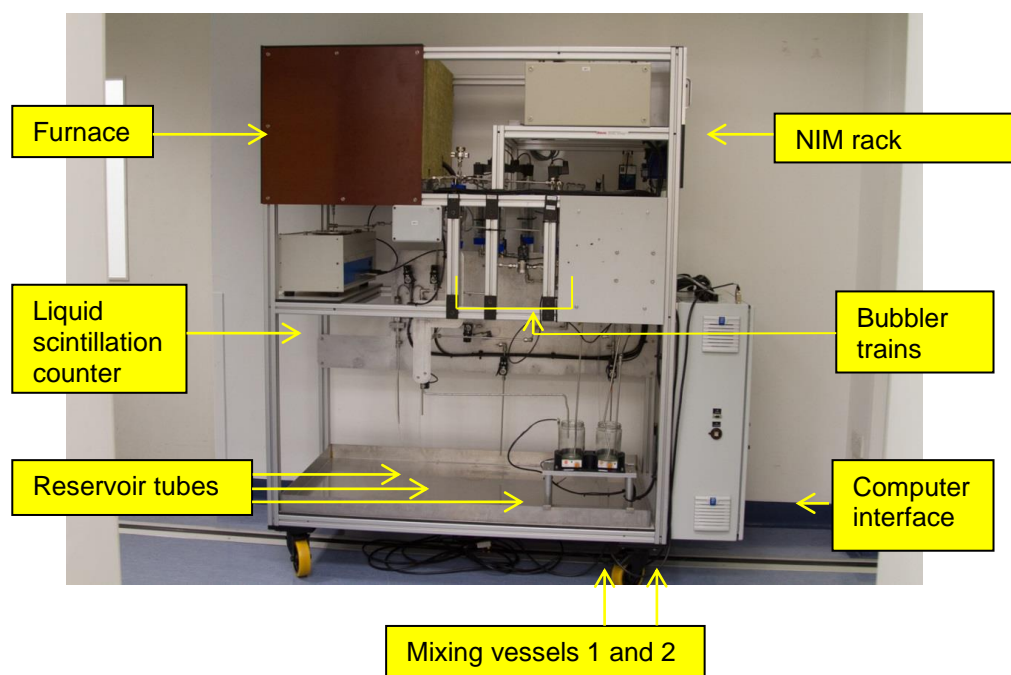


Figure 13: AERGMS system

The project has demonstrated the effective application of the AERGMS system for trapping and counting of  $^{14}\text{CO}_2$  at concentrations representative of those in a waste repository. Future work can build on the findings of this project by further investigating the effect of air flow rate, in-line pressure drops, ambient air temperature, and sampling time on factors including the trapping efficiency and sensitivity.

### 3.3.2 Real-time gas-in-air monitoring

There is a need for monitoring of gaseous species in the workplace in real time for worker safety and to meet regulatory requirements. Current practice is to use radioactive gas-in-air monitors (e.g. ion-chamber based), but these cannot differentiate between different species. The aim of this task was to design, build and test equipment for the real-time monitoring of individual radionuclide species. This was done in two parallel stages:

- building and testing a cryogenic system for the separation of  $\text{CO}_2$  from air to demonstrate the feasibility of this generic method for isolating individual  $^{14}\text{C}$ -labelled gases from air prior to radioassay;
- calibration of a radioactive gas-in-air monitor for  $^{14}\text{CO}_2$  to demonstrate its response to this species.

A cryogenic system would allow the components gases of an air sample to be separated on the basis of the differences between the phase transition properties of the gases. The method used involved de-sublimating  $\text{CO}_2$  at low temperature and pressure and was accomplished as follows:

- aspiration of air from the environment of interest, followed by compression;
- cooling to the sublimation temperature of  $\text{CO}_2$ ;
- pumping out and discharging other main gaseous components of air (e.g.  $\text{N}_2$ ,  $\text{O}_2$  and Ar);
- warming up the  $\text{CO}_2$  and storing it in a suitable receptacle prior to radioassay.

Figure 14 represents the initial 'conceptual design' of the cryogenic system. The final equipment was built by the Italian company '5Pascal'. The system is large (170 cm high, 170 cm wide and 110 cm deep), but



building a more compact system would have significantly increased the costs and manpower required to produce an adequate design.

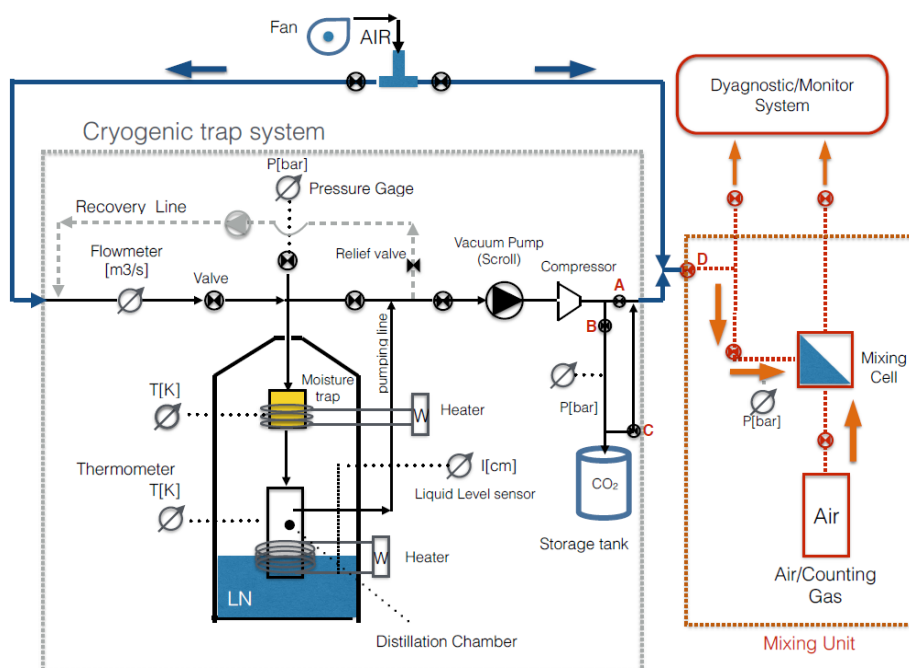


Figure 14: Conceptual design of cryogenic system

The equipment has demonstrated the feasibility of separating CO<sub>2</sub> from air by de-sublimation, although only a limited amount of CO<sub>2</sub> capture was achieved. However, significant experience has been gained in the design of such a system and its operational procedure. The main issue is to devise a suitable heat exchanger to enable the adjustment of the equilibrium temperature of the mixture inside the condenser unit and which can maintain the temperature in the range 120 - 140 K at a pressure of about 3 - 5 bar. The condenser must be redesigned so that flow-rate pressure loss is reduced and the surface on which CO<sub>2</sub> can be frozen by de-sublimation is maximised.

In parallel with the development of the cryogenic system, a radioactive gas-in-air monitor was calibrated using a standardised <sup>14</sup>CO<sub>2</sub> cylinder (see Chapter 3.4). The monitor selected was an Overhoff 200SB tritium monitor. A calibration factor was derived for low levels of <sup>14</sup>CO<sub>2</sub> in an air mixture containing ~3% CO<sub>2</sub>. Its response to <sup>14</sup>CO<sub>2</sub> in this gas composition was found to be ~3.7 times that of tritium.

A prototype gas transfer and measurement system (incorporating the monitor) was also constructed for connecting to the cryogenic system. Due to time limitations, it was not possible to use this manifold in the course of the project, but a method has been developed and can be applied in future studies.

This task has demonstrated that using a cryogenic system to separate CO<sub>2</sub> from an air sample prior to radioassay is feasible, although further work is required to optimise this process. The project has demonstrated that a commercial radioactive gas-in-air monitor will respond adequately to <sup>14</sup>CO<sub>2</sub> in a gas composition that the cryogenic system would generate. Further studies can build on this work, e.g. by further developing the cryogenic separation process and by producing a more compact system.

### 3.3.3 Testing of gas samplers

The ability to rapidly assay packages or areas suspected as having high gaseous activity content would complement the use of monitoring instruments, enabling priority packages or areas to be identified quickly and at low cost. The aim was to identify suitable sampling devices and to evaluate them using standardised atmospheres of radioactive gases. Various samplers were considered, and a type of passive sampling device designed by the Institut de Radioprotection et de Sûreté Nucléaire (IRSN) for sampling HTO was selected for testing. The basic device was modified by IRSN to enable the simultaneous collection of <sup>14</sup>CO<sub>2</sub>

and tritium species. Three devices were tested, each designed for a different combination of these species. Each device was exposed for ~ 120 hours to an appropriately characterised atmosphere at NPL. The atmospheres were (ii)  $^{14}\text{CO}_2$  and HT, (iii)  $^{14}\text{CO}_2$  and HT gas and HTO vapour, and (iii)  $^{14}\text{CO}_2$  and HTO vapour. Temperature and humidity were monitored throughout. Atmospheres of HT and  $^{14}\text{CO}_2$  were generated from cylinders containing the individual standardised gases, whereas HTO vapour atmospheres were generated from a standardised solution in a Drechsel flask.

Estimates of the activities of  $^{14}\text{CO}_2$  absorbed by the samplers were made by collecting  $^{14}\text{CO}_2$  remaining in the enclosures and carrying out system pressure measurements, and by trapping of  $^{14}\text{CO}_2$  and assay by liquid scintillation counting. Similarly, residual HTO was trapped in a dry ice / acetone bath (or sampled from the enclosure) prior to liquid scintillation counting. Table 1 gives the results of measurements made by IRSN of  $^{14}\text{CO}_2$  and HTO in samplers exposed to known atmospheres and the predicted activities. The results are not in agreement, and the reasons for this need to be further investigated, but the data are of the same order of magnitude and indicate that samplers of this type have potential to be deployed in repository environments for assay of these species in containers or areas. (NPL acknowledges the co-operation of IRSN in providing these samplers, analysing them and providing data.)

Table 1: Results of measurements of samplers at NPL and IRSN

Atmosphere	Compound	Activity predicted by NPL (Bq)	NPL unc. (%)	Activity measured by IRSN (Bq)	IRSN unc. (%)
$^{14}\text{CO}_2$ , HT, HTO	$^{14}\text{CO}_2$	640	12	522.7	5
$^{14}\text{CO}_2$ , HTO	HTO	320	12	-	-
	$^{14}\text{CO}_2$	166	12	156.3	5

#### 3.3.4 Mid-infrared spectroscope for carbon isotope analyses

Gaseous radioactive emissions from stored wastes are dominated by C-14, which is present in all parts of nuclear power plants. Sensitive and fast measurement of C-14 is thus needed to allow better monitoring and control of releases from nuclear power plants and radioactive waste repositories. In addition to the methods described above in 3.3.1 and 3.3.2, a mid-infrared spectrometer was developed for the detection of C-14. It uses a quantum cascade laser (QCL) as light source and is therefore compact and well-suited for on-site measurements. The results presented here show that this instrument is ideal for field measurement as it is compact and the achieved sensitivity is sufficient in the context of radioactive waste management, where elevated levels of C-14 are found.

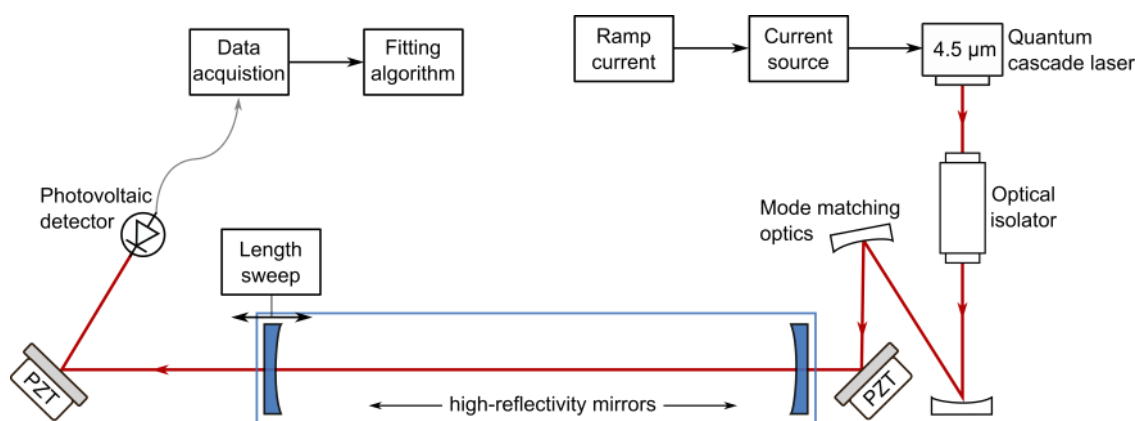


Figure 15: Schematic illustration of the experimental arrangement

To reach the necessary sensitivity, cavity ring-down spectroscopy (CRDS), one of the most sensitive spectroscopic techniques, was used. This technique allows for an absorption path length of several kilometres owing to high-reflectivity mirrors placed around the measurement cell. The sensitivity is thus greatly increased in comparison with traditional spectroscopy techniques. CRDS relies on the measurements of decay rates after switching off the light source. Once no more light is entering the cavity, the light inside the cavity slowly leaks out. Without absorption, the decay rate depends mostly on the reflectivity of the mirrors. When the laser is tuned over an absorption line, additional losses occur due to absorption and a larger decay rate is observed. By comparing the inverse of the decay rate, the ring-down time  $\tau$ , with  $\tau_0$ , the ring-down time in vacuum, one can directly infer the strength of the absorption line  $\kappa(\nu)$ , and the concentration of the species of interest according to  $\kappa(\nu) = \sigma(\nu)N = (\tau_0 - \tau)/(c\tau\tau_0)$ , where  $\sigma(\nu)$  is the absorption cross-section and  $N$  the number density. The ring-down time is determined by fitting the experimental signal with an exponential decay model.

Instead of detecting C-14 directly,  $^{14}\text{CO}_2$ , carbon dioxide, produced through microbial cell respiration, is targeted. First, a suitable absorption line has to be found.  $\text{CO}_2$  absorption lines are situated around  $2300\text{ cm}^{-1}$  ( $4.3\text{ }\mu\text{m}$ ). Isotopic shifts are relatively important in carbon dioxide, and a shift of about 70 wavenumbers (or 120 nm) is observed between  $^{13}\text{CO}_2$  and  $^{14}\text{CO}_2$ . It is thus possible to find a strong absorption line of  $^{14}\text{CO}_2$  that does not interfere with absorption lines of other isotopes. For the detection of  $^{14}\text{CO}_2$ , the strongest conceivable absorption band corresponds to the fundamental asymmetric stretching vibration band  $\square\square$ , and in particular, the P(20) line at  $4.527\text{ }\mu\text{m}$  ( $2209.1\text{ cm}^{-1}$ ).

The experimental arrangement is schematically shown in Figure 15. The measurement cell is formed by a 40 cm long cavity with high reflectivity mirrors (99.98 %). A typical vacuum ring-down time of  $5.5\text{ }\mu\text{s}$  is obtained. The novelty of this CRD spectroscope is the use of a continuous-wave QCL as a light source for the detection of  $^{14}\text{C}$ . Using two spherical mirrors, the mode of the laser is matched to the mode of the cavity. The light exiting the cavity is focussed onto an InAsSb photovoltaic detector. The absorption spectrum is inferred from the ring-down times recorded as a function of the laser frequency. A metering valve allows for a controlled injection of the gas, and the pressure is measured with a capacitance manometer. A ramp is applied to the laser current to get light coupled into the cavity, and at the same time, the cavity length is modulated at a slower rate to obtain frequency points between the fixed points determined by the free spectral range of the cavity. The relationship between the current and wavenumber is roughly linear. A ring-down event is produced by applying a rapid step to the laser current. The data are processed using LabView and a fitting algorithm determines the ring-down time. The absorption coefficient is computed using  $\tau_0=5.45\text{ }\mu\text{s}$  which is determined from the baseline.

A reference spectrum of pure  $\text{CO}_2$  with a standard isotopic ratio was first analysed and is marked red in Figure 16. The natural abundance of C-14 is only 1.2 ppt and it was not expected to distinguish the  $^{14}\text{CO}_2$  peak in this spectrum. The peaks visible here correspond to different stable isotopologues of  $\text{CO}_2$ . This spectrum provides the background for our measurement of enriched C-14 samples. A sample with enriched C-14 content was then placed in the measurement cell. Figure 16 shows its absorption spectrum in blue; an additional absorption peak can also be observed. As expected, this is the P(20) peak of  $^{14}\text{CO}_2$  at  $2209.11\text{ cm}^{-1}$ . The absorption spectrum, consisting of about 30000 ring-down events (averaged using a

moving average filter), was recorded over a 30 min time period. Spectra can also be recorded with acquisition time as short as 10 seconds, with still a good signal to noise ratio.

The absorption spectrum shown in Figure 16 was fitted by a sum of Voigt profiles using a non linear least square fitting routine. The obtained fit is plotted in Figure 16 in yellow. The line strength of this line had been measured experimentally before, and found to be  $S_0 = 2.5 \times 10^{-18} \text{ cm}^{-1}/\text{molecule cm}^{-2}$ . The line parameters of the  $^{14}\text{CO}_2$  line, obtained from the fitting of the experimental spectrum, are used to calculate the line area,  $S$ . The density of  $^{14}\text{CO}_2$  molecules is then obtained using  $n_{^{14}\text{C}} = S/S_0$ . With the half-life of  $^{14}\text{C}$ ,  $t_{1/2} = 5730$  years and the pressure in the cell,  $p$ , the activity of the sample,  $A$ , at atmospheric pressure,  $p_0$ , is given by  $A = n_{^{14}\text{C}} \ln 2 / t_{1/2} p_0 / p = 0.101 \text{ Bq ml}^{-1}$ . The activity concentration of the sample was measured independently using primary gas counting techniques, and was determined to be  $0.096 \text{ Bq/ml}$ , which is in good agreement with the MIKES measurement.

It was shown that the mid-infrared spectroscope was capable of detecting low levels of  $^{14}\text{C}$  from a gas sample. A real sample would not be pure  $\text{CO}_2$ , but the air.  $\text{CO}_2$  first needs to be extracted from the air using, for example, a cryogenic trap. The sensitivity of  $0.1 \text{ Bq/ml}$  can be extrapolated to a measurement of  $\text{CO}_2$  extracted from an air sample. The  $\text{CO}_2$  concentration in a typical air sample is 400 ppm, therefore a sensitivity  $0.1 \text{ Bq/ml}$  for pure  $\text{CO}_2$  corresponds to  $40 \times 10^{-5} \text{ Bq/ml}$  or  $40 \text{ Bq/m}^3$  in air. The sensitivity achieved here is thus sufficient for applications in a nuclear power environment.

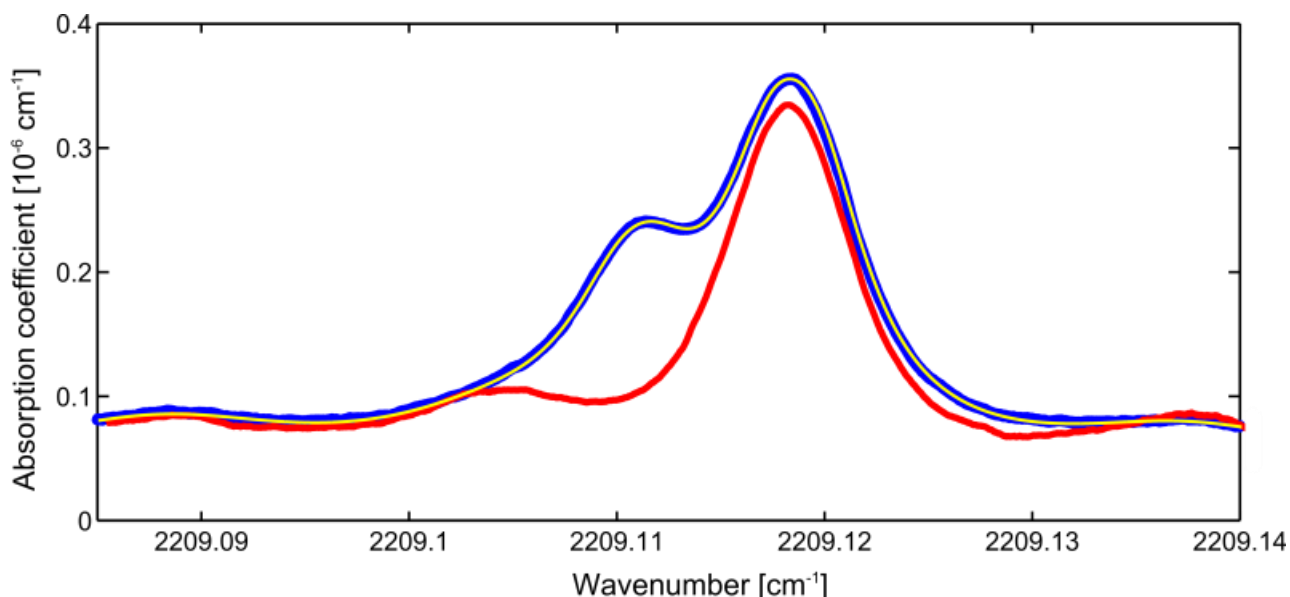


Figure 16: Absorption spectra of two different samples at 22 mbar

### Summary of 3.3 results

A vital aspect of radioactive waste management is that of monitoring the radiation doses both to workers in waste repositories and to the general public. Wastes from decommissioned nuclear power plants can contain trapped radioactive gases (e.g. tritium,  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$ ) and also tritiated (radioactive) water. All may be released into the atmosphere creating a potential dose hazard to site and repository workers, the general public and to the environment. Gas sampling and monitoring is a legal requirement for all sites that can potentially produce radioactive gases. New and improved automated radioactive monitoring systems are required for existing and future nuclear sites and storage facilities.

Within the project prototypes were developed to evaluate the feasibility of:

- Automated radioactive gas sampling and analysis system for long term environmental monitoring
- A real-time cryogenic gas separation and monitoring system suitable for future deployment in a nuclear waste repository

- Devices for passive sampling of multiple radioactive gaseous species
- Using a novel mid-infrared detector specifically for radioactive carbon dioxide

A prototype automated radioactive gas sampling and analysis system was designed, built, calibrated and tested with  $^{14}\text{CO}_2$  at levels predicted to be present in a future nuclear waste repository. The feasibility of automating current gas collection and off-site radioactive assay into a single unit with potential for data networking of several units at a remote central location has been demonstrated. By using an additional gas trapping fluid and a furnace it would be possible to expand the automation of the system to incorporate tritium, tritiated water,  $^{14}\text{CO}_2$  and  $^{14}\text{CH}_4$ .

A prototype gas monitoring system for the cryogenic separation of individual radioactive gases from air has been built and tested demonstrating the feasibility of using this technique for real time radioactive gas-in-air monitoring. The separation of  $\text{CO}_2$  from air has been demonstrated to illustrate the principle of the generic method.

Three novel passive gas samplers, each designed to measure a different combination of  $^3\text{H}$  and  $^{14}\text{C}$  gaseous species, were evaluated in an enclosure containing atmospheres of tritium, tritiated water and  $^{14}\text{CO}_2$  in air to determine gas trapping efficiencies. These samplers are potentially applicable to screening measurements for specific repository areas or waste containers.

Spectroscopy in the mid-infrared enables identification of the presence of different isotopes of a gaseous molecule e.g.  $^{12}\text{C}$  and  $^{14}\text{C}$  in  $\text{CO}_2$ . The use of mid-infrared quantum cascade lasers and cavity ring-down spectroscopy is now offering greater technique sensitivity and much more compact instrumentation making this a viable method for use outside the laboratory. These developments make this technique a candidate for future compact instrumentation for measuring the concentrations of  $^{14}\text{CO}_2$  present in nuclear repositories and facilities or in buildings undergoing decommissioning. The feasibility of measuring very low concentrations of  $^{14}\text{CO}_2$  in a standardised gas sample containing trace  $^{14}\text{CO}_2$  in a  $\text{CO}_2$  carrier gas mixture has been successfully demonstrated within this project.

### 3.4 Calibration reference materials and standard sources

Reference materials and standard sources were developed and manufactured for calibration of measuring devices for free release measurement, *in-situ* radiochemical analysis and measurement of gases in radioactive waste repositories.

#### 3.4.1 Reference materials and standard sources for free release and repository acceptance measurements

##### 3.4.1.1 Standard sources

A set of 36 point-like standard sources of Co-57, Co-60, Cs-137, and Am-241 (9 activity levels for each nuclide in the range of 30 Bq to 1 MBq) were produced by three partnering laboratories.

The sources were used for hot-spots simulation in phantoms filled with 'inactive' steel, building or light material material (petanque balls, low activity gravel, plastic balls). Metal phantom and standard source are shown in Figure 17.





Figure 17: Metal phantom with Am-241 standard source

#### 3.4.1.2 Building reference material

As the building reference material, natural radioactivity activity gravel was chosen and standardised within an interlaboratory comparison by five partnering laboratories/by five participating partner laboratories. Mass activities of Ra-226, Th-228 and K-40 were measured and reference values determined. The measurement results for Ra-226 are in Figure 18.

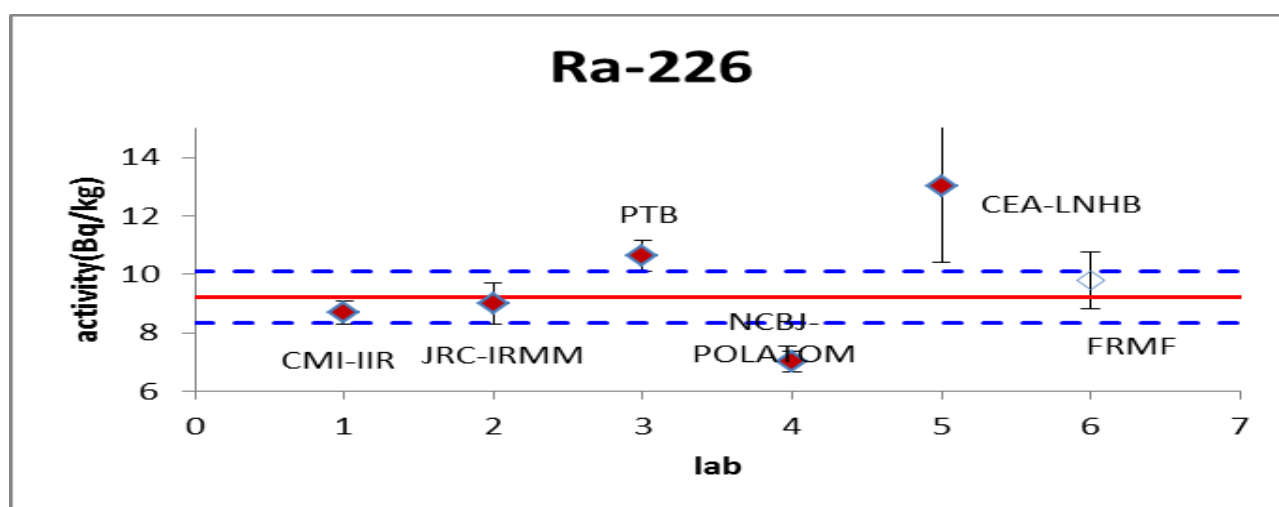


Figure 18: Results of Ra-226 measurement in gravel

Based on the results of the interlaboratory comparison, the reference activity concentrations of natural radionuclides in gravel reference material are  $(8.83 \pm 0.44)$  Bq/kg for Ra-226,  $(3.16 \pm 0.16)$  Bq/kg for Th-228, and  $(95.6 \pm 3.8)$  Bq/kg for K-40.

#### 3.4.1.3 Metal reference material

As a metal reference material, steel tubes were produced using horizontal centrifugal casting from a smelt into which Co-60, in the form of Fe-alloy, was first added and then one piece of neutron irradiated silver wire containing Ag-110m was progressively diluted. The source of Co-60 was contaminated steel from accidental melting of an orphan source. An 80 cm long tube was casted from each of the six basins/batches containing 100 kg of melted iron. The casting was in turn cut in two pieces that were machined to the desirable dimensions. The final material, shown in Figure 19, consists of 12 steel tubes of 20 cm outer diameter, 17.6

cm inner diameter, 40 cm length/height and 245.9 kg total mass. The total volume occupied is 192 L (half-filled container) and the apparent density (mass/occupying volume) is 1.28 g/cm<sup>3</sup>.



Figure 19: Steel tubes with Co-60 and Ag-110m in the measuring container

The reference material was standardised within an interlaboratory comparison, where 10 disc samples, made from the same material as tubes, were measured. The results are given in Figure 20.

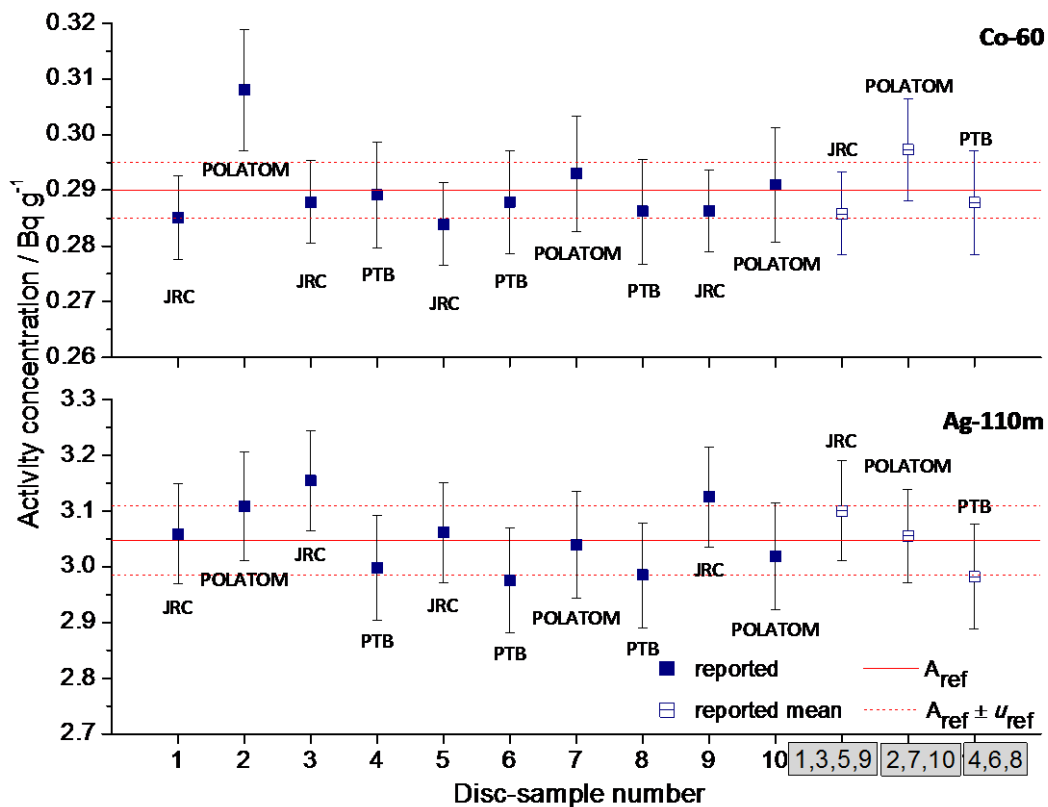


Figure 20: Activity concentration results for Co-60 and Ag-110m in steel tubes.

Based on the results of the interlaboratory comparison, the reference activity concentrations of the tubes standard are  $(0.290 \pm 0.006)$  Bq/g for Co-60, and  $(3.05 \pm 0.09)$  Bq/g for Ag-110m (reference date: September 30, 2013).

#### 3.4.1.4 Light reference material

For the light reference material, clay balls material was chosen and standardised within an interlaboratory comparison by seven partnering laboratories/participating partner laboratories. Mass activities of Ra-226, Th-228 and K-40 were measured and reference values determined. The measurement results for Ra-226 are given in Figure 21.

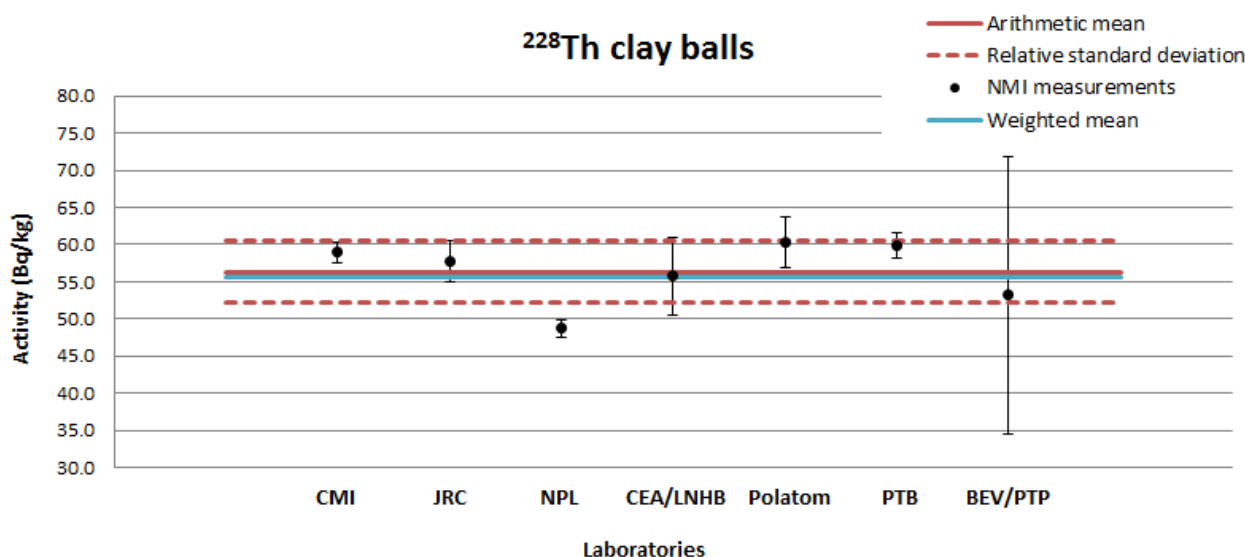


Figure 21: Results of Th-228 measurement in clay balls

Based on the results of the interlaboratory comparison, the reference activity concentrations of natural radionuclides in light reference material (clay balls) are  $(60.5 \pm 1.7)$  Bq/kg for Ra-226,  $(56.4 \pm 4.2)$  Bq/kg for Th-228 and  $(800 \pm 80)$  Bq/kg for K-40.

#### 3.4.2 Reference materials and standard sources for *in-situ* radiochemical analysis

##### 3.4.2.1 Concrete powder

This was generated from a ground concrete material obtained from the bioshield of the Windscale AGR in the UK. This material was analysed to determine pre-existing levels of  $U_{nat}$ , Pu-240 and Sr-90, which were found to be ~2.7% of the spike levels for  $U_{nat}$ , <0.04% for Pu-240 and <0.4% for Sr-90. Due to the technical challenges associated with spiking the matrix of the concrete itself, a series of standard aliquots were prepared to directly spike the concrete, immediately before the analysis with reference solutions containing  $U_{nat}$ , Pu-240 and Sr-90 at an activity of ~1 Bq/g.

The measurement of the concrete was carried out by borate fusion, as described in Chapter 3.2, followed by radiochemical analysis. The actinide analysis results were good, with a maximum bias of ~12% on the measurement results. This was not the case for Sr-90, where bias of ~30% may be incurred. The reason for this is not known, but high levels of calcium in concrete may be the issue here.

##### 3.4.2.2 Concrete solution

A total of 2 g concrete was fused as described above and made up to a solution of 2 dm<sup>3</sup> with 1M HNO<sub>3</sub> and then spiked with 1.2-1.4 Bq/kg of U-238, Pu-240 and Sr-90. After mixing, aliquots of this solution were analysed. Again, the bias on the actinide data was <10%, but the Sr-90 was again biased high, by ~30%, with no identifiable cause.

### 3.4.2.3 Outcomes and overview

Concrete reference materials both solid and dissolved were prepared, and this was delivered successfully. These materials were used to evaluate the method described in Chapter 3.2 performance. The main conclusions are:

- simultaneous radiochemical separation of U, Pu and Sr is achievable in mineral matrices applying the proposed procedures.
- separation and determination of all radionuclides is done without crossed interference among them.
- high bias observed in the case of Sr analysis suggests that there is an uncontrolled factor in the case of mineral matrices analysis that should be investigated.

### 3.4.3 Gaseous reference materials

To enable the testing of instrumentation and devices developed within the project it has been necessary to develop a new traceable carbon-14 reference material in the form of a radioactive gas standard and to provide well characterised contained test atmospheres.

The potential activity concentration of gaseous tritium and carbon-14 species inside a repository or waste store were estimated to be in the range 1 - 100 Bq ml<sup>-1</sup>. A lower level activity concentration standard (0.1 Bq ml<sup>-1</sup>) was requested during the project to enable the performance of the mid infra-red system to be quantified. Testing of the developed instrumentation required the production of a new traceable pressurised gas standard based on existing techniques routinely used at NPL to meet this activity concentration range for <sup>14</sup>CO<sub>2</sub>. This new low activity concentration reference material will enable further studies on the performance of environmental monitoring and sampling devices in current use at nuclear facilities.

Test atmospheres were produced using the carbon-14 reference material, traceable tritium gas (HT) and vapour from tritiated water (HTO) standards contained within an enclosure to enable the evaluation of the passive gas sampling devices and to enable demonstration of the automated environmental radioactive gas monitoring system performance (AERGMS).

#### 3.4.3.1 Production of <sup>14</sup>CO<sub>2</sub> gas cylinders at 10 and 0.1 Bq ml<sup>-1</sup>

These cylinders were prepared in a series of stages:

- generation of <sup>14</sup>CO<sub>2</sub> from a solution of NaH<sup>14</sup>CO<sub>3</sub> followed by standardisation;
- production of a master gas cylinder of ~10 Bq ml<sup>-1</sup> <sup>14</sup>CO<sub>2</sub> followed by confirmation of activity concentration;
- production of a cylinder of ~0.1 Bq ml<sup>-1</sup> and activity concentration confirmation.

#### 3.4.3.2 Generation of <sup>14</sup>CO<sub>2</sub> from a solution of NaH<sup>14</sup>CO<sub>3</sub>

A technique previously developed at NPL for the production of <sup>11</sup>CO<sub>2</sub> was used for the gas generation. An alkaline solution of NaH<sup>14</sup>CO<sub>3</sub> was degassed by the addition of concentrated HCl using the NPL gas conversion rig (Figure 22). The gas was transferred to a gas handling manifold maintained at pressures of 10<sup>-2</sup> mb. The gas was dried by repeat passing through a condensing flask maintained at ~-80 °C by immersion in a Dewar of acetone and solid CO<sub>2</sub> and collected in another vessel immersed in a Dewar of liquid nitrogen.

The vessel containing the condensed <sup>14</sup>CO<sub>2</sub> was transferred to the NPL gas monitor calibration rig. The rig was filled with inactive CO<sub>2</sub> to approximately 1000 mb and the active and inactive gases were mixed. A sample of this gas was isolated and removed from the rig for primary measurement by internal gas proportional counting<sup>2</sup>. The activity concentration of <sup>14</sup>CO<sub>2</sub> derived by this method was 3608 Bq ml<sup>-1</sup> ± 2% (k =2) at STP.

Liquid scintillation counting of the  $\text{NaH}^{14}\text{CO}_3$  starting solution was performed as a check on the gas-counting value, and the  $\text{CO}_2$  conversion efficiency was confirmed as 100% by pressure measurements. The gas activity concentration predicted by LSC was in statistical agreement with the value determined by internal gas proportional counting.



Figure 22: The gas conversion rig for the generation of  $\text{CO}_2$ .

#### 3.4.3.3 Production of a master gas cylinder of $\sim 10 \text{ Bq ml}^{-1} \text{ }^{14}\text{CO}_2$

A sample of  $\sim 400 \text{ ml}$  of gas from the rig was transferred to a previously-evacuated  $5 \text{ L}$  cylinder by expansion and the cylinder was then further pressurised by the addition of  $285 \text{ g}$  of inactive  $\text{CO}_2$  from another cylinder. The mass of gas transferred was determined gravimetrically. The activity concentration in the active cylinder based on the internal gas proportional counting and gas dilution was  $10.09 \text{ Bq ml}^{-1} \pm 12 \% (k=2)$  at STP.

The dilution of the  $^{14}\text{CO}_2$  within the active cylinder was confirmed by sampling the cylinder gas, mixing with ambient air and passing through a  $\text{CO}_2$  trapping medium contained in a Drechsel flask. The rig was maintained at atmospheric pressure by regular additions of air, and each pressure change within the system was monitored to enable the fraction of  $\text{CO}_2$  trapped to be determined. Liquid scintillation counting of the trapping medium was used to confirm the activity concentration of the gas in the cylinder.

#### 3.4.3.4 Production of a cylinder of $\sim 0.1 \text{ Bq ml}^{-1} \text{ }^{14}\text{CO}_2$

The cylinder at  $\sim 0.1 \text{ Bq ml}^{-1}$  was produced in a similar manner. A second evacuated cylinder was filled from the original ( $10 \text{ Bq ml}^{-1}$ ) cylinder to a pressure of  $300 \text{ mb}$ . Inactive gas was transferred with weighing as before. The activity concentration in the cylinder based on the dilution of the master cylinder was  $0.0963 \text{ Bq ml}^{-1} \pm 17 \% (k=2)$  at STP. Again, the gas dilution factor was confirmed by sampling and trapping of gas followed by Liquid Scintillation Counting of the trapping medium.

#### 3.4.3.5 HT, HTO and Ra-226 sources

HT is available in pressurised gas cylinders for use in the calibration of tritium-in-air monitors used for radiation protection purposes. NPL is one of a few NMI worldwide that is able to standardise artificial radioactive gases (e.g.  $^{11}\text{CO}_2$ , HT, Kr-85, Xe-133) using the internal gas proportional counting primary measurement technique. A standardised cylinder of HT in nitrogen carrier gas is maintained at NPL for internal and monitor calibration service use. This cylinder was used to generate the HT atmosphere used for the testing of the passive sampling devices.

HTO vapour was added to the atmosphere of the samplers undergoing testing by the passage of air through a Drechsel flask of standardised HTO solution attached to the enclosure inlet. The activity concentration of the solution before and after air passage was determined by liquid scintillation counting and the mass of



solution removed determined by weighing. This enabled the estimation of the activity concentration produced in the enclosure during the sampler testing.

The testing of the AERGMS' response to Rn-222 was performed by degassing a Ra-226 solid source of nominal activity 105 kBq (Pylon Electrical Development Company, Model RN-1025) into an evacuated volume (2 L nominal) and circulating the gas through the AERGMS in a closed circuit.

### Summary of 3.4 results

New radioactive reference materials and standardised sources have been developed for the calibration of the devices and methods developed within the project enabling achievement of lower uncertainties and more accurate measurement of radionuclide activities.

Radioactive reference materials and standardised sources for the calibration and validation of the free release measurement facility were defined, produced and characterised for the types of materials and radioactive contamination found in waste during decommissioning. Waste containers were prepared using quantified reference materials formed from steel tubes fabricated with  $^{60}\text{Co}$  and  $^{110\text{m}}\text{Ag}$  contamination, and from naturally radioactive pieces of gravel or clay formed into balls. A number of spherical steel containers for standardised point sources ( $^{241}\text{Am}$ ,  $^{57}\text{Co}$ ,  $^{137}\text{Cs}$  and  $^{60}\text{Co}$  at activities between 1 MBq and 30 MBq) were also used to simulate waste containers containing radioactivity 'hot spots'.

For radiochemical analysis, inactive and active concrete material has been characterised and is readily available. Sellafield bio-shield concrete powder was selected as a reference material for spiking with standardised radioactive solutions containing  $^{90}\text{Sr}$ ,  $^{\text{nat}}\text{U}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Am}$ ,  $^{41}\text{Ca}$  to simulate expected contaminants in concrete. A 'concrete solution' containing U, Pu nuclides and  $^{90}\text{Sr}$  was used as another radiochemical reference material.

For validation of the radioactive gas sampling prototypes and devices standardised radioactive gas cylinders of tritium or  $^{14}\text{CO}_2$  with traceability to national standards of radioactivity and tritiated water standards were used to create test atmospheres simulating the activity concentrations of radioactive species predicted to be present in a nuclear waste repository.

## 3.5 Improved nuclear data for long-lived radionuclides

The aims of this task were to enhance the reliability of the international system of references at BIPM by organising international comparisons and to determine the half-life of I-129 and Sm-151 with an uncertainty less than 3%.

### 3.5.1 Intercomparison of Ho-166m

A prerequisite for the project was a Ho-166m solution free of radioactive impurities. Such a solution was provided by PTB. However, the solution still contained inactive Erbium which would lead to interference at mass number 166 when carrying out mass spectrometry measurements. Thus, great efforts were exerted to reduce the Er/Ho ratio.

#### 3.5.1.1 Activity standardisation and comparison

The activity was then determined and this task extended and organised as the EURAMET project 1257 comparison with the BIPM identifier EURAMET.RI(II)-K2.Ho-166m. In this way, the participants can demonstrate their calibration and measurement capabilities (added value). A Draft B report was submitted to the BIPM and published.

The laboratory final results for the activity concentration are shown in Figure 23. All results agree very well and no outlier can be identified. Details about the comparison and its result were published (Kossert et al., 2014).

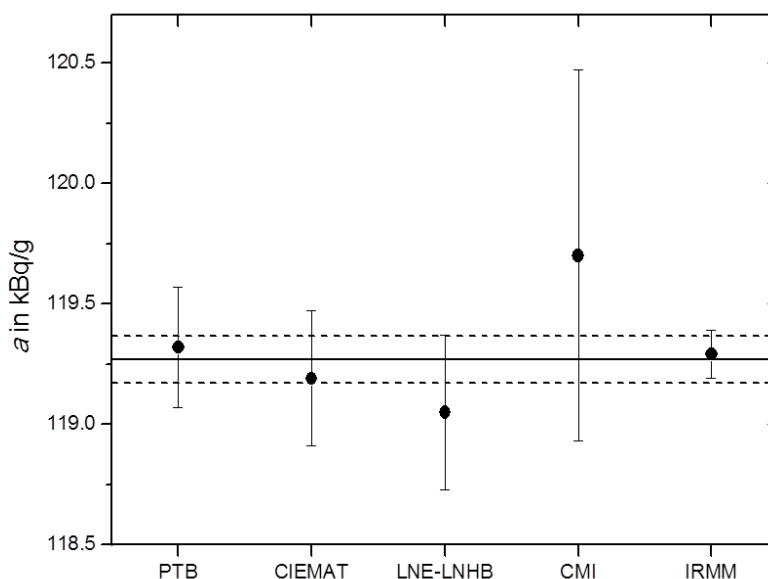


Figure 23: Final laboratory results for the activity concentration of aliquots of the same Ho-166m solution. Uncertainty bars indicate standard uncertainties ( $k = 1$ ). The horizontal line corresponds to the power-moderated mean of all 5 results.

A comparison reference value (CRV) for the EURAMET.RI(II)-K2.Ho-166m comparison has been calculated as the power-moderated mean (PMM) of all final laboratory results, using the method adopted in 2013 by the CCRI(II) for all future evaluations of key comparisons. The resulting CRV is  $119.27(10) \text{ kBq g}^{-1}$ . The stated uncertainty corresponds to the one standard uncertainty.

#### 3.5.1.2 SIR submission

In addition, an ampoule traceable to the solution used within the framework of the EURAMET.RI(II)-K2.Ho-166m comparison was sent to the International Reference System (SIR) at BIPM. Then, the activity results obtained in the EURAMET comparison are compared with the results from IRA (Switzerland) in the BIPM.RI(II)-K1.Ho-166m comparison. Preliminary results indicate an excellent agreement between the EURAMET.RI(II)-K2.Ho-166m result and the IRA result.

#### 3.5.2 Intercomparison and half-life of I-129

This task concerns the measurement of the half-life of I-129. It includes three steps: the acquisition of an I-129 solution of high purity, the measurement of its activity concentration, and the determination of the mass concentration by mass spectrometry.

##### 3.5.2.1 Standardisation and intercomparison of I-129

Measurement of activity concentration took place at the participating laboratories using several techniques.

The final results for the activity concentration are listed below. Although from a strict point of view the CIEMAT values could not be considered as outliers, some problems were identified at source preparation and data processing and, in some cases corrected later. They were therefore classified as outliers and excluded from the comparison value calculation.

Table 2: Final results for the activity concentration  $A$ , as reported by the participants. The stated uncertainties  $u$  are standard uncertainties ( $k = 1$ ).

Participant	$A$ in $\text{kBq g}^{-1}$	$u$ in $\text{kBq g}^{-1}$	Measurement methods
CIEMAT	32.14	0.11	4P-LS-BP-00-00-CN 4P-NA-GR-00-00-00
CMI	33.10	0.57	4P-PC-BP-NA-GR-CO
JRC	33.0	0.1	4P-LS-MX-00-00-CN 4P-LS-MX-00-00-TD
CEA	33.16	0.06	4P-LS-BP-00-00-TD 4P-LS-BP-GH-GR-AC
PTB	33.003	0.099	4P-LS-MX-00-00-CN 4P-LS-MX-00-00-TD

The proposed comparison reference value (CRV) of the present EURAMET.RI(II)- S6.I- 129 Supplementary Comparison was defined as the power-moderated mean of 4 final laboratory results. Consequently, the CRV is  $A = 33.10$  (5)  $\text{kBq g}^{-1}$  using the final laboratory results in Table 2.

### 3.5.2.2 Determination of the I-129 concentration

The mass concentration was determined following similar approaches although the equipments used were different.

The solution was diluted and aliquoted after reception in order to perform activity and mass concentration measurements. Two closed vials containing diluted solutions in NaI and  $\text{Na}_2\text{S}_2\text{O}_3$  media were prepared. The first vial, containing around 1 mL of solution was dedicated to the determination of the I-127/I-129 isotope ratio by Multi Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS). The second vial, containing around 5 mL of solution, was dedicated to mass concentration determination.

The mass concentration of the I-129 in solution was determined using the isotope dilution (ID) technique associated to isotope ratios measurements by MC-ICPMS and using a I-127 spike. The I-127 spike was provided by the National Institute of Standards and Technology (NIST SRM 3180). It was sent in five independent closed vials in  $\text{Na}_2\text{SO}_3$  and NaOH media to ensure the stability and conservation of these solutions. The concentration for each vial was certified at 1.0006 (24)  $\text{mg.g}^{-1}$  (relative uncertainty of 0.24% at  $k=2$ ).

The value of I-129 concentration in the aliquot solution T was found to be: 5.170 (36) ( $k=1$ )  $\text{mg.g}^{-1}$ .

### 3.5.2.3 Half-life determination of I-129

The I-129 half-life can be then derived from the basic relation:

$$T_{1/2} = \frac{\ln(2) \cdot N_0 \cdot m}{A \cdot M}$$

where  $N_0 = 6.022\,141\,79$  (30)  $\times 10^{23} \text{ mol}^{-1}$  is the Avogadro constant,  $M$  is the atomic mass of I-129,  $m$  is the mass and  $A$  the activity concentration of the I-129 solution as determined in this study.

Then, a provisional half life value of  $1.614 (15) \times 10^7$  y is proposed.

### 3.5.3 Intercomparison and half-life of Sm-151

Sm-151 is a relatively long-lived nuclide produced during the irradiation of uranium fuel rods in nuclear reactors.

In order to enhance the reliability of the activity measurements carried out in this exercise an international comparison was organised. It was registered as EURAMET.RI(II)- S7.Sm-151 Supplementary Comparison, (EURAMET Project 1292), then a Comparison Reference Value (CRV) was established and a Draft B report was submitted to the BIPM for publication in Metrologia Technical Supplement.

The number of Sm-151 atoms in the solution was determined using the isotope dilution (ID) technique associated to isotope ratio measurements by TIMS and using a Sm natural spike solution.

#### 3.5.3.1 Standardisation and intercomparison of Sm-151

The intercomparison participants made use of Liquid Scintillation Counting (LSC) for the activity determination by applying the CIEMAT/NIST efficiency tracing method and the TDCR method.

The final results for the activity concentration adopted by each participant are listed in Table 3 and plotted in Figure 24.

Table 3: Final results for the activity concentration  $A$ , as reported by the participants

Participant	$A$ in $\text{kBq g}^{-1}$	$u$ in $\text{kBq g}^{-1}$	Measurement methods	Comments
CMI	77.9	0.93	4P-LS-BP-00-00-TD	
JRC	78.7	0.4	4P-LS-MX-00-00-CN 4P-LS-MX-00-00-TD	The final result is the mean value of the results obtained by the LSC CN and the LSC TDCR methods.
CEA	77.87	0.41	4P-LS-BP-00-00-TD	
NCBJ	79.51	0.48	4P-LS-BP-00-00-TD	
PTB	79.22	0.41	4P-LS-MX-00-00-CN 4P-LS-MX-00-00-TD	The final result is the weighted mean of the results of the CIEMAT/NIST and the TDCR methods.
SMU	80.247	0.376	4P-LS-BP-00-00-TD	

The proposed comparison reference value (CRV) is the power-moderated mean of all six values *i.e.* 78.98 (38)  $\text{kBq g}^{-1}$  rounded to 79.0  $\text{kBq g}^{-1}$ , with an associated uncertainty of 0.4  $\text{kBq g}^{-1}$  ( $k=1$ ).

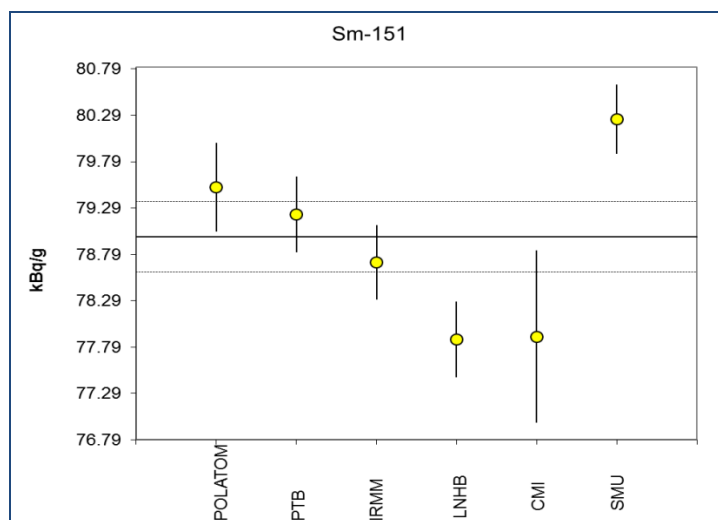


Figure 24: Final laboratory results for the activity concentration of aliquots of the same Sm-151 solution. The horizontal line corresponds to the value of the power-moderated mean of all six results.

### 3.5.3.2 Determination of the Sm-151 concentration

The CEA received two solutions in HCl 1M media. The first vial, containing around 1 mL of solution, was employed to measure the samarium isotope ratios by Thermal Ionisation Mass Spectrometry (TIMS). The second vial, containing around 2.5 mL of solution, was dedicated to the mass concentration determination, which was carried out using the isotope dilution (ID) technique associated to isotope ratio measurements by TIMS and using a Sm natural spike solution. The samarium natural spike solution was provided by the National Institute of Standards and Technology (NIST SRM 3147a). It was sent in independent closed vials in nitric acid at a molarity of approximately 1.6 mol.L<sup>-1</sup> to ensure the stability and conservation of the solution. The concentration of each vial was certified at 9.94 (3) mg.g<sup>-1</sup> (relative uncertainty of 0.15 % at  $k=1$ ).

The final result for the Sm-151 concentration in the solution sent was evaluated as the average of the six independent mixtures. The final result was carried out and is: 0.0853 ± 0.0003 µg.g<sup>-1</sup> with an associated uncertainty of 0.4% ( $k=1$ ).

### 3.5.3.3 Half-life determination of Sm-151

The Sm-151 half-life is then derived from the basic relation:

$$T_{1/2} = \frac{\ln(2) \cdot N_0 \cdot m}{A \cdot M}$$

where  $N_0 = 6.022\,141\,79\,(30) \times 10^{23} \text{ mol}^{-1}$  is the Avogadro constant,  $M = 150.919\,939\,8\,(18) \text{ g} \cdot \text{mol}^{-1}$  is the atomic mass of Sm-151,  $m$  is the mass and  $A$  the activity concentration of the Sm-151 solution as determined in this study.

Then, the Sm-151 half-life value and its associated standard uncertainty is  $94.6 \pm 0.6 \text{ y}$ .

## Summary of 3.5 results

Improvements were made to decay data for selected radionuclides present in nuclear wastes, focusing on half-life measurements of long-lived fission and activation products. Long-lived fission products <sup>166m</sup>Ho, <sup>129</sup>I and <sup>151</sup>Sm can occur in nuclear decommissioning waste streams and all require improved international measurement comparability which has been addressed by comparison exercises performed in the project and new mass spectrometry half-life determinations for <sup>129</sup>I and <sup>151</sup>Sm.



Holmium isotopes are good neutron absorbers and are used in nuclear reactor control rods, with a half-life of 1132.6 years and very few previous comparable measurements, it was selected by the project for an intercomparison measurement exercise. These measurement results have been reported as the EURAMET.RI(II)-K2.Ho-166m comparison which is linked to the BIPM comparison BIPM.RI(II)-K1.Ho-166m bringing the number of recognised internationally comparable measurements for this nuclide to 15 since 1989.

<sup>129</sup>Iodine, a long-lived fission product (half-life  $16.1 \times 10^6$  years), is one of the major contributors to radiation dose from a deep geological repositories. A lack of previous comparative radioactive measurements for <sup>129</sup>I has been filled by the projects performance of the EURAMET.RI(II)-S6.I-129 Supplementary Comparison exercise.

Samarium-151 is produced by fission during the irradiation of uranium fuel rods in nuclear reactors and has a half-life of 90 years. Up until this project no previous international accepted activity measurement intercomparisons had been conducted. During this project the EURAMET.RI(II)- S7.Sm-151 Supplementary Comparison was performed enabling measurement comparability for this nuclide between participating institutes to be established.

## 4 Actual and potential impact

### 4.1 Metrology achievements

For free release measurement of radioactive waste fixed and transportable facilities based on germanium detectors with special shielding and appropriate evaluating methods were developed within the project. Typical relative uncertainties of the developed facilities are in the order of 10 %. New spectrometric software was created enabling determination of mass and surface activities and minimum detectable activities of individual radionuclides and their uncertainties for various types of the measured material. In the developed methods, scale factors for individual types of nuclear facilities were included that enable the evaluation of indirectly measurable radionuclides. Similar results were achieved for repository acceptance criteria measurements.

For in-situ measurements, a traceable transportable integrated radiochemical analysis laboratory was designed for rapid on-site measurement of pure  $\alpha$ -,  $\beta$ - or X-ray emitting radionuclides, such as Sr-90 or transuranics. This facility includes a standardised traceable radiochemical procedure that allows the analysis of the activities of the radionuclides in different types of samples thus securing relative measurement uncertainties be lower than 10 %.

For traceable radioactive gases measurement, automated trapping, separation and counting of individual radioactive species were build and validated including an integrated measurement system for monitoring of radioactive gases and vapours containing H-3, C-14, Rn-222 and non-active 'bulk' gases arising from stored wastes based on monitors that are low-maintenance and at the same time field-deployable for a long time.

For the calibration of measurement instruments, calibration standards and reference materials were produced. They are traceable to national standards for free release measurement, repository acceptance measurement, radioactive gases in repositories measurement and in-situ measurement. These materials were adapted to the needs of the newly developed measurement systems and adjusted to the typical composition of materials and activity levels relevant for radioactive waste.

In the framework of the project, half-live data and gamma-ray intensities of long-lived radionuclides relevant in radioactive waste management were improved; their relative uncertainties are lower than 3 %.

## 4.2 Dissemination activities

### 4.2.1 Scientific publications

The project generated eleven high impact publications in key journals. These incorporate the significant scientific outputs of the project (see Chapter 6).

### 4.2.2 Conferences =

The work carried out in the project has already reached both the wider scientific audience in general at conferences, such as ICRM-LLRMT 2012, Jeju, DRO conference 2012, Decay Data Working Group, ICRM 2013, Antwerp, ICEM 2013, Brussels, ICER 2014, Barcelona. In total, 33 invited lectures, oral presentations and poster presentations were given by the partners during the lifetime of the project. Much of the dissemination of the project's findings consisted of presentations at meetings of the EURAMET Technical Committee for Ionising Radiation (TC-IR)) with about 35 attendees from across the European metrological community. Appropriate parts of the project have been also presented to the International Committee for Radionuclide Metrology (ICRM) working groups for gamma spectrometry (GS WG), nuclear data (ND WG) and low level measurement techniques (LL WG), each with an audience of about 20 stakeholders. Positive reactions were received to all these contributions, attracting discussions and comments.

### 4.2.3 Stakeholder Engagement and Standards

A link to the EU Parliament, Committee on the Environment, Public Health and Food Safety has been established and input to the 'COUNCIL DIRECTIVE COM(2012)0242 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation' submitted by CMI. This comprised requirement for radionuclide specific free release measurement. Also, a link to the IAEA (International Atomic Energy Agency) Network of Laboratories for Nuclear Waste Characterisation (LABONET) has been realised and research results of the project were presented at LABONET's meeting in Vienna in 2013. National representatives were identified for the major standard committees related to the scientific developments of the project, and project information has been provided to them. These committees include ISO(TC147/WG4, REMCO/WG9/WG14/WG15/WG16, TC85/SC2/WG17, IEC(TC45A, TC45B), CEN(TC351) and CENELEC(TC45B). Following standardisation projects and comparisons were organised and performed:

EURAMET Project 1257 and CCRI(II) key comparison EURAMET(II)-K2.Ho-166m; CCRI(II) supplementary comparison EURAMET RI(II)-S6.I-129; BIPM International Reference System (SIR) submission Ho-166m; CCRI(II) supplementary comparison Sm-151; EURAMET Project 1292 and BIPM-CCRI(II) Supplementary comparison Sm-151.

More than one hundred stakeholders and end-users were integrated in the project.

### 4.2.4 Workshops

During the course of the project, over one hundred stakeholders in the nuclear industry showed interest in project outcomes. Three project workshops were held for the stakeholders at CEA in Paris, CIEMAT in Madrid and UJV in Rez near Prague. The first two workshops presented research results to an audience of about 20 stakeholders from nuclear industry, decommissioning companies, nuclear regulators, radioactive waste agencies, measuring instruments producers, research institutes and universities. The third workshop was held at the Institute for Nuclear Research (UJV), where the experimental free release measurement facility was demonstrated to some 35 delegates. The following topics were presented and discussed:

- standardised traceable gamma assay methods for 'free release' measurement of solid materials and objects from nuclear facilities, and methods for the characterisation of radioactive waste prior to storage in repositories
- in-situ radiochemical analysis methods
- measurement methods for radioactive gases and vapours present in radioactive waste repositories and facilities

- development of reference materials and standard sources for the calibration of measurement devices
- improved half-life data for long-lived radionuclides present in wastes

### 4.3 Effective cooperation between JRP-Partners

The European Metrology Research Programme (EMRP) is a metrology-focused European programme of coordinated R&D aimed at facilitating closer integration of national research programmes and ensuring collaboration between National Measurement Institutes, thus reducing duplication and increasing impact. This project is a good example of the implementation of this programme, gathering thirteen NMIs/DIs and one integral REG from twelve European Countries and from the EC. Also a few NMIs from the countries that are smaller contributors to the EMRP were involved in the project. Moreover, this project is the first collaborative project in the field of radioactive waste management metrology involving partners with great expertise both in radionuclide metrology and in nuclear physics. The participation of a large number of research groups from several countries shows the general interest in the topic and represents the first valuable impact created by the project. Many exchanges between the partners took place. Several tasks benefited from the collaboration between the partners, as demonstrated by several joint publications and presentations. Furthermore, various analytical methods were validated thanks to the joint collaboration of partners.

### 4.4 Examples of early impact

#### Standards and regulation:

Scientific and operational results of the project have been directly adopted by national authorities (e.g. Slovenian Ministry of Education, Science, Culture and Sport), European regulators, BIPM (CCRI(II)), EURAMET (TC-IR), and the international organisations (e.g. IAEA, Committee for Radionuclide Metrology - ICRM).

#### End-user uptake:

An experimental Free Release Measurement Facility was built, calibrated and tested at ENVINET a.s. in Trebic (Czech Republic). It was then disassembled, transported and reassembled at another site in the Czech Republic all within a three week turn-around time. It is now being used to monitor metal radioactive wastes prior their designation as free release. The design of the Free Release Measurement Facility has been finalised and will be built in a cooperation with NUVIA a.s. on the JRC Ispra (Italy) site to enable ongoing decommissioned radioactive waste monitoring. An experimental Repository Acceptance Measurement Facility has also been built, calibrated and tested at ENVINET a.s. before relocation to a nuclear facility site in the Czech Republic where solid nuclear wastes are being measured prior to storage in a repository. These measurements will continue beyond the end of the project.

#### Scientific uptake and impact:

The project has so far contributed with 42 presentations at meetings, conferences and workshops and with 15 presentations or contributions to standards, regulatory bodies and working groups. Eleven scientific articles have been published or submitted to peer-reviewed scientific journals, 5 scientific visits and 3 workshops for stakeholders have been organised.

### 4.5 Potential impact

The development of a standardised traceable method for free release measurement will lead to a reduction in waste disposal costs by limiting the quantities of material incorrectly sentenced to repositories; also, trade disputes (especially between waste producers, scrap factories and metallurgical works) will be less likely at both the national and international levels.

The development of standardised traceable rapid methods for on-site radiochemical analysis will reduce costs. The new radioanalytical methods enable quicker turnaround times of nuclear waste samples and reduce operating costs for the nuclear supply chain. These processes have also found application in radiopharmaceuticals and nuclear forensics.

The validated protocols for radiochemical analysis using commercially available instrumentation (KATANAX, PERALS and TriAthler) developed within the project play a significant role in enabling on-site measurements. The passive sampling devices for radioactive gases are now being deployed at nuclear facilities in France to support staff radiation protection and gaseous release monitoring. They are also being deployed in environmental monitoring in the vicinity of nuclear sites. This will help to improve the accuracy of dose estimates for emissions of radioactive gases such as  $^{14}\text{CO}_2$  and tritiated water vapour.

All of the methods developed in the project are directed at protecting the environment and human health. Improved assessments of radioactive waste and environmental during nuclear decommissioning as well as environmental monitoring at waste repositories contribute to more effective radioactive waste management.

## 5 Website address and contact details

A public website has been made available: [www.radwaste-emrp.eu](http://www.radwaste-emrp.eu).

A partners' restricted area has also been created at the NPL's SharePoint site.

The contact person for general questions about the project is Petr Kovar, CMI ([pkovar@cmi.cz](mailto:pkovar@cmi.cz)).

The contact person for the free release measurement and repository acceptance measurement is Jiri Suran, CMI ([jsuran@cmi.cz](mailto:jsuran@cmi.cz)).

The contact person for the in-situ radiochemistry is Simon Jerome, NPL ([simon.jerome@npl.co.uk](mailto:simon.jerome@npl.co.uk)).

The contact person for the measurement of gases in radioactive waste repositories is Julian Dean, NPL ([julian.dean@npl.co.uk](mailto:julian.dean@npl.co.uk)).

The contact person for the reference materials and standard sources is Dirk Arnold, PTB ([dirk.arnold@ptb.de](mailto:dirk.arnold@ptb.de)).

The contact person for the nuclear data is Marie-Martine Be, CEA-LNHB ([mmbe@cea.fr](mailto:mmbe@cea.fr)).

## 6 List of publications

F. J. Maringer et al.: Metrology for radioactive waste management: Clearance levels and acceptance criteria legislation, requirements and standards, *Applied Radiation and Isotopes*, 81(2013) 255-260

J. Solc et al.: Optimization of a measurement facility for radioactive waste free release by Monte Carlo simulation, *Applied Radiation and Isotopes*, 87(2014) 348-352

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G. Genoud et al.: Mid-infrared spectroscopy for radiocarbon detection, Optic days 2013, Helsinki

V. Peyres et al.: Ionizing Radiation for Radioactive Waste Management, Congreso Español de Metrología, Madrid, 2013

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M. Merimaa et al.: Isotope ratio measurements of emissions from energy production, World Metrology Day, MIKES open house, Espoo, 2014

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