Milestone 9
State of the art of waste form characterisation methods

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Abstract

The milestone document (delivered by Task 2.3 Waste acceptance systems) collects the latest state-of-the-art technologies and methods used for the classification of radioactive waste. The content of this document will form part of PREDIS Deliverable 2.5 Assessment of feasibility of waste form characterisation methods (M36, August 2023).

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MILESTONE DESCRIPTION

Milestone No 9, associated with Work package 2, Task 2.3 has been completed on 7.8.2022.

In this document, state-of-the-art methods and techniques for waste characterisation are collected. The focus is on radiological testing, as this is the area where the most progress is being made, with the adjective state-of-the-art being interpreted as the most modern and recent tests using the latest methods and technologies and recent development in older routinely used methods rather than the most advanced tests in the field, however old they may be.

The readiness of the milestone was reviewed and agreed upon by Lumír Nachmilner, CVRez (T2.3 leader) and Anthony Banford, NNL (WP2 leader).

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LIST OF ABBREVIATIONS

NDA	Non-destructive analysis/assay
DA	Destructive analysis/assay
IGS	Integral gamma scanning
SGS	Segmented gamma scanning
ASGS	Absolute SGS
FEP	Full energy peak
TCT	Transmission computed tomography
ECT	Emission computed tomography
TGS	Tomographic gamma scanning
HRGS	High resolution gamma spectrometry
ART	Algebraic reconstruction technique
IART	Improved ART
SNS	Segmented neutron scanning
LINAC	Linear accelerator
PGNAA	Prompt gamma radiation induced by neutron activation
CRDS	Cavity ring down spectroscopy
DTM	Difficult-to-measure
HLW	High level waste
IER	Ion exchange resin
ILW	Intermediate level waste
LILW	Low and intermediate level waste
LLW	Low level waste
NPP	Nuclear power plant
RW	Radioactive waste
SF	Spent fuel
WAC	Waste acceptance criteria
WF	Waste form
WFQ	Waste form qualification
TTA	thenoyl-tri-fluor acetone=1-(2'-thenoyl)-3,3,3-trifluoroacetone
TOA	tri-octylamine

CMPO	octylphenyldiisobutylcarbamoylmethyl posphineoxide
PMBP	benzoyl pyrazolone
Cupferron	N-nitroso-N-phenyl-hydroxylamine
DMG	dimethylglyoxime
ABO	α-benzoinoxime=(2E)-2-hydroxyimino-1,2-di(phenyl)ethanol
AMP	ammonium phosphormolybdate
CFC	copper ferrocyanide
Sr resin	4,4’(5’)-di-t-butylcyclohexano-18-crown-6 in octanol
TEVA resin	Aliquat 336 loaded resin
UTEVA resin	dipentylpentyl phosphonate coated resin
TRU resin	CMPO and TBP coated resin
DGA resin	diglyolamide coated resin
LN resin	HDEHP coated resin
DIPHONIX resin	diphosphonic acid covalently bound to polystyrene
DIPEX resin=ACTINIDE resin	bis(2-ethylhexyl) methanediphosphonic acid coated resin
Zr resin	hydroxamate coated resin
AMP-PAN	ammonium molybdophosphate impregnated resin
TK 201 disc	TOA impregnated membrane
TK202 resin	polyethyleneglycol coated resin
AAS	atomic absorption spectrometry
OES	optical emission spectrometry
ICP-OES	inductively coupled plasma - optical emission spectrometry
MS	mass spectrometry
ICP-MS	inductively coupled plasma - mass spectrometry
SF-ICP-MS	sector field ICP-MS
ICP-Q-MS	quadrupole ICP-MS
TIMS	thermal ionization MS
AMS	accelerator MS
RIMS	resonance ionization MS
TOF-MS	time-of-flight MS

LA-ICP-MS	laser ablation ICP-MS
GDMS	glow discharge MS
NAA, RNAA	neutron activation analysis, radiochemical NAA
LSC	liquid scintillation counting

1 Introduction

In any waste management strategy, the proper control of physical, chemical, radiochemical and radiological parameters of radioactive waste and thorough testing of the quality of the final waste forms and waste packages is essential. Failing to carry out control procedures properly at any step of the waste life cycle can have significant consequences like non-compliance with nuclear safety or the generation of waste packages that do not meet the waste acceptance criteria for long-term storage or disposal.

Not all parameters can be measured easily (if at all) throughout the life cycle of radioactive waste, and it is therefore important to test and document raw radioactive waste as thoroughly as possible. Performing characterization at the earliest practical stage of waste production results in more accurate data. This also helps to avoid overly conservative assumptions later on, which leads to reduced cost. Characterization of raw waste allows their classification. The different waste forms produced from raw waste must meet the criteria laid down in the WAC.

In this document, state-of-the-art methods and techniques for waste characterisation are collected. Obviously, not all parameters are subject to breakthrough developments in the testing methods (like measurement of physical parameters of the waste package such as mass, shape, dimensions, etc.). Therefore, the focus is on radiological testing, as this is the area where the most progress is being made, with the adjective state-of-the-art being interpreted as the most modern and recent tests using the latest methods and technologies and recent development in older routinely used methods rather than the most advanced tests in the field, however old they may be.

2 Non-destructive analysis

Non-destructive assay (NDA) is a very effective tool for quality control, it is commonly used to check the radioactive content of waste packages without the need of sampling. The two most widely used techniques are gamma spectrometry and neutron counting. While NDA techniques are relatively very simple, they are very sensitive to measurement bias when no appropriate item-specific calibrations or correction techniques are applied (or even exist). This bias is mainly caused by the unknown density and activity distribution inside the waste package. Correction techniques are usually based on additional measurements like dedicated scanning methods in combination with transmission experiments or tomography, which allows the missing information to be reconstituted to some degree.

Passive non-destructive assay techniques measure radiation from the spontaneous decay of the nuclear material. Active non-destructive measurement methods use an external source of radiation, and are inherently more complex to implement than passive methods.

2.1 Gamma measurements

Radionuclides that emit characteristic X-ray and gamma radiation with specific energies and intensities can be identified and even quantified by non-destructive measurement. Gamma-ray spectrometry provides the most detailed analysis of the gamma emitting radionuclides, the energy of the emitted gamma photons is measured by a detector which delivers a signal proportional to this energy. These signals are then analysed and classified in the form of a histogram called a gamma spectrum [1].

The detector type can be a gas detector, semiconductor, or scintillator. The first two exploit the phenomenon that ionisation generates charges in a non-conducting material which are converted into electric pulses or currents by electric polarisation and the signal is amplified by special electronics, while in the latter the primary ionisation is converted into photons of light which are amplified by a photomultiplier or a photodiode. The main detectors used in gamma-spectrometry are organic (plastic or liquid) scintillators (NaI, CsI, LaBr, BGO) and semiconductors (HPGe – high-purity germanium, silicon, CdTe, CdZnTe, GaAs) [1].

Scintillators can be produced in large volumes, but their energy resolution is generally lower. They are typically used for low intensity photon fluxes and simple gamma spectra. Since most scintillators are very fast (signal on the order of nanoseconds), they can be used for coincidence counting at high counting rates. The crystal size of room temperature semiconductor detectors is very small (mm^3 to cm^3), which allows them to withstand intense photon fields. Their spectral resolution is slightly better than that of scintillators. HPGe detectors have excellent energy resolution, which allows them to distinguish between the numerous gamma and X-ray lines emitted by nuclear materials and to deduce their isotopic composition. HPGe detectors need refrigeration (liquid nitrogen, cryogenic compressor or the combination of both), because at room temperatures the noise caused by thermal excitation is very high. Generally, a gamma-spectrometry measuring setup consists of a detector, electronics system (analogue or digital) and an analysis system [1]. A typical gamma measurement setup is shown on Figure 1. The IAEA-TECDOC-1537 Report (2007) [2] Annex I. presents the various gamma-scanning methods.

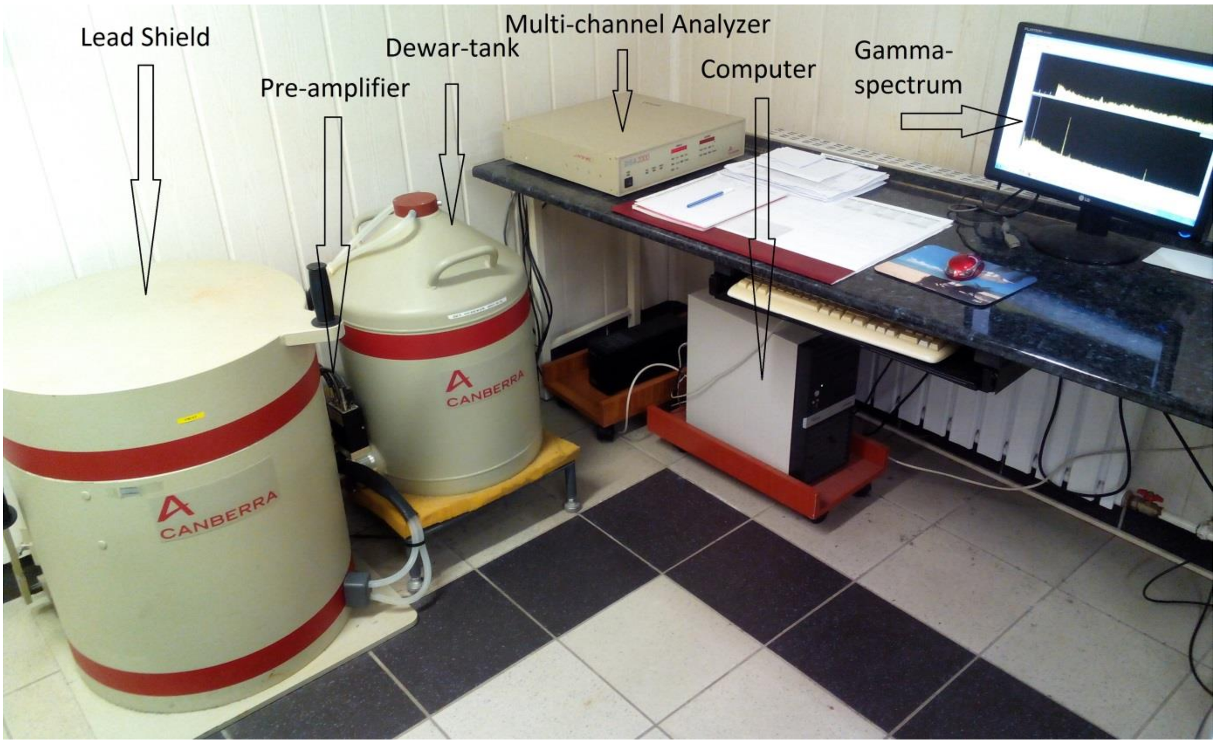

Figure 1 Gamma measurement station at ISOTOPTECH, Hungary

2.1.1 Integral Gamma Scanning (IGS)

Integral Gamma Scanning (IGS) is routinely used to characterize the nuclide inventory of a waste package, being a simple, cheap and fast method. It is usually performed in open detection geometry. In a classical setup, a single detector is used, and the waste drum is continuously rotated using a turntable during the spectrum acquisition. The measurement geometry is set-up in a way that all parts of the waste package contribute to the response of the detector. The peak efficiency is calculated after performing a single measurement, with the basic assumption that the waste is homogeneous.

The advantage of the open geometry procedure is that it has less complicated hardware and generally has a higher detection efficiency compared to collimated geometry measurements, and usually leads to lower detection thresholds. As this method is generally more sensitive to the distribution of activity and density of the waste matrix, it is usually applied for NDA of low-level waste (LLW) packages, with homogeneous or well-characterized filling.

However, there are attempts on extending the applicability of Integral Gamma Scanning to the measurement of waste drums with relatively homogeneous matrix and heterogeneous activity. This new approach is based on solving a first-kind Fredholm integral equation using a small number of measurements. A model for computing the peak efficiency was developed to discretize the first-kind Fredholm integral equation and obtain an ill-conditioned system of equations which was solved using the Tikhonov regularization with non-negativity constraint. The performance of the approach was firstly investigated using synthetic data. Numerical experiments showed that accurate results can be obtained in the measurement of waste drums with relatively homogeneous matrix and heterogeneous activity distributions especially for nuclides emitting two or more gamma rays, and that reasonable results can be obtained for multi-gamma emitters even if the mass distributions are highly heterogeneous [3].

2.1.2 Global measurement of waste containers

Gamma spectrometry is frequently used to measure waste packages because it can meet the characterization requirements for a wide range of very different types of containers (polyethylene bins of a few litres, metal drums ranging from 100 L to 1 m^3, concrete packages, etc.), the physicochemical nature, density, volume, activity level, isotopic spectrum and localization of radioelements. However, this measurement technique may prove to be limited by the attenuation of the radiation in the material. For very dense materials (e.g., concrete of a 2-3 $g \cdot cm^{-3}$ density), the measurable depth of matrix is only a few centimetres for the gamma emissions of the major radioactive isotopes (50 keV to 2 MeV) [1].

Done et al. (2014) [4] describes the use of gamma spectrometry for the characterization of 100 L drums containing radioactive waste placed in 200 L drums with concrete shield for final disposal. In order to simulate situations as close as possible to real waste container configurations, different geometrical configurations of measuring were built by distributing the cylindrical standard sources, from the linear standard source of ^{152}Eu, in different holes. Activity calculation was performed with the gamma-spectrometric installation and ORTEC software, considering the radioactive matrix homogeneously distributed only in the 100 l drum, the remaining volume of 200 l being considered as concrete shield. Depending on the actual configuration of the sources, ~40 – 100% efficiencies were obtained.

2.1.3 Segmented Gamma Scanning (SGS)

In most cases, gamma emitting radioisotopes are not distributed homogeneously inside the waste package and the waste matrix is not uniform. Measurement of these inhomogeneous packages can be performed with Segmented Gamma Scanning (SGS), which is less sensitive to this heterogeneous isotope distribution. In this case, the drum is usually rotated and shifted vertically in front of a collimated detector, measuring only thin segments of the drum at a time. Spectra are recorded for segments of the waste package, representing specific volume parts of the waste. Segmentation can be vertical, horizontal or angular. Acquisition of segment spectra is performed at a set of predefined positions of the detector relative to the waste drum. A SGS instrument is shown on Figure 2.

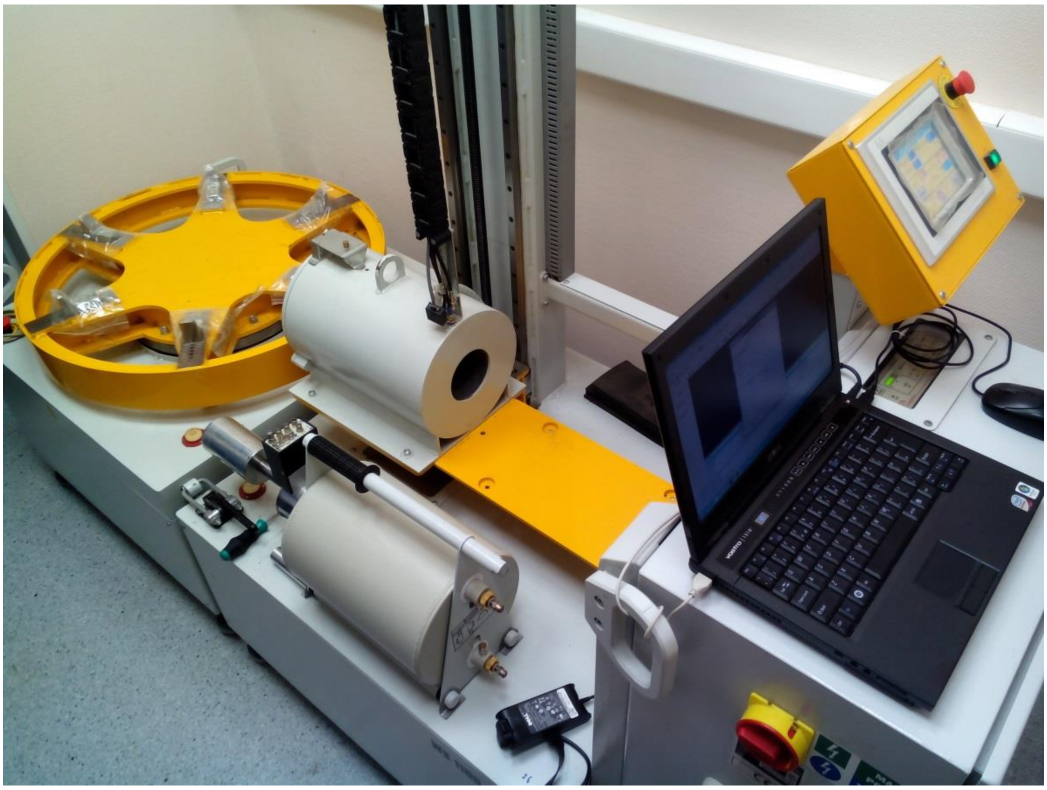

Figure 2 SGS instrument at ISOTOPTECH, Hungary

Bai et al. (2009) [5] describes an improved method based on the analysis of the angular dependent count rate distributions recorded during the waste drum rotation in SGS to localize spatially concentrated gamma-emitting isotopes (‘hot spots’) inside the waste package and to determine the gamma attenuation properties of the waste matrix. To achieve this, numerical simulations and χ^2 fits of the angular dependent count rate distributions were performed using an analytical expression derived from a geometrical model.

Krings and Mauerhofer (2012) [6] present a new concept for the isotope specific activity reconstruction assuming that the radioactive waste contains activity point sources as well as homogeneous activity contaminations in different regions of the drum. The concept accounts for information of the waste’s composition due to the conditioning and packaging process as well as to the framework requirement of industrial application. They present an improved method to quantify the activity of spatially concentrated gamma-emitting isotopes (point sources or hot spots) in heterogeneous waste drums with internal shielding structures. The isotope activity is reconstructed by numerical simulations and fits of the angular dependent count rate distribution recorded during the drum rotation in SGS using an analytical expression derived from a geometric model.

Patra et al. (2019) [7] reports on a non-conventional absolute segmented gamma scanning (ASGS) methodology for the assay of 200 L waste drums, avoiding the use of a standard drum. The analysis employs the full energy peak (FEP) efficiency, ingeniously determined using a standard ^{152}Eu point source. From combined experiment and Monte Carlo simulation the FEP efficiencies of the detector for a 200 L cylindrical sample can be well reproduced using a point source. While verifying the applicability of the point source FEP efficiencies for the assay of plutonium in 200 L drums, an energy dependent bias has been seen, which confirms the presence of lump attenuation in addition to the general matrix attenuation. An infinite energy extrapolation of apparent mass approach has been adopted for the assay of large volume waste drums which takes care of the gamma-ray attenuation from all sources that is otherwise difficult to correct for in a sample drum of unknown history.

2.1.3.1 Multi-rotational Vertical Scanning

This mode consists of measuring the emission of gamma rays from different horizontal segments of the waste package, with the assumption that the matrix is uniform, and the activity is homogeneous in these slices. During the measurement the detector is moved vertically past the waste package (or the waste package is moved in front of a fixed detector) in specific points along the rotational axis of the waste package. In order to minimise the angular distribution of activity and matrix, the separated segment measurements are made at a fixed height and continuous rotation of the waste package. The geometry of each slice is defined by the intersection of the solid angle of the detector and the waste packages.

Spiral-scanning mode is a variation of multi-rotational scanning, in which the measurement is taking place with the vertical movement linked with rotational movement while scanning. This method is often used as a pre-scan to identify hot-spots of activity, because it allows the entire vertical surface to be viewed systematically.

2.1.3.2 Angular Scanning

During angular scanning mode the measurements of the waste package are performed in a determined horizontal section at discrete angular steps instead of continuous rotation. This way the angular and radial non-uniform activity distribution can be determined. Angular scanning is usually performed in a combination with vertical scan mode. It can be carried out in two ways:

- Acquiring one energy dependent spectrum for each angular segment, which allows the determination of the radial and angular position of the hot-spot as well as their nuclide composition. This method needs more time than the multi-rotational vertical SGS method.

- Acquiring total gamma activity per determined sector in each slide. For this method, an MCS acquisition mode and module is needed. It allows the determination of angular and radial position of the hot-spots, and does not take longer than multi-rotational vertical SGS. The drawback is that it is not possible to determine the nuclide composition of the hot-spots with this method.

2.1.3.3 Horizontal/Swivelling Scanning

This method is based also on the multi-rotational vertical scanning mode. A predefined number of rotational/horizontal scans are performed at each height positions, differing by the swivelling angle/horizontal position of the detector. This way, the waste package is subdivided into a number of rings which may overlap. Each measurement is correlated to the activity of the region seen by the detector. This scan mode is appropriate for radial and angular non-uniform activity distribution in the slide, like in case of inner shielding in the waste package.

2.1.3.4 Attenuation Correction

State of the art Scanning Gamma Spectrometry systems use techniques to determine the attenuation properties of the matrix experienced by the radiation emitted from the nuclides inside the waste package.

Methods for performing attenuation correction:

— *Weight correction:* This involves the determination of the apparent density of the waste matrix which is a fundamental technique in SGS because the weight can always be determined.

— *Differential peak absorption technique (DPA)*: This technique may be applied if gamma rays with different energies can be detected from the same nuclide.

— *Evaluation of scattered gamma rays*: The technique is based on a detailed evaluation of the pulse height spectrum to assess the ‘amount’ of scattered gamma rays.

— *Transmission corrected gamma ray scanning:* This method implies the use of an external gamma ray source to measure the transmission at one or more energies for a segment.

— *Transmission computed tomography (TCT)*: This method yields a two-dimensional distribution of attenuation factors within a (usually) horizontal slice of the waste package.

Transmission computed tomography (TCT): An NDA method which allows the distribution of matrix density to be determined within sections of waste package. The technique is based upon the detection of gamma rays emitted from a known source and the calculation of transmission ratios through specific paths within the waste matrix

Emission computed tomography (ECT): An NDA method which allows the distribution of nuclide activity to be determined within sections of waste package. The technique is based upon the measurement of segmented spectra from known sections of the waste matrix in order to obtain accurate results it is necessary to know the distribution of matrix density within the section (typically by TCT).

2.1.4 Tomographic Gamma Scanning (TGS)

Tomographic Gamma Scanning (TGS) is an improvement of Segmented Gamma Scanning (SGS). It combines High Resolution Gamma Spectrometry (HRGS) with 3D spatial resolution transmission and emission image reconstruction techniques. The technique can yield accurate quantitative results for low-to-moderate matrix densities (0-1.0 $g.cm^{-3}$) and for contact dose rates less than 6 $mSv.h^{-1}$. A Tomographic Gamma Scanner setup is shown on Figure 3.

Figure 3 Photo of a Tomographic Gamma Scanner

A tomographic gamma scanner has the same basic components as the SGS, but it has a more stringent detector collimation, turntable rotation is incremental, and the detector can be moved in a transverse direction to the axis of the sample. Using a gamma transmission source, the unknown matrix inside the drum can be mapped and the attenuating object revealed. This allows to acquire a 3D transmission and emission tomographic projection data, from which the spatial attenuation maps and spatial emission can be determined.

Emission tomography relies on a collimation reduced to a segment of the package and requires a horizontal scan coupled with angular acquisitions, making it possible to reconstitute the spatial distribution of the activity in the tomographic section. This operation can be repeated in different sections to reconstruct the 3D activity of the waste. The tomographic reconstruction step requires knowledge of the gamma attenuation by the materials in the waste container and therefore complementary photon transmission measurements [1]. Figure 4 shows the principle of gamma emission tomography.

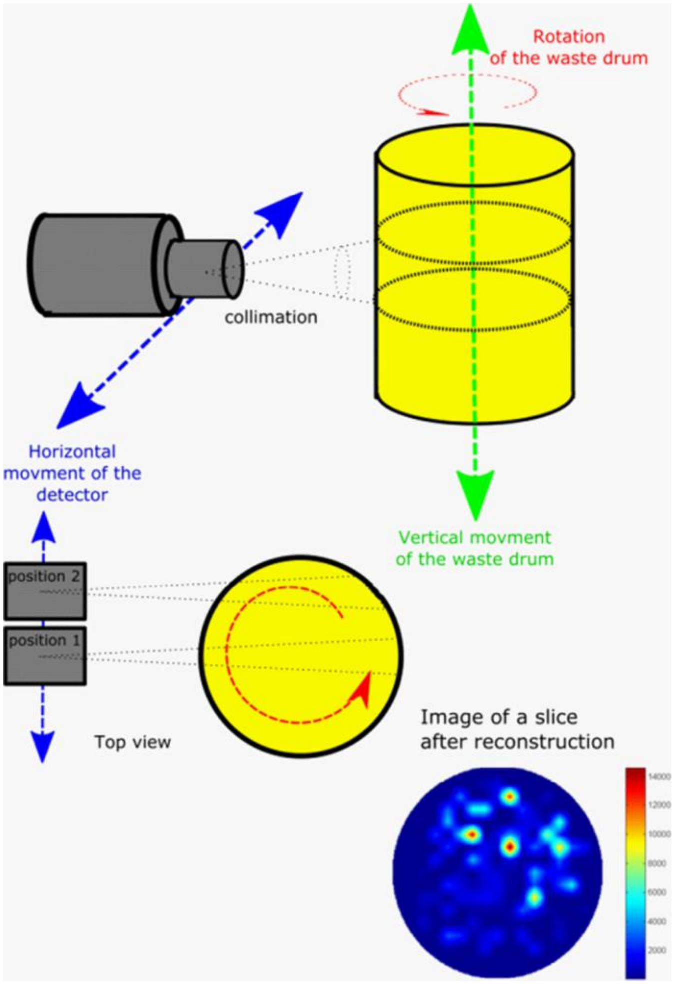

Figure 4 Principle of gamma emission tomography (Pérot et al., 2018)

Venkataraman et al. (2007) [8] reports on designing and building an integrated waste assay system was designed and built to extend the dynamic range of matrix densities to 3.0 g.cm^{-3} and dose rates up to 0.1 Sv.h^{-1}. This was achieved by implementing a design that allowed the system to be configured as a Segmented Gamma Scanner (SGS).

Zheng et al. (2018) [9] proposes an improved algebraic reconstruction technique (IART) to reconstruct TGS images, applying the total variation minimization method and the self-adaptive relaxation factor to improve the iterative process of traditional algebraic reconstruction technique (ART). Results show that this IART algorithm can accurately reconstruct TGS images simply based on small amount of measurement data. Compared with traditional technique, this method can reduce the mean square error and improve the signal-to-noise ratio of transmission images. And it can improve the positioning accuracy of radioisotope and the accuracy of reconstructed activity.

2.1.5 Compton Suppression Spectrometry

The presence of Compton scattered gamma rays of higher energy during gamma ray spectrometry performed with HPGe detectors complicates the measurement. The main interaction in the relatively low Z HPGe crystal above a few hundred keV is via Compton interaction. Compton scattered gamma rays cause a rise in continuous background in the spectrum and by this raising the detection limit for lines at low energies.

One way to deal with these Compton scattered gamma rays is surrounding the HPGe crystal with scintillation material. When Compton scattered gamma rays escape from the HPGe detector and are absorbed and detected in the scintillation material (Compton Suppression Shield or Anti-Compton Shield), they are coincident with the gamma photons detected in the crystal in time. In case of coincident signals in the HPGe detector and the Compton Suppression shield, the registration of the Compton interaction event can be blocked with a veto signal. The suppression shield should be capable of detecting low energy gamma rays down to 15 keV for an optimum suppression.

Although Compton Suppression Spectrometry has been used for several decades, the improvement of the method is still ongoing. In case of radionuclides with complex decay schemes such as ^{60}Co, ^{106}Rh, ^{110}mAg, ^{124}Sb, ^{134}Cs, and ^{154}Eu, many gamma rays can be emitted in coincidence. There is a possibility of the detection of two gamma rays from the same disintegration by both detectors at the same time. Rejecting these events as Compton events leads to undesired full-energy peak (FEP) loss. Zhang et al. (2019) [10] proposes a solution by using digital list-mode data acquisition in conjunction with time stamped pulse analysis method to overcome this disadvantage and recover the undesired FEP coincidence losses for cascade radionuclides.

2.1.6 Dose rate measurements

Dose rate measurements are the simplest form of passive measurements, and several types of detectors are readily available on the market, including Geiger-Müller counters, ionization chambers, and (NaI) scintillation counters. In order to convert dose rate to radiological inventory, dose conversion factors need to be determined, for example by comparing equivalent dose rate measurement to results from gamma spectrometry. Application of conversion factors can only be achieved successfully when the considered waste stream is stable in time (no change in isotopic vector), when the waste form content and activity distribution are sufficiently homogeneous, and when measurements are performed using the same procedure for all drums. Dulama *et al*. (2010) [11] developed a mathematical model for dose rate estimation of quasi-homogeneous batches of spent ion exchange resins and liquid radioactive wastes, to optimize quantities of waste per unit volume of conditioned waste form, in order to meet the acceptance criteria for transport and final storage. The main contributors to dose rate were gamma emitting radionuclides like ^{54}Mn, ^{60}Co, ^{57}Co, ^{124}Sb, ^{125}Sb, ^{65}Zn, ^{134}Cs and ^{137}Cs. Model validation was performed for a set of 23 conditioned spent ion exchange waste drums which were also characterized by gamma ray spectrometry. Dose rate was measured with a hand-held device (factory set to achieve a 15% relative uncertainty in direct reading mode) at contact with the side of the waste drum. The selected representative value for the dose rate at contact was the average of readings registered at the half-height on the side of the waste drum. Main discrepancies were found due to internal inhomogeneities of the waste form which can alter both the dose rate measurement and spectrometric results. Abd *et al*. (2016) [12] calculated the dose conversion factor for ^{137}Cs contaminated waste (soil) packed in metallic drums by comparison with gamma spectrometric data. They measured the dose rate at multiple points on the drum surface and calculated the average for these measurements. In a follow-up study, Sabeeha *et al*. (2017) [13] examined the dose rate assessment for dummy waste drums containing metallic waste (15-20%), encapsulation material and ^{137}Cs gamma point sources placed at different distances from the outer wall. The detection system was a NaI-type handheld device with 40% efficiency of gamma-ray at 0.661 MeV, in contact with the outer side of the waste package. Sabeeha *et al*. (2017) [13] report on dose rate measurements using a NaI detector for the acceptance of radioactive waste generated from decommissioning operations for transport, storage and disposal based on national regulations. They used dummy 220 L carbon steel waste drums in which metallic pieces contaminated with ^{137}Cs were conditioned with cement matrix to verify and calibrate the methodology [14].

2.1.7 Passive gamma radiation measurements

For many organizations, the priority is the research and development of new non-destructive methods capable to detect the radiological (including difficult-to-measure alpha and beta emitters) and fissile mass content with an acceptable uncertainty, compatible with the waste acceptance criteria (WAC) for storage, transportation, and final disposal. Ideally, these methods should be able to be applied in homogeneous and heterogeneous waste in packages of different sizes.

Passive non-destructive measurements refer to those methods consisting in measuring the radiation emitted spontaneously by the radioactive materials. In case of characterization of radioactive waste, gamma methods are effective when a measurable amount of gamma photons are able to penetrate the package to be measured

[2]. In conditioned radioactive waste, very low energy gamma photons (or X rays) and beta and alpha emitters cannot be detected by this method (for instance long-lived radionuclides such as ^{36}Cl, ^{129}I, ^{41}Ca, ^{10}Be, but also the low energy 59.54 keV gamma line of ^{241}Am). These difficult to measure radionuclides are therefore often scaled to an easily measured gamma emitter such as ^{60}Co or ^{137}Cs. Also, radionuclides that decay by positron emission (e.g., ^{22}Na) are often detected by measuring the 511 keV annihilation photons with gamma instrumentation. If there is no measurable gamma emitter present in the wastes, then gamma measurement will not be suitable as a characterization method [14].

2.2 Neutron measurements

2.2.1 Passive neutron measurement

In some cases, gamma emission from radioactive material can be masked by more intense emitters (e.g., activation products or fission products). Neutron counting can be used to characterize these types of nuclear wastes, or to obtain complementary information and to reduce measurement uncertainties. Used for the purpose of radioactive waste characterization, it can provide information on the quantity of actinides present in the waste package, and it is mainly used for the quantification of Pu, taking advantage of the spontaneous emission of neutrons, mainly coming from spontaneous fission, or the (alpha, n) reaction which produces a single fast neutron from the interaction of the alpha particle emitted during the disintegration with a light element present in the medium (Be, B, C, O, F, etc.). This method has a relatively low sensitivity to the density of materials surrounding the nuclear material, but hydrogen or other light elements present in the matrix slow down neutrons, making some of them undetectable. As it is not very sensitive to metallic materials present in the matrix compared to gamma spectrometry, these two techniques can complement each other. Neutron emission from different isotopes does not show characteristic differences, so neutron counting cannot distinguish between different neutron emitting radionuclides. As the identification and quantification of these isotopes is not possible with this method, the measured fission rate is expressed in the terms of ^{240}Pu equivalent mass, used for quantification of the neutron emitting nuclides ([15]; [1]; [14]).

2.2.1.1 Total neutron counting

This is the simplest mode of application of passive neutron measurement. Total neutron counting is an integral measurement method and aims to detect all neutrons without distinction of the process of emission. Detectors are placed near the object to be measured, and signals of all individual detectors are summed up. The waste package may be rotated during the measurement to level out smaller inhomogeneities of the emission-rate distribution on the surface of the measured object. This type of measurement is only representative for a nearly homogeneous distribution of neutron emitters in the waste package in a nearly homogeneous matrix. ([15], [14])

2.2.1.2 Segmented neutron counting

Segmented neutron counting (or Segmented Neutron Scanning, SNS) can be used to determine the distribution of neutron emission-rates on the surface of the waste package. The surface of the waste package is subdivided into equidistant segments, and each segment is subdivided into sectors. The neutron emission rate for each sector is determined by either position sensitive detectors (2-dimensional) or using a special arrangement of neutron detector tubes (in vertical and horizontal arrangement) combined with rotation of the waste package. Deconvolution of the measured data provides a set of data giving information on the distribution of the neutron emission rate on the surface of the waste package [15]. The application of this configuration allows to verify the assumption of homogeneity required for applying the total neutron counting evaluation procedure, and the detection of hot spots [14].

2.2.1.3 Neutron radiography/tomography

Neutron radiography is, until now, not routinely applied on radioactive waste packages and results of previous R&D projects did not show convincing results [16], probably related to both the low neutron flux used in these projects, and the low spatial resolution. To investigate the general applicability of fission neutron radiography for the non-destructive characterization of radioactive waste packages, a feasibility study was initiated with the NECTAR fission neutron facility (which offers neutron fluxes up to 4.7×10^{7} $cm^{-2}s^{-1}$) of the Technical University of Munich (TUM) [16]. For this feasibility study, several mock-up drums were used bearing different typical, but non-radioactive matrices (PE grains, bitumen, concrete, supercompacted pellets, lead-shielding containers and heavy concrete – densities ranging from 1 g/cm^3 up to 4.6 g/cm^3), as well as a specially designed mock-up drum simulating raw waste. To compare neutron radiography with more currently used techniques, all samples were also measured by a tomography system using ^{60}Co (activity 2.1×10^{13} Bq) as transmission source [16]. Results showed that fission neutron radiography, and therefore fission neutron tomography too, of 200 l (radioactive) waste drums is possible, provided that a minimum neutron fluence of about 10^{7} cm^{-2} at the detector plane is achieved. Further improvements are needed regarding image processing and image quality [14].

2.3 Other methods

2.3.1 Digital autoradiography for beta and alpha measurements

Digital autoradiography is a non-destructive nuclear analysis method used to produce and quantify an image of the radioactivity present in the sample. It has proven to be applicable on solid materials (metals, powder, smears, concrete, wood, etc.) resulting from dismantling operations. The first operational developments on actual dismantling sites implemented reusable autoradiographic screens sensitive to all types of radiation, allowing the non-intrusive detection of difficult-to-measure radionuclides (low energy b-emitters such as ^{3}H and ^{14}C, as well as alpha-emitters), in particular with improved sampling of low-tritiated waste.

Potentially radioactive waste is placed on the screens; after a certain time of exposure, screens are developed, and an image is obtained revealing the presence of radioisotopes. Images taken using this technique have allowed the mapping of traces of tritium, radiocarbon, and uranium on concrete.

Current developments aim at optimizing the technique for dismantling operations by making it possible to move from offline detection to detection in real time [17].

2.3.2 Calorimetry

Calorimetry is the quantitative measurement of heat, and it can be used as a non-destructive assay technique for determining the thermal power output of heat-producing nuclear matter contained in waste or waste packages. Radioactive decay energy is eventually converted into heat by the interaction of the emitted particles with the surrounding matter. This technique is not able to distinguish between different radioisotopes, so it is necessary to support the method with complementary gamma and neutron emission measurements.

As any radiation that escapes from the calorimetric instrument remains undetected and unaccounted for, detailed numerical simulation and proper calibration of the instrument is needed.

Calorimetry has been successfully applied in the nuclear industry for the accurate quantification of nuclear matter contained in drums for inventory or classification purposes. It is a Non-Destructive Assay (NDA) technique that consists in precisely measuring the thermal power generated by the nuclear decays within the radioactive matter and relate it to the specific power of the isotope to deduce the mass of the assayed matter. It is suited for nuclear materials that generates heat by alpha and beta particle decays in the range of thermal power spanning from 0.001 W to 135 W. It is mainly used for the assay of Plutonium and ^{241}Am (either as a single isotope or mixed with Plutonium). Calorimetry can be coupled with a spectroscopic technique when the sample contains different isotopes [14]. Figure 5 shows a schematic design of a basic calorimeter.

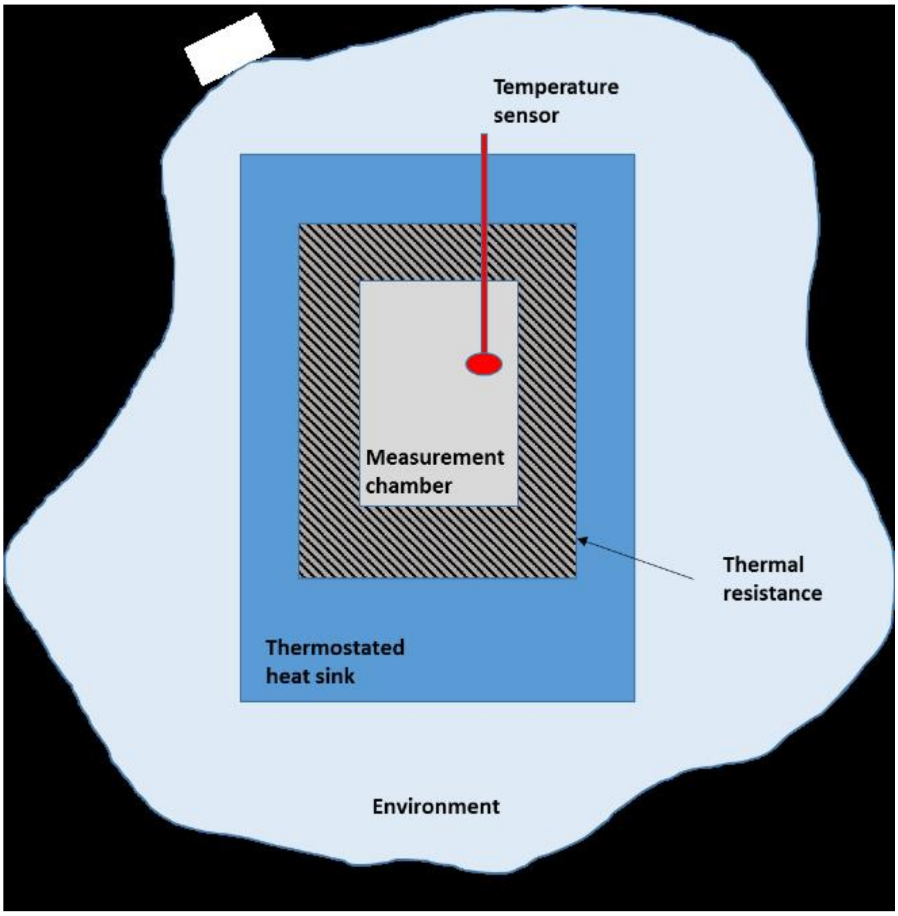

Figure 5 Schematic design of a basic calorimeter (CHANCE (D2.3) - R&D needs for conditioned waste characterization, 2022)

In the frame of the Task 3.2 of the CHANCE Project a calorimeter has been developed that can assess cylindrical samples (industrial drums) with a volume up to 260 litres. It can measure thermal power ranging from 100 to 3500 mW with a measurement accuracy lower than 2.5% and a precision better than 2% in the whole measurement range.

An exhausting description can also be read in Deliverable 2.3 (R&D needs for conditioned waste characterization) of the CHANCE Project [14].

2.3.3 High-energy photon imaging

High-energy photon imaging provides very rich information about the internal structure of packages (density, shape, position, etc. of the waste, coating and blocking matrices, internal screens, containers, etc.), and can be used in the manner of a medical scanner to inspect the interior of a waste package. The package is placed between a photon source and a detector. The image delivered by the detector shows the absorption of photons through the package. In contrast to medical scanners, which are optimised for scanning the human body, i.e., water a few tens of centimetres thick, there can be large variations in the size (60-100 cm diameter) and density (0.5-2 g.cm^{-3}) of the object to be scanned in case of analysing radioactive waste packages. In order to deal with such objects, a high intensity and energy photon source is required. This needed photon source can be produced by an electron linear accelerator (LINAC). In this apparatus, the electron packets produced by an electron cannon are accelerated in a network of cavities by a stationary high-frequency wave and their energy is raised up to a few MeV. The electrons are then focused and projected onto a heavy material target (tungsten or tantalum), then they yield a fraction of their energy by emitting a braking radiation (or Bremsstrahlung). This equipment can deliver very high dose rates, ranging from 10 to 100 Gy/min at a distance of 1 m from the target in the axis of the beam. The radiographic image represents the attenuation experienced by the beam along a linear path. The tomographic image is obtained by acquiring different angular projections (radiographies) of the package. The tomographic reconstruction is then carried out by dedicated algorithms allowing precise visualization of the interior of an object (values of the density) in planar sections [1].

Figure 6 shows the main components of such a system.

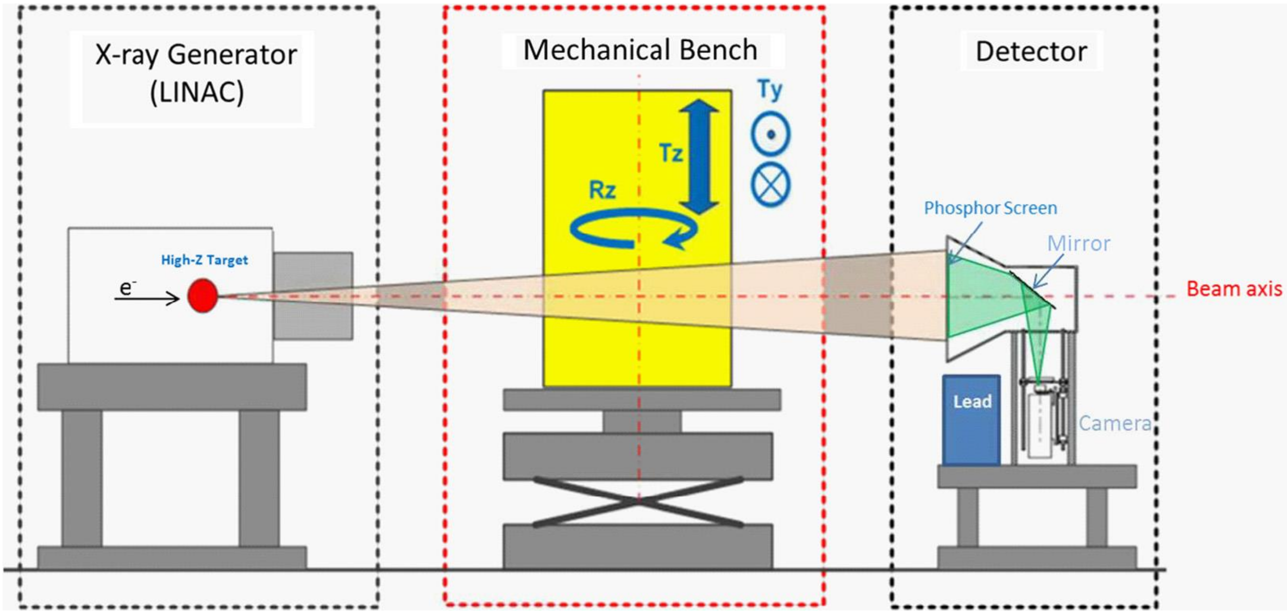

Figure 6 Main components of the high-energy imaging system (Pérot et al, 2018)

With these levels of intensity and energy, it is possible to cross through more than a meter of concrete while keeping a detectable signal behind the object to be radiographed. However, it is absolutely necessary to set up highly efficient biological protection in order to protect the personnel. In CEA Cadarache, such a system is implemented in the CINPHONIE buried casemate containing a 9MeV LINAC, see Figure 7.

Figure 7 The CINPHONIE cell hosting a high energy photon imaging system in the CHICADE basic nuclear facility, at CEA Cadarache (Pérot et al., 2018).

This high-energy photon imaging system allows the realization of X-ray radiographies (2D imaging) or tomographies (sectional reconstruction of the interior of the package, 3D imaging), shown on Figure 8.

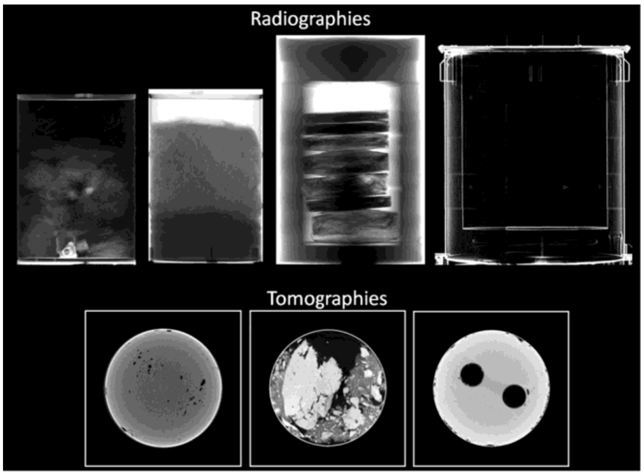

Figure 8 Examples of X-ray radiographies and tomographies on packages of different diameters (Pérot et al., 2018)

Using standards of known and calibrated materials, it was possible to qualify the performances of the high energy (9 MeV) tomograph of CINPHONIE: the spatial resolution is 1.5 mm and the precision on density is less than 10%. Typical 1 m^3 packages can be inspected in less than 10 min for a complete radiography, and about 30 min for a tomographic cut. Two acquisition systems developed by CEA LETI are currently available: (1) a 2D wide-field screen of 80-60 cm^2 with a Gadox (Gd2O2S) phosphor coating for rapid imaging, with attenuation dynamics of about 3 decades, or in other words 1 m of concrete or 25 cm of steel, and (2) a system of 25 CdTe semiconductor bar detectors, with collimators oriented towards the focal spot of the photon beam, for quantitative computed tomography with attenuation dynamics of approximately 5 decades, i.e. 1.5 m of concrete or 40 cm of steel. Newer detectors (large and continuous line of scintillator needles) are under test to avoid the horizontal sweeping scan of the package imposed by dead layers between the collimated CdTe, and thus to reduce acquisition time. Short-term evolutions include the use of a higher energy and intensity LINAC to interrogate larger and heavier waste packages (up to 5 T), and acquisitions at different energies to determine the mean atomic number of objects, by taking advantage of the differences in attenuation according to the photon beam energy spectrum and the atomic number of the elements. In addition to the already measured density, this information will make it possible to refine the identification of the materials [1].

2.3.4 Active neutron interrogation

Active neutron interrogation consists in measuring the fast and delayed neutrons of neutron-induced fissions and allows it to quantify the fissile materials, for example when passive neutron measurement is inoperative because their spontaneous neutron emission is insufficient or is masked by that of more intense emitters such as curium and americium. Active neutron interrogation is based on the detection of neutrons emitted as a result of fission induced by an external neutron source. The extraction of the useful signal due to induced fission neutrons, embedded in the interrogating flux which is several orders of magnitude higher, uses techniques of time and energy discrimination [1].

This technique can be subdivided into two approaches.

Measuring prompt neutrons

This method uses a pulse-mode neutron generator to detect prompt fission neutrons induced by thermal neutrons.

The principle can be described in three steps:

– the neutron generator emits a short pulse (typically a few dozen to hundred ms) of neutrons of 14 MeV (during which fissions induced by fast neutrons are produced whose prompt neutrons cannot be used because it is impossible to distinguish them from the interrogating neutrons);

– the fast neutrons of the generator slow down in the constituent materials of the measuring device (notably graphite, see Fig. 15) and the object to be characterised;

– when the interrogating flux is essentially thermal (a few hundred ms after the end of the neutron pulse), it becomes possible to discriminate energy between the interrogating neutrons (thermal) and the prompt fission neutrons (fast). This is accomplished with blocks of ^{3}He detectors surrounded by polyethylene, coated with cadmium and/or B_4C to absorb the interrogating thermal neutrons that will nevertheless let the fast prompt fission neutrons through, the latter being then thermalized by the polyethylene and detected by the ^{3}He counters.

The measured signal contains a component due to prompt fission neutrons proportional to the amount of fissile material. The coefficient of proportionality, called the calibration coefficient, is estimated for the different waste matrices likely to be measured [1].

Measuring delayed neutrons

Measurement of delayed neutrons involves two phases, first with an irradiation of the package intended to cause fissions (with fast, epithermal and thermal neutrons) and then a counting of the delayed neutrons resulting from induced fissions. Since each of these phases lasts for several seconds or minutes, the emission of the generator is not necessarily pulsed and the use of an isotopic source of neutrons is possible.

The neutron interrogation method essentially makes it possible to characterise the fissile nuclei (^{235}U, ^{239}Pu and ^{241}Pu). The signal due to fertile nuclei (^{238}U and ^{240}Pu) may nevertheless be significant for some measurements of delayed neutrons (with a harder interrogating flux). Whatever the mode of interrogation (isotopic source, neutron generator), they allow an overall characterisation of the waste package, but they are sensitive to the nature of the matrix (its density and chemical composition), the position of the contaminant in the package and the self-shielding effect in fissile materials. These penalties may be extensive but when these effects are controlled, the method is very sensitive and detection limits can reach a few tens of milligrams of fissile materials. As in the case of passive neutron counting, it is not possible to distinguish the contribution of the different isotopes and the isotopic composition needs to be known a priori (reference spectrum) or determined through other complementary methods (gamma spectroscopy) [1].

2.3.5 Active photon interrogation (Photofission)

High energy photon interrogation (detection of photofission delayed neutrons or gamma rays) is studied to characterise the same nuclear materials in large-volume concrete packages for which neutron interrogation is limited due to strong neutron attenuation by hydrogen nuclei. The use of high-energy photons and of the photofission phenomenon, a physical phenomenon similar to neutron fission but induced by photons with energy greater than 6 MeV, allows the actinides to be assayed within a waste package. In the same way as high-energy photon imaging, this method uses a high-energy photon beam produced with a LINAC and a conversion target (Bremsstrahlung). The photons, beyond threshold energy of about 6 MeV, have the power to cause the fission of heavy nuclei with a mass greater than that of lead (see Figure 9) [1].

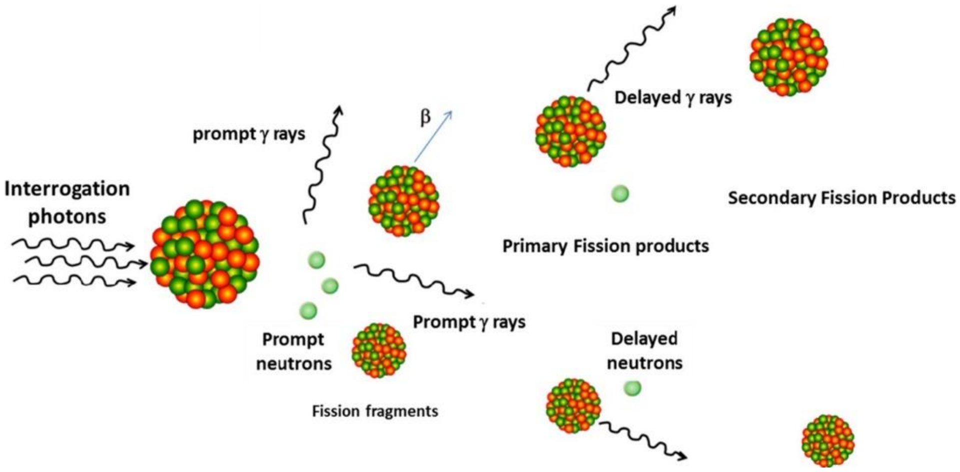

Figure 9 Basic diagram of photofission (Pérot et al., 2018)

By knowing the characteristics of the interrogating high-energy photon beam (energy, intensity, direction...), the measurement of delayed neutrons or gamma radiations from photofission allows the dosage of the quantity of actinides present in a radioactive waste package, photofission prompt particles being difficult (prompt neutrons) or impossible (prompt gamma rays) to detect due to the intense background following the LINAC pulses.

The photofission cross-section exhibits a maximum for photons of 15 MeV energy (exciting the giant dipole resonance of the target nucleus, with decreasing of the said resonance by the fission path). In contrast to thermal neutron fission, all actinides are likely to undergo photofission with similar probability, even isotopes (^{234}U, ^{238}U, ^{238}Pu, ^{240}Pu, ^{242}Pu) as well as the odd ones (^{233}U, ^{235}U, ^{239}Pu, ^{241}Pu) of uranium and plutonium.

The first photofission waste characterisation studies developed at the CEA exploited the detection of delayed neutrons. The methods used to detect delayed gamma rays are more recent [14]. Evaluations on waste packages were carried out in particular at the SAPHIR facility in CEA Saclay (Saclay photonic activation and irradiation activation system, Fig. 18) and continued at CEA Cadarache, by simulation and experimentation in the CINPHONIE facility (photonic and neutron interrogation cell, Fig. 13, Sect. 3.2 on high-energy photon imaging) with an electron LINAC (currently 9 MeV, short term, 20 MeV).

Delayed neutrons are emitted by the precursor nuclei of fission products up to a few tens of seconds after photofission. They are counted during irradiation, between each pulse of the LINAC.

The prompt neutrons of photofission are produced a few fractions of picoseconds after photofission, with a production rate much higher than that of delayed neutrons (about a factor of 100) but their detection is made very difficult by the intense photon flash of the LINAC, accompanied by an intense photo-neutron flux that blinds the generally used ^{3}He neutron counters. New types of activation sensors, including fluorine for instance, are now being studied to gain access to information from prompt neutrons, not just after the LINAC pulses but after stopping irradiation, in view to provide additional data in the interpretation of photofission measurements.

As mentioned above, the measurement of delayed gamma rays of fission is the only possible one, the prompt gamma rays being masked by the intense photon flash of the LINAC pulse. Today it is applied after irradiation in two forms: on the one hand in total high energy gamma counting (Eg>3 MeV) using detectors with high stopping power (BGO scintillator), and on the other hand in HPGe.

The method has been evaluated in particular by tests on package mock-ups and real packages by global gamma counting. On the other hand, Figure 19 shows the spectrum of the delayed gamma rays of a 100 g uranium sample centred in a large concrete package (about 1.2 m^{3}), obtained by a Monte Carlo simulation for a 2 h irradiation with a 15 MeV LINAC followed by a 3-hour post-irradiation counting period using a HPGe detector.

The use of multiple detectors, placed all around the examined package, also allows tomographic information to be produced from high-energy delayed neutrons or gamma rays. This photofission tomography technique offers the possibility to locate nuclear material that has undergone photofission within the waste package, after computer reconstruction of the detectors data, and to thereby reduce the uncertainties by making it possible to focus the interrogation and the detection on the specific zone of interest in case of hot spot. As mentioned above, the fissile actinides (^{235}U and ^{239}Pu) and fertile ones (^{238}U) undergo photofission with a probability of the same order of magnitude. Their discrimination is therefore necessary to estimate certain quantities of interest such as the fissile matter mass.

Different methods are possible, such as the analysis of delayed gamma ratios, the time evolution of the delayed gamma signal, or the ratio of delayed gamma and neutron signals. Photofission is a promising technique for the characterisation of large-volume concrete waste packages for which other non-destructive nuclear measurement methods are reaching their limits. The feasibility studies referred to above are therefore being pursued as part of a major development programme to bring it to the industrial application stage [1].

2.3.6 Prompt gamma neutron activation analysis

Neutron activation analysis (radiative capture prompt gamma radiations or fission delayed gamma rays) is studied to characterise chemical toxics or nuclear materials. Many nuclei are identifiable by their prompt gamma radiation induced by neutron activation (PGNAA) in particular that which is emitted after the radiative capture (n, g) of a neutron, the reaction being all the more likely as the energy of the neutron is low. It is generally characterised by the cross section of radiative capture with thermal neutrons (0.025 eV), of which Figure 20 gives an order of magnitude for most elements of the Mendeleev periodic classification, taking into account their natural isotopes. If a few elements such as boron, gadolinium, cadmium, or mercury have a very high radiative capture cross-section of more than 100 barns, most elements such as iron, chlorine or nickel have a lower cross-section, of the order of the barn, which nevertheless authorises their characterisation by measuring their prompt gamma radiation. Only a few elements such as carbon, oxygen or lead have capture cross-sections that are too low to be assayed by PGNAA. For these elements, reactions involving fast neutrons can be preferred, such as inelastic scattering (n, n’g) that also produces gamma ray characteristics of the interrogated elements. Detection limits are however much smaller because cross sections are well below 1 barn for all the elements, and the larger fast neutron flux (compared to the thermal flux) does not compensate for that.

Since interrogation sources produce fast neutrons of a few MeV, they are surrounded, as well as the analysed object, by a moderating material to promote capture reactions at thermal energy. The most commonly used neutron generators are based on the DD or DT fusion reaction, which produces 2.5 MeV or 14 MeV neutrons, respectively, depending on whether the target on which the deuterium ions are accelerated contains deuterium or tritium. These generators operate in pulsed mode, which makes it possible to favour the measurement of the radiative capture gamma radiations between the pulses, once the neutrons have been thermalized to eliminate the noise of the abovementioned reactions with fast neutrons, such as inelastic scattering (n, n’g). Indeed, the later may induce a significant background on the major elements constituting the waste or the measurement system, when capture gamma rays of minor elements (traces) are searched. Gamma radiation is analysed by high resolution spectrometry with an HPGe detector.

PGNAA can be used to characterise radioactive waste, revealing the presence of toxic or reactive substances (boron, chlorine, cadmium, gadolinium mercury, aluminium, nuclear materials, etc.), or the presence of neutron moderators (carbon, hydrogen) and neutron absorbers (boron, cadmium, gadolinium) in order to correct neutron measurements for matrix effects in a waste package. This technique is also applied for online analysis of cement- or coal-based crusts, in petroleum prospecting, and its use is also being considered to retrieve precious metals and rare earths from electronic waste (computers, mobile phones, etc.). It is even possible to characterize nuclear materials through neutron activation by measuring delayed gamma radiation of the induced fissions, between the pulses of the generator or after irradiation according to the radioactive period of the fission fragments emitting these radiations [1].

2.3.7 ^{3}H/^{3}He Noble Gas Mass Spectrometry

As decay products, helium isotopes can clearly indicate the presence of tritium and alpha decaying isotopes in a closed system. Palcsu et al. (2010) [18] presents a study of helium and neon measurements and their interpretation of long-term head- space gas investigations in L/ILW waste drums from Paks Nuclear Power Plant and closed vaults of the Radioactive Waste Treatment and Disposal Facility, Püspökszilágy, Hungary. Development of special sampling methods and preparation lines as well as isotope-analytical measurements of the headspace gas samples were done in the Hertelendi Laboratory of Environmental Studies in the ATOMKI. In the gas samples helium isotopes as well as neon isotopes have been determined mass spectrometrically. While neon content can be of atmospheric origin only, helium can be produced either by alpha decay (^{4}He) or decay of tritium (^{3}He). ^{3}H/^{4}He and He/Ne ratios have been used to determine the different origin of the helium isotopes. Helium isotope ratios always represented ^{3}He enrichment in the headspace gases produced by the decay of the tritium in the waste. Using the recent ^{3}He concentration in headspace gas the total amount of ^{3}H restored in L/ILW vaults was estimated. The investigated seven different vaults were closed between 1979 and 1995 when they had been full of L/ILW. The calculated tritium activities based on the He measurements showed good agreement with the documented isotope inventory of the vaults. Typical tritium activity concentrations were between 0.1 and 10 Bq.l^{-1} gas in the drums and between 10 and 1000 Bq/L gas in the vaults. Additionally, one drum showed a higher He/Ne ratio compared to air, which clearly indicates ^{4}He excess, thus the presence an alpha source in the waste. The study has demonstrated that helium and neon measurements are a powerful tool to reveal tritium activities in radioactive waste. In some cases, the presence of alpha decaying isotopes can also be detected.

2.3.8 ^{129}I/^{129}Xe Noble Gas Mass Spectrometry

The activity concentration of ^{129}I can be determined indirectly by mass spectrometric measurement of its daughter element ^{129}Xe by noble gas mass spectrometry. The practical implementation of the procedure is as follows.

After sampling, the sampled material is placed under vacuum in a hermetically sealed container and the degassed sample is left in a sealed state for several months, if possible. At the end of the storage period, the amount of ^{129}Xe produced in the meantime from ^{129}I is determined by mass spectrometry. The ^{129}I activity concentration is calculated using the following formula:

$$C = N_{daughter} \cdot \frac{e^{\lambda t_{sd}}}{(1 - e^{-\lambda t_{dm}})} \cdot \lambda \cdot \frac{1}{V_{\mathrm{sample}}}$$

where C is the activity concentration of ^{129}I in Bq.m^{-3}, $N_{daughter}$ is the number of ^{129}Xe daughter elements produced, λ is the decay constant of ^{129}I, V_{sample} is the volume of adsorbed air sample in m^3, t_{sd} is the time between sampling and degassing, t_{dm} is the time between degassing and measurement, i.e. the storage time. It is necessary to take into account the time between sampling and degassing when determining the concentration of a radioiodine with a shorter half-life, such as ^{131}I.

2.3.9 Cavity Ring Down Spectroscopy (CRDS)

As the CHANCE project deliverable 2.3 [14] deals in detail with the topic of CRDS and state of the art developments in this field, the section on CRDS is quoted from this document.

The CRDS can provide the sensitivity required to detect fugitive radioactive emissions from nuclear waste outgassing. In CRDS, the gas sample is placed inside an external resonant optical cavity consisting of high-reflectivity mirrors with an effective path length of several kilometres. A laser beam is coupled into the cavity, and the light exiting the cavity is focussed onto a detector, as shown in *Figure 10*. The laser coupling is suddenly switched off and the light decaying out of the cavity recorded. The signal is fitted with an exponential curve and the decay time, also called ring- down time (τ) determined. Additional losses due to analyte absorption result in a shorter ring-down time. Spectra are recorded at low pressure (~ 10 mbar) such that the absorption features are narrow and the peaks of the different molecules and isotopologues are well separated. Quantum cascade lasers (QCLs) are ideal to probe molecules, as they emit light in the mid-infrared region, where strong molecular vibrational levels are present. They are compact and relatively low cost, and high resolution can be achieved, as they typically have a linewidth of a few tens of MHz. The recent rise of commercial QCLs has paved the way for a field deployable CRDS system for radionuclide detection. For the highest sensitivity, the strongest absorption feature of the target isotopes must be identified. Interferences from other molecules and isotopes should also be taken into account as well as availability of lasers and other optical components. For instance, one of the strongest lines of ^{14}CO$_2$, with minimum interference from other isotopologues of CO_2 and molecules, is situated at 2209.1 cm^{-1} (4.52 µm). This line has been used for highly sensitive detection of radiocarbon with CRDS below ppb levels ([19], [20], [21], [22], [23]), with detection levels as low a few ppq ([24]). An example of a spectrum of tritiated water recorded with a CRDS system is shown in Figure 11 where it is seen that in this case the central wavelength of the targeted absorption line is at 4596.48 cm^{-1} or 2.175 µm.

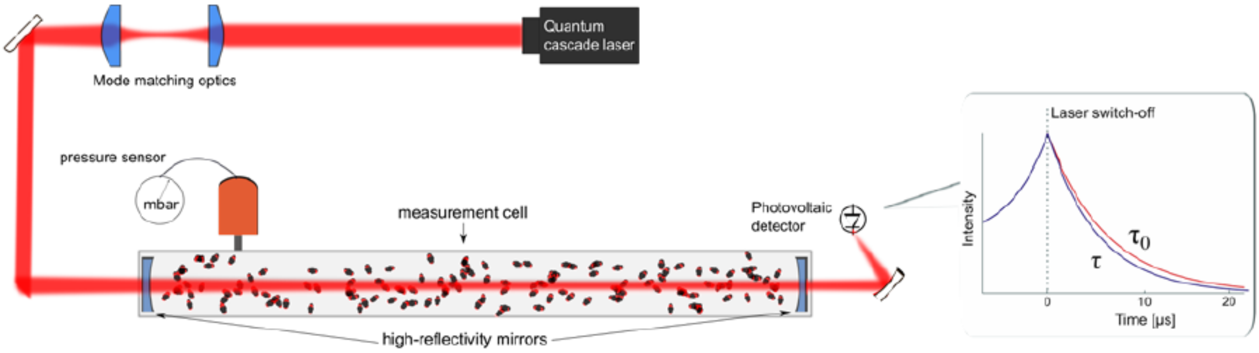

Figure 10 PRINCIPLE OF THE CRDS TECHNIQUE (CHANCE (D2.3) - R&D needs for conditioned waste characterization, 2022)

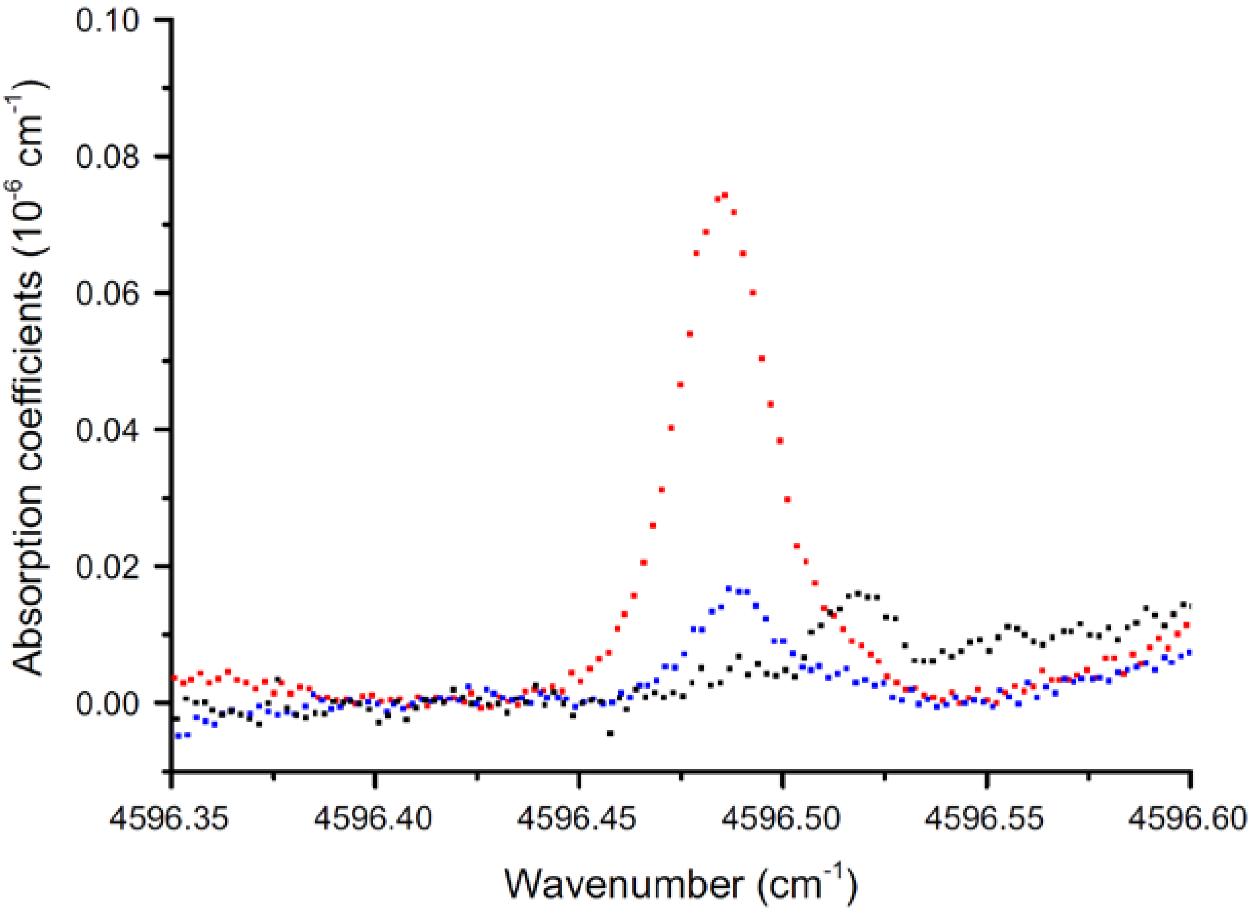

Figure 11 Experimental absorption spectra CHANCE (D2.3) - R&D needs for conditioned waste characterization, 2022)

For many applications, including nuclear waste outgassing monitoring, the direct detection of the target radionuclide by CRDS is not feasible, as the molecular species is diluted in an atmospheric matrix. It is therefore necessary to first trap the molecules of interest (CO_2, H_2O…) and then release an almost pure sample into the CRDS cell. In this manner the highest sensitivity can be achieved, and trace amount of the radionuclide can be detected. It is however crucial to maintain the advantages of using an optical method to enable in situ measurements. The sampling method must be automated and performed on-line and should for example not result in trapping the gas in a liquid medium. This way, no complex sampling preparation is needed. There are several options to trap the gaseous molecules. A cryogenic trap, with a "freeze-and-release" method or cryofocusing can be used to trap CO_2 and has been previously explored. However, the relative slow cooling and heating cycle and the cost of a cryogenic unit is not ideal. Selective CO_2 trapping can be achieved using an adsorbent. A weak anion exchange resin can for example efficiently trap CO_2 while instantaneously releasing CO_2 at only 100°C, making them ideal for in situ monitoring. For detection of tritium in the form in tritiated water, water vapour can easily be trapped using a standard cold trap. If rapid sampling is necessary, several sampling modules in parallel can be used, as illustrated in Figure 12. A catalytic converter can be added in order to convert other molecular forms of the radionuclide of interest into the molecular form used for the measurements (e.g., $^{14}CH_4$ can be converted in $^{14}CO_2$ or HT into HTO).

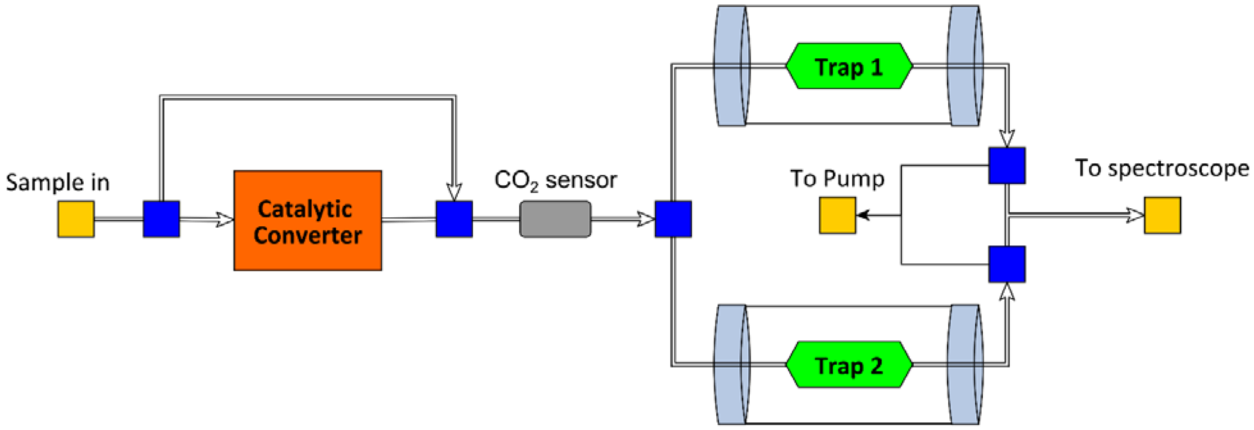

Figure 12 Possible configuration of a sampling system CHANCE (D2.3) - R&D needs for conditioned waste characterization, 2022)

This approach of combining on-line sampling with CRDS has been successfully used to monitor the radiocarbon emissions from a nuclear power plant stack ([25]). High sensitivity was achieved as well as a measurement time of only 50 min, which is an order of magnitude faster than conventional techniques currently used, such as LSC. The same method is currently being used in CHANCE for characterisation and monitoring of nuclear waste outgassing. A CRDS instrument for the detection of radiocarbon compounds will be used to study in detail their outgassing rate on various types of waste. A novel instrument for the detection of $H^{36}Cl$ based on CRDS is also being developed. This is the first time that CRDS is used to detect this molecule, which is highly relevant in the case of outgassing from graphite waste. This will advance the use of CRDS as an innovative technique to characterize outgassing of radioactive waste. It will result in a major step forward in the development of the use of CRDS to detect radioactive gas emissions, with the demonstration of its use for a new application [14].

2.3.10 Muon tomography

As the CHANCE project deliverable 2.3 deals in detail with the topic of muon tomography and state of the art developments in this field, the section on muon tomography is quoted from this document.

Because of their unique ability to penetrate matter, cosmic ray muons can be used to image the interiors of structures and can be applied as a non-destructive characterization method. It can be a very useful tool in case of legacy nuclear waste [26].

Muons are charged particles, created by the interaction of cosmic radiation with the upper layer of the atmosphere. They have the same electric charge as electrons, which make them easy to detect, but they are much more massive ($m_\mu \approx 207m_e$) and have a high momentum, which confers them with their strong penetrating ability. The vertical flux of energetic muons, above 1 $GeV.c^{-1}$, at sea level is about 70 m^{-2} s^{-1} sr^{-1} (or an integrated vertical flux ≈ 1 cm^{-2} – min^{-1}) (Amsler et al., 2008). The mean muon energy is 3–4 GeV, which is sufficient to allow them to penetrate several meters of rock before being stopped. Muon imaging is not new, the first measurements date back to the 1950s [26].

As the muons pass through matter, some of their energy is transferred from the muon to the electrons and nuclei in the material, resulting in an energy loss and direction change of the muon, a process called multiple scattering. Because of this multiple scattering, the muon either gets absorbed in the material or comes out under an angle, and the spectrum of the angles depends on the muon momentum and the charge number Z of the material traversed. Muon tomography allows discriminating between low, medium and high Z materials. Image reconstruction techniques and/or statistical analysis of the muon tracks are performed to image target objects. To use muons for radiography, the number of muons absorbed in the material is recorded. This technique is particularly relevant for the scanning of large objects like waste silos. For smaller objects like waste drums or cargo containers, tomography is used, where the scattering of the muons is measured. In muon tomography, the incoming and outgoing directions are recorded for each muon, therefore, the entire scanned volume needs to be placed in between detectors. During the passage of the muon through the target material, the muon undergoes a random walk as a result of multiple scattering. To analyse the data, many algorithms have been developed [14].

An exhausting description of the muon tomography technique and newest developments in the field are presented in CHANCE (D2.3) - R&D needs for conditioned waste characterization (2022) [14].

3 Destructive analysis

Destructive measurement complements non-destructive measurement of radioactive waste, and has an important role particularly in case of historic/legacy wastes when there is little or insufficient data available. Destructive analysis involves sampling, sample preparation and chemical separation methods. Sampling is a critical step in the characterization process. Designing the sampling procedures and checking the homogeneity and representation of the samples assures the reliability of the final results. Sample preparation by dissolution/mineralization has to be applied in accordance with the physicochemical characteristics of the matrix of waste forms or primary wastes and as a function of the behaviour of the specific element in the dissolution media (volatilization, precipitation). In some cases, it is possible to do a direct measurement of the radionuclide after dissolution/mineralization if the determination technique has the resolution required for it. Chemical separation involves the chemical strategy to eliminate chemical interference (e.g., Ca in Sr determination) and radiological interference in the measurement through a chemical process such as precipitation, solvent extraction, or chromatography.

Radiometric determination is performed by instrumental analysis. Sophisticated methods are used such as liquid scintillation counters that allow beta spectrometry, alpha spectrometry with semiconductor detectors, high resolution gamma spectrometry for high and low energy gamma emitting nuclides, mass spectrometry that gives an accurate and efficient response for the analysis of the prepared and/or separated waste samples [14].

3.1 Major radionuclides in radioactive and nuclear waste and destructive methods for their determination

There is a great variety of radionuclides and nuclear material in radioactive and nuclear waste. Regarding the long storage and processing period between production and final disposal of waste the radionuclides in the waste packages can be all regarded long-lived isotopes. To select the half-life of radiologically relevant radionuclides is always arbitrary, we are going to discuss the nuclides with half-lives longer than one year (not excluding those short-lived nuclides that have long-lived daughters).

According to the source of production two major groups of radionuclides can be distinguished, i.e., radionuclides of activation origin and those of contamination origin.

- **Radionuclides of activation origin in nuclear waste**

  Material in the reactor core and nuclear explosions is exposed to neutron irradiation. The highly exposed part of the reactors is the core that contains various alloys, steels, zirconium alloys. The biological shield containing concrete and steel is exposed to smaller neutron flux but the irradiation time covers years, decades. All the long-lived radionuclides may appear in the waste, the latter ones preferably in the decontamination waste.

- **Radionuclides of contamination origin in nuclear waste**

Radionuclides of contamination origin are divided according to their way of production in two groups.

Fission products are produced during the burning process in the fuel of nuclear reactors and during explosions of nuclear bombs. They are released from the fuel elements through cladding failure into the primary coolant which is the major source of contamination in reactors during operation. Fission products can be released into the environment through nuclear accidents and explosions of nuclear bombs resulting in contamination of the facilities and possibly the environment.

Actinides: Chemically the major fissile materials, ^{235}U, ^{239}Pu, ^{233}U (produced from ^{232}Th) are actinides. Actinides are partially of natural origin and are partially produced via a series of nuclear reactions and radioactive decay (transmutation) during the burnout processes of nuclear fuel and the explosion of nuclear bombs. Some of them are further generated from their parent radionuclides after shutdown of the chain reaction, e.g., ^{241}Am is produced in the decay of ^{241}Pu(β^-) therefore their amounts in wastes or in nature are with time increasing.

A comprised review about the relevant radionuclides, their properties and the characterization methods was given in the IAEA document TRS No. 389 on Radiochemical Characterization of Shut Down Nuclear Reactors for Decommissioning Purposes already in 1998 [28]. Another document with similar objectives on Development of methods to provide an inventory of radiologically relevant radionuclides was issued in the same year as the Final report of a 4-year long project of the European Atomic Energy Community FI2W-CT90-0034/FI2W-CT91-0109 [29]. A more detailed and up-to-date review was issued also by the IAEA in the TECDOC series No. 1537 with the title Strategy and Methodology for Radioactive Waste Characterization in 2007 [30]. In the chapter 5.3 on destructive analysis (DA) a list of DTM nuclides with their basic separation methods and analytical techniques are summarized. The present classification of nuclides and the methods for their destructive analysis (DA) are based on these publications. The OECD-NEA publication discussing R&D and Innovation Needs for Decommissioning Nuclear Facilities from 2014 [31] was also taken into consideration but the work focusses on non-destructive assay (NDA). The relative short list of DTM nuclides was enlarged according to the recent R&D works that revealed the significance of further radioisotopes in waste composition. Method description has been extended significantly according to the state-of-the-art knowledge on radiochemical separations and radiometric and non-radiometric measurement techniques. A list of the major activation nuclides, and those of fission products and actinides is given in Table 1, 2, 3, respectively. An excellent summary on Laboratory Techniques and Methodology was prepared by J. LEHTO and X. HOU and published by Wiley-VCH in 2011 under the title: Chemistry and Analysis of Radionuclides [32]. The work was supported by Nordic collaboration within NKS-R-NorDec project.

Table 1 An up-dated list of major long-lived activation nuclides based on IAEA TRS. No. 389

Some activation products are fission products, as well: ^{93}Zr, ^{94}Nb, ^{93m}Nb, ^{93}Mo, ^{151}Sm

Target	Reaction	Radionuclide	Decay mode	Half-life (year)	Target nuclide abundance, %
^{6}Li	n,α	**^{3}H**	**β^-**	**12.3**	7.5
^{13}C	n,α	**^{14}C**	**β^-**	**5730**	1.1
^{14}N	n,p	^{14}C			99.6
^{23}Na	n,2n	^{22}Na	β^+, EC	2.6	100
^{23}Na	γ,n	^{22}Na			100
^{35}Cl	n,γ	**^{36}Cl**	**β^-(β^+, EC)**	**301000**	75.8
^{39}K	n,p	^{39}Ar	β^-	269	93.3
^{40}Ca	n,γ	**^{41}Ca**	**EC**	**103000**	96.9

Target	Reaction	Radionuclide	Decay mode	Half-life (year)	Target nuclide abundance, %
^{54}Fe	n,γ	**^{55}Fe**	**EC**	**2.7**	5.9
^{54}Fe	n,p	^{54}Mn	EC,γ	0.86	5.9
^{55}Mn	n,2n	^{54}Mn			100
^{58}Ni	n,γ	**^{59}Ni**	**EC**	**76000**	68.3
^{62}Ni	n,γ	**^{63}Ni**	**β^-**	**100**	3.6
^{59}Co	n,γ	^{60}Co	β^-,γ	5.3	100
^{64}Zn	n,γ	^{65}Zn	β^+, EC	0.67	48.6
^{92}Zr	n,γ	**^{93}Zr**	**β^-**	**1500000**	17.1
^{92}Mo	n,γ	**^{93}Mo**	**EC**	**3500**	14.8
^{93}Nb	n,γ	**^{93m}Nb**	**IT**	**15.8**	100
^{93}Nb	n,γ	**^{94}Nb**	**β^-,γ**	**20000**	100
^{94}Mo	n,p	^{94}Nb			9.3
^{98}Mo	n,γ	**^{99}Tc**	**β^-**	**213000**	24.1
^{107}Ag	n,γ	^{108m}Ag	EC, γ	130	51.8
^{109}Ag	n,γ	^{110m}Ag	β^-,γ	0.68	48.2
^{124}Sn	n,γ	**^{125}Sb**	**β^-,γ**	**2.76**	5.8
^{132}Ba	n,γ	^{133}Ba	EC, γ	10.5	0.1
^{151}Eu	n,γ	^{152}Eu	EC,β^-,γ	13.5	47.8
^{153}Eu	n,γ	^{154}Eu	β^-,γ	8.6	52.2
^{154}Eu	n,γ	^{155}Eu	β^-,γ	4.76	0
^{165}Ho	n,γ	^{166}Ho	β^-,γ	1200	100
^{150}Sm	n,γ	^{151}Sm	β^-	90	7.4

Red letters indicate the DTM nuclides. DTM nuclides for which detailed method descriptions are given below are written with **Bold** letters.

Table 2 An up-dated list of major fission products based on IAEA TRS. No. 389

Nuclide	Production	Decay mode/emitted radiation	Half-life (year)
^{90}Sr	**fission**	**β^-**	**28.7**
^{90}Y	**fission, ^{90}Sr decay**	**β^-**	**(64 h)**
^{99}Tc	**fission, ^{98}Mo activation**	**β^-**	**211000**
^{106}Ru	fission	β^-	1.02 y
^{106}Rh	^{106}Ru decay	β^-, γ (512 keV)	(30 s)
^{126}Sn	fission	β^-	$1*10^5$
^{129}I	**fission**	**β^-**	**$1.6*10^7$**
^{135}Cs	**fission**	**β^-**	**$2.3*10^6$**
^{137}Cs	fission	β^-, γ (662 keV - ^{137m}Ba daughter)	30
^{144}Ce	fission	β^-, γ (133 keV)	(285 d)
^{147}Pm	fission	β^-	2.62

Red letters indicate the DTM nuclides. DTM nuclides for which detailed method descriptions are given below are written with **Bold** letters. Some fission products are activation products, as well: ^{93}Zr, ^{94}Nb, ^{93m}Nb, ^{93}Mo. They were listed in Table 1.

Table 3 List of major actinides based on IAEA TRS. No. 389

Nuclide	Main production	Decay mode/emitted radiation	Half-life (year)
^{238}Pu	**^{242}Cm α decay, ^{238}Np β decay**	**α**	**88**
^{239}Pu	**^{238}U(n,γ), then ^{239}Np β decay**	**α, fissile**	**24110**
^{240}Pu	**^{239}Pu(n,γ)**	**α**	**6570**
^{241}Pu	**^{240}Pu(n,γ)**	**β^-**	**14**
^{241}Am	**^{241}Pu β decay**	**α, γ (59 keV)**	**432**
^{244}Cm	**n captures**	**α**	**18,1**
^{242}Cm	**^{242}Am β decay**	**α**	**163 d**
^{237}Np	**^{238}U(n,2n) or ^{235}U(n,γ), then β decay**	**α**	**$2{,}14\text{x}10^6$**
^{233}U	**^{232}Th(n, γ), then β decay**	**α, fissile**	**$1{,}6\text{x}10^5$**
^{234}U	**natural, 0,005%**	**α**	**$2{,}5\text{x}10^5$**
^{235}U	**natural, 0,7%**	**α, fissile**	**$7\text{x}10^8$**
^{236}U	**^{235}U(n,γ)**	**α**	**$2{,}3\text{x}10^7$**
^{238}U	**natural, 99,27%**	**α**	**$4{,}5\text{x}10^9$**

Red letters indicate the DTM nuclides. DTM nuclides for which detailed method descriptions are given below are written with **Bold** letters.

It is under consideration whether the present list should be updated by including ^{232}Th, ^{230}Th, ^{228}Th, ^{231}Pa, ^{252}Cf and ^{226}Ra as the decay product of ^{238}U.

In the following section the nuclear properties, the nuclear and non-nuclear measuring techniques of the DTM nuclides are briefly summarized, and the basic chemical properties and the separation procedures of the elements are discussed focusing on the individual solutions. A short list of the standardized methods (ISO and ASTM) and the recommended methods (if available) of the IAEA is shown in Table 4 at the end of the session. Data on DTM nuclides will be summarized in the PREDIS Deliverable 2.5 Assessment of feasibility of waste form characterisation methods with estimated detection limits of the methods. A list of symbols is at the end of the document.

3.2 Major radionuclides of activation origin in nuclear waste and destructive methods for their determination

3.2.1 ^{36}Cl

It is a long-lived ($T_{1/2}$=3.01*10^5 y) radionuclide decaying basically (98%) by emission of β^- electrons (β_{Max} 709 keV) and additionally by electron capture and β^+ emission. It is produced from ^{35}Cl in the ^{35}Cl(n,γ)^{36}Cl reaction (target abundance 76 %, cross section σ=10 mb), it is also produced from ^{39}K by (n,α) reaction (σ=2 b) and from ^{34}S. ^{36}Cl is present in concrete biological shield, in graphite, it is an impurity in steels and alumina construction materials. Due to its solubility and mobility, it is radiologically important radionuclide as a contaminant in radioactive waste and the environment of nuclear facilities.

It is a DTM nuclide that can be measured after chemical separation by LSC at lower (10 mBq/sample) or by AMS at higher sensitivity (10^{-15} ^{36}Cl/Cl ratio). For LSC measurements the sample matrix and most likely all β^- emitting radionuclides have to be removed. The removal of other volatile radionuclides such as ^{129}I is especially important. For AMS measurements stable Cl (^{35}Cl) is the major interference but for the stability of the chemical processes Cl carrier is added to the sample. The measuring source in AMS is usually AgCl.

Chlorine is separated from the samples as Cl_2 by vaporization that can be performed by heating (pyrolysis above 900°C) or by oxidizing the sample with strong oxidizing agents. The evaporated Cl_2 can be trapped by graphite cooled with liquid nitrogen or by absorbing the vapours in NaOH solution containing a reducing agent, e.g., $NaNO_2$ that turns chlorine to chloride ions Cl^-.

Chloride like iodide ions form insoluble **AgCl and AgI precipitate**.

Chlorine and iodine have to be separated before LSC measurements. The separation can be performed by repeated precipitations, selective oxidation and using specific resin:

- AgCl precipitate can be selectively dissolved by the addition of ammonia while AgI remains un-attacked.
- **Iodide can be oxidized** selectively to I_2 with H_2O_2 or $NaNO_2$, followed by the **extraction of I_2** with CCl_4.
- Chlorine can be separated from iodine using the **CL resin** that is a Pd and Ag selective resin retaining these noble metals partially irreversible. The sample is loaded from 1M H_2SO_4 on the Ag treated CL resin. Chloride is eluted with 0.1M NH_4SCN and iodide is stripped with 0.35M Na_2S.

Chloride can be purified on **anion exchange resin**. AgCl is dissolved with ammonia and loaded on the column. Chloride ions are eluted with 0.2M NH_4NO_3 – 0.6M NH_4OH.

Chemical recovery of Cl can be determined by measurement of stable Cl by ICP-MS or ion chromatography before and after separation of the sample.

3.2.2 ^{41}Ca

It is a long-lived ($T_{1/2}$=1.03*10^5 y) radionuclide decaying by electron capture, it emits X-rays (3.3 keV, 11.4%) and Auger electrons (3.0 keV, 77%). It is produced from ^{40}Ca in the ^{40}Ca(n,γ)^{41}Ca reaction (target abundance 97 %, cross section σ=0.4 b). Calcium is major component of concrete, biological shield, soils and sediments, it is an impurity in graphite. ^{41}Ca is radiologically important radionuclide in decommissioning waste and a possible contaminant in radioactive waste in nuclear facilities.

It is a DTM nuclide that can be measured after chemical separation by LSC or AMS. The major difficulty in LSC measurement is the extremely low energy of X-rays and Auger electrons that fall in the range of electronic noises. A good separation from the matrix and the radionuclides emitting low energy electrons or X-rays is necessary. Another problem arises from the usually big Ca concentration of many sample types. The detection limit of LSC is around 10^{-1} Bq/g Ca using 1 g soil/concrete. AMS is at present the most sensitive detection technique for ^{41}Ca, with a detection limit of 10^{-6}- 10^{-8}Bq/g Ca. X-ray spectrometry and RIMS can also detect ^{41}Ca but they are not more sensitive than LSC.

The major difficulty in selective separation of Ca is that there are no highly selective separation procedures for Ca. Ca forms many precipitates like alkaline earth metals. The classical procedures are based on many repeated precipitations to obtain a pure Ca fraction. Ca forms **carbonate precipitate** together with Sr and Ba, while alkali metals remain dissolved and can be separated. Ca is precipitated as **$Ca(OH)_2$** together with the hydroxides of Sr, Ba from NaOH solutions of 0.5M or higher. Ca is separated more selectively as $Ca(OH)_2$ from NaOH solutions of pH 9 while Sr, Ba remain in the filtrate. These two separation steps are combined and repeated 2-3 times. Ca and Sr form precipitate in acid solutions (pH 5) with **oxalate**, while Ba and Ra are partially separated. Ba can be separated from Ca as **Ba chromate** precipitate. Sr and partially Ba can be separated by retaining them on **Sr resin** from ≥ 3M HNO3 while Ca gets in the effluent.

Additionally $Fe(OH)_3$ precipitations are performed to remove various contaminants such as actinides, lanthanides, Fe, Co, Ni etc. by **scavenging**. Many contaminants can be removed by **anion exchange** chromatography loading the sample from 8M HNO_3 and/or 9M HCl. The use of **TRU resin** for further purification of Ca from Ac, lanthanides was also proposed.

Sample preparation for AMS measurement is somewhat simpler, a Ca hydroxide precipitation at pH 9 can assure the required purification from many contaminant (Fe, Co, Ni, Mn, U, Ac, Al) followed by carbonate and nitrate precipitations to remove alkali and alkaline earth metals (Sr, Ba, Ra). Ca can be further purified on a **cation exchange resin** where it is retained from dilute HNO_3 (0.08M) and stripped with 5M HNO_3. For AMS measurement purified CaF_2 source is prepared and mixed with Ag powder and pressed in copper sample holder.

For measurement of the chemical recovery ^{45}Ca tracer can be used that is a pure β emitter (β_{Max} 257 keV) and its half-life is 163 days. It can be measured by LSC after correction for spectrum overlapping. Chemical recovery of Ca can be determined by measurement of stable Ca in the sample by AAS, ICP-OES, ICP-MS before separation and afterwards.

3.2.3 ^{55}Fe

It is a pure β^- decaying isotope, it decays through electron capture to ^{55}Mn emitting characteristic X-rays of 5.9 keV (24%) and Auger electrons of 5.2 keV (60%). Its half-life is 2.73 y.

^{55}Fe is produced by n capture from ^{54}Fe (5.8% of stable Fe) with high neutron cross section (σ=2.25 barn). Since iron is a major construction material in nuclear facilities ^{55}Fe is responsible for a significant part of the induced radioactivity on relatively short term: More than 50% of the total activity accumulated in a nuclear reactor is due to ^{55}Fe a couple of years after reactor shutdown, thus it is a major contributor to decommissioning waste.

^{55}Fe can be determined by X-ray spectrometry using low energy Ge or Si detectors or by LSC. ^{55}Fe is a DTM nuclide, due to the low energy of the emitted radiations radiochemical separation is necessary. Stable Fe presents the most significant limitation in the sensitive determination of ^{55}Fe. It produces intensive colour in the LSC source resulting in strong quenching and makes X-ray sources thick causing self-absorption losses. To reduce quench effect complexing agent such as HF, oxalic acid or reducing agent such as ascorbic acid are given to the LSC source. Counting efficiency is calculated as a function of quench parameter. The chemical recovery can be determined by measuring stable Fe content of the sample before and after the chemical operations using optical (AAS, ICP-OES) or mass spectrometric techniques (ICP-MS).

For Fe separation precipitation, LLE, ion exchange and ECh are used often combining the various separation steps:

- Fe(II) and Fe(III) –although to different level – form sparingly soluble **hydroxides and sulphides**. Hydroxide precipitate is often used to pre- concentrate Fe from bigger sample volumes. pH is adjusted with ammonia to 8 or 10.5 to reach solubility minimum in case of Fe(III) and Fe(II), respectively. Fe(III) forms soluble **oxalate complexes** if pH is below 6 while Fe(II) oxalates are insoluble.

- Fe forms different neutral or acidic chloro-complexes, such as $FeCl_2$, $FeCl_3$, $[FeCl_4]^-$ in HCl solutions. Many of the separation techniques are based on the extraction and ion exchange of these species. The classical and fairly selective method of Fe separation is the LLE of the neutral $FeCl_3$ complex with **di-isopropyl ether** from about 8M HCl. Fe is back-extracted with water. Similarly, $FeCl_3$ can also be extracted with methylisobutylketone (MIBK) from 6M HCl. The extraction of Fe with **MIBK** can be performed as ECh when MIBK is supported on an inert resin. Fe-nitroso complexes formed with **Cupferron** can also be extracted from 2M HCl in $HCCl_3$ followed by back-extraction with 6M HNO_3.
- Fe(III) can be separated using ion exchange chromatography. It is well retained by **cation exchangers** from 0.2M HCl and can be separated from possible interfering anion species such as Sb, Ru followed by its elution with 0.5M oxalic acid. A more selective separation of Fe(III) is performed by the retention of $[FeCl_4]^-$ on **anion exchange resin** from concentrated HCl solution, it can be eluted with dilute acid.
- ECh is used as a more efficient method for Fe separation than LLE. Fe(III) nitrate complex is well retained by **TRU resin** from 8M HNO_3 and can be stripped with 2M HNO_3. This property was used effectively in combination with hydroxide precipitation for the DA of ^{55}Fe. **DGA resin** has high distribution coefficient for $FeCl_3$ from HCl solutions of 4M or higher concentrations.

For purification purposes the single separation steps are usually combined, e.g., hydroxide precipitation- AEC – ECh with TRU resin.

3.2.4 Nickel isotopes: ^{59}Ni, ^{63}Ni

^{59}Ni decays by electron capture to stable ^{59}Co emitting characteristic X-rays of 6.9 keV (31%) and Auger electrons of 6.1 keV (54%), its half-life is $7.6*10^4$ y. ^{63}Ni is a pure β- emitter, it decays to stable ^{63}Cu. The maximum energy of the β electrons is 67 keV, its half-life is 100.1 y.

Both Ni isotopes are produced from stable Ni by neutron capture in the $^{58}Ni(n,\gamma)\,^{59}Ni$ and $^{62}Ni(n,\gamma)\,^{63}Ni$ reactions, respectively, with high cross sections (σ_{Ni-59}=4.6 b, σ_{Ni-63}=14.2 b). ^{58}Ni (68% abundance) and ^{62}Ni (3.6% abundance in Ni) are important components of the steel construction materials and therefore ^{59}Ni and especially ^{63}Ni contribute significantly to the accumulated activity in nuclear reactors. The activity of ^{63}Ni is comparable with that of ^{60}Co at the end of operation and a couple of years after reactor shutdown and its relative activity increases with longer cooling time. The typical activity ratio of $^{63}Ni/^{59}Ni$ is around 100.

^{59}Ni can be detected by X-ray spectrometry and ^{63}Ni by LSC. Because the activity of ^{63}Ni is much higher than that of ^{59}Ni, and the LS spectra of ^{59}Ni (X-ray and Auger electron spectrum) and ^{63}Ni (β spectrum) are overlapping therefore only ^{63}Ni is measurable by LSC. For high sensitivity measurements of ^{59}Ni AMS can be used. Both isotopes are DTM nuclides. Ni has to be separated from the matrix, any other radionuclides that would interfere in LSC or X-ray detection. For X-ray spectrometry thin sources have to be prepared to reduce self-absorption. If ^{59}Ni is detected by AMS stable Co has to be completely removed.

In acidic solutions Ni forms Ni^{2+} ions, it hydrolyses at pH 7 and above and forms a sparingly soluble precipitate. Precipitation of **Ni hydroxide** is a standard technique to pre-concentrate or purify Ni. There is a very specific reagent making complex almost exclusively with Ni, i.e. dimethylglyoxime (DMG: $C_4H_8O_2N_2$). **DMG can precipitate** Ni as $NiDMG_2$ at pH 8-9. After filtration the bright red precipitate can be decomposed by evaporation with concentrated nitric acid and the residue is dissolved in 0.1M HCl. The colourless solution can be mixed with LS cocktail. Ni can be separated by “ECh” also using DMG that is bound to an inert support. The commercially available **Ni resin** contains DMG bound to polymethacrylate resin. The mechanism is not a true extraction but formation of a Ni-DMG precipitate on-column. After destruction the Ni containing sample is dissolved in 1M HCl, the pH of the solution is adjusted to 8-9 with ammonium citrate and ammonia and the solution is loaded on Ni resin. Ni precipitate is eluted with 3M HNO_3.

In the complete separation and purification procedures the separation steps are combined, and Fe is removed from the sample before Ni separation otherwise Fe would precipitate in the load solution at pH 8-9. Usually, Fe is separated preliminary by extraction with diethylether or MIBK from 6-8M HCl where Ni remains in the aqueous phase, recently more often by AEC from 8-9M HCl or by ECh on TRU resin from 8M HNO_3 where Fe is retained and Ni gets in the effluent of the resins. (For Fe removal possibilities see the methods in chapter on ^{55}Fe.)

For the measurement of Ni radionuclides by AMS high decontamination factors against Co and Cu have to be assured. For this purpose Ni is separated as volatile **Ni tetracarbonyl** $Ni(CO)_4$.

The chemical recovery is determined by the measurement of stable Ni (together with the Ni carrier) in the sample and in the measuring source by AAS, ICP-OES or ICP-MS.

3.2.5 ^{93}Zr

It is a pure β^- decaying radionuclide emitting low energy β^- electrons (β_{Max} 60 keV), its half-life is long ($T_{1/2}=1.5*10^6$ y). It is produced by neutron capture from stable $^{92}Zr(n, \gamma)$ where the isotope abundance of ^{92}Zr is 17.1% and the reaction cross section is moderately high (σ=0.26 b). The cladding material of the fuel elements in the thermal reactors operated world-wide is Zr alloy, and soil and concrete also contain some Zr. Due to its very long half-life ^{93}Zr is a radiologically important radionuclide on long-term in nuclear facilities and radioactive wastes.

^{93}Zr is a DTM nuclide that can be detected by ICP-MS and LSC. ICP-MS is theoretically more sensitive for ^{93}Zr but the presence of stable Zr in the samples reduces the sensitivity because of the abundance sensitivity due to the presence of stable ^{92}Zr and ^{94}Zr nuclides and isobaric interferences first of all due to ^{93}Nb (isotope abundance of ^{93}Nb is 100%) and the radioactive ^{93}Mo ($T_{1/2}=4*10^3$ y) that is also produced from stable Mo in steel samples in nuclear reactors. When measuring by LSC, complete separation from the matrix and pure low energy β- and X-ray/Auger electron emitting radionuclides (e.g., ^{3}H, ^{14}C, ^{55}Fe, ^{63}Ni, ^{93}Mo, ^{241}Pu) is necessary.

One of the major issues in Zr chemistry is the strong affinity to hydrolyse and form polymers. Hydrolysis already starts in 1M acid solutions. Increasing the pH various hydroxide complexes appear and the very low solubility $Zr(OH)_4$ precipitate forms. Zr oxides are soluble in HF. Zr can be pre-concentrated as **ZrO_2*nH_2O or as $BaZrF_6$ precipitates**.

For chemical separation of Zr from radioactive wastes liquid-liquid extraction and extraction chromatography can be used.

- Zr has affinity for formation of ion association complexes: it readily forms complexes with **TBP and TOPO**. It is well known that Zr is a major interfering component in the LLE of Pu and U by TBP in the PUREX process. Many liquid-liquid extraction procedures have made use of the formation of an organic solvent soluble chelate of zirconium such as **Zr-TTA**, **Zr-HDEHP** complexes. E.g., Zr can be extracted from 2 M HNO_3 using 0.5 M TTA and re-extracted with 2 M HF. Zr can also be extracted from 4 M HCl / 1 M $AlCl_3$ solution using 0.5 M TTA in xylene and re-extraction of Zr with 0.25 M HNO_3 / HF. Zr can be extracted with **ABO** (α-benzoinoxime). Zr can form a complex with 5% **Cupferron** that is extracted with $HCCl_3$ and back-extracted with 6M HNO_3.
- For ECh of Zr TBP, TEVA, UTEVA, TRU, DGA resins can be used. Zr can be retained from 7 M HNO_3 on **TBP resin** and stripped with 0.3 M HNO_3. Zr, Nb and Mo were retained on **TEVA resin** (conditioned with 8 M $LiNO_3$ / 0.01 M HNO_3) from 9 M HCl. Zr was eluted with H_2O to separate it from Nb and Mo. Recent studies showed that Zr is better retained on TEVA if the HCl concentration is higher than 9M, but TEVA does not retain Zr from nitric acid solutions. Zr, Nb, Hf and Ta can be retained on **UTEVA resin** from 8 M HNO_3, but using 8 M HNO_3 / 0.2 M HF these elements are not retained. Zr is also retained on UTEVA fom 9M HCl solution, and is stripped with 4M HCl. The retention of Zr on **TRU resin** from 8-10M HNO_3 is much stronger than that of Nb offering a possibility to separate Zr from Nb. Studies on the retention of Zr on **DGA resin** and its separation from Nb are ongoing. Recently a new resin called **Zr resin** containing hydroxamate has become commercially available that has extremely high distribution coefficient for Zr from HCl and HNO_3 of a wide range of acidity, but the resin is not selective for Zr against Nb.

The complete separation procedures for the determination of ^{93}Zr usually consist of sample destruction including the use of HF, Zr pre-concentration by precipitation, separation by LLE, ion exchange or ECh followed by a final purification. For ICP-MS measurement of ^{93}Zr the separation of Nb and probable that of Mo is critical.

The chemical recovery can be determined by measuring stable Zr with elemental analytical techniques such as AAS, ICP-OES, ICP-MS. The relatively short ^{95}Zr can be used as radioactive tracer in ICP-MS measurements detecting the emitted γ radiation.

There are no standard analytical techniques for the determination of ^{93}Zr, there are no national or international standard procedures, the few methods applied and published are still under development. No intercomparison data are available.

3.2.6 Niobium isotopes: ^{93m}Nb, ^{94}Nb

^{94}Nb is a β^- decaying radionuclide emitting medium energy β^- electrons (β_{Max} 472 keV) and easy to measure γ radiation at 703 keV (98%) and 871 keV (100%), its half-life is long ($T_{1/2}$=2.03*10^4 y). It is produced by neutron capture from stable Nb: ^{93}Nb(n, γ) where the isotope abundance of ^{93}Nb is 100% and the reaction cross section is moderately high (σ=1.15 b).

^{93m}Nb decays by isomer transition to stable ^{93}Nb that emits by internal conversion X-rays at 16.6 keV (about 10%), its half-life is in the medium range ($T_{1/2}$=16.1 y). It is also produced by neutron capture from stable Nb: ^{93}Nb(n, n) where the isotope abundance of ^{93}Nb is 100%. ^{93}Nb is the decay product of both ^{93}Zr and ^{93}Mo.

Stable Nb is a structural component of the Zr alloys used as cladding material in most of the nuclear reactors. Therefore, both ^{93m}Nb and especially ^{94}Nb are radiologically important components in radioactive wastes. ^{94}Nb is not strictly a DTM nuclide but due to its relatively small specific activity radiochemical separation is needed for the radiometric determination using γ spectrometry.

^{93m}Nb can be measured by X-ray spectrometry while ^{94}Nb is measured by γ spectrometry or LSC or ICP-MS. ^{93m}Nb cannot be detected by LSC in the presence of ^{94}Nb.

In aqueous solutions the typical oxidation state is Nb(V) that forms anionic niobate NbO_3- or $Nb(OH)_6$- species. Nb is found in many samples as insoluble pentoxide that can be dissolved only with HF: $Nb_2O_5 + HF \rightarrow NbOF_5^{2-}$ therefore to destruct and dissolve Nb containing waste samples HF has to be used besides other mineral acids. For radiochemical separation of Nb precipitation, LLE, ion exchange and recently ECh are used:

- Nb is usually (pre-)concentrated as **Nb pentoxide** by evaporating the sample with concentrated nitric acid to dryness and removing many interfering components with 4M HCl while Nb_2O_5 remains a precipitate. After this simple separation ^{94}Nb can be determined by γ spectrometry. Precipitation of Nb_2O_5 is also a usual technique for preparation Nb source for X-ray spectrometry of ^{93m}Nb.
- Nb together with Mo can be extracted with α-benzoinoxime (**ABO**) from 4M HCl/1M $AlCl_3$ followed by stripping them together with 4M NH_4OH. Nb and Mo are separated then by co-precipitating Nb with $Fe(OH)_3$ precipitate. This separation is usually preceded by the removal of cations on a cation exchanger and Zr^{4+} e.g., by extraction with TTA.
- Zr, Nb together with Sb are well retained on **anion exchange resins** from 7M HF solutions as anionic fluoride complex. Zr is removed with 6M HCl, Nb (together with Sb) is stripped from the resin with 7M HNO_3 or Nb is stripped 2M HBr/0.5M HF while Sb remains on the column. (If concentrated HF is used for loading Zr is slightly retained and can be eluted with excess concentrated HF rinse.)
- Recently ECh has been applied for the selective separation of Nb. Analogous to anion exchangers **TEVA resin** has been used to separate Nb. Nb together with Zr and Mo can be retained on TEVA from dilute HF. Nb is stripped with 1M HNO_3 (after removal of Zr and Mo). In another experiment Zr, Nb and Mo are retained on TEVA resin from 11M HCl. Zr is stripped with 8M HCl/0.01M HF, Mo with 4M HCl and Nb with 7M HNO_3. Other possibilities to separate Nb from Zr with other ECh resins are under investigations at various laboratories (see also the chapter on determination of ^{93}Zr).

The chemical recovery of Nb is determined by the measurement of stable Nb by AAS, OES, ICP-MS, or by γ spectrometric determination of ^{95}Nb tracer.

3.2.7 ^{125}Sb

It is a long-lived ($T_{1/2}$=2.76 y) β^- decaying radionuclide emitting high energy β^- electrons (β_{Max} 2350 keV) and easy to measure γ radiation at 428 keV (30%) and 601 keV (18%). It is produced from ^{124}Sn in the ^{124}Sn(n,γ) ^{125}Sn reaction (target abundance 5.8 %, cross section σ=0.13 b) and consecutive β^- decay. Tin is an alloying metal of Zircaloy (0.25-1.7%) the main cladding material of nuclear reactors in western countries. It is also produced by fission but the fission yield is low (0.03% for ^{235}U). It is basically an ETM nuclide that can be measured by high resolution γ spectrometry, but to increase the detection sensitivity it has to be radiochemically concentrated.

Antimony forms insoluble **Sb_2S_3 precipitate** that can be used for pre-concentration.

Antimony has volatile $SbBr_3$ and SbH_3 compounds that can be separated by distillation. The **volatile hydride of Sb** together with those of As, Se and Te are produced by the reaction with sodium borohydride.

Antimony is retained on anion exchange resin from 10M HNO_3. It is eluted using 2M H_2SO_4/4M HBr.

Antimony forms SbF6- anions in HF and is retained together with Zr and Nb fluoride complexes on **anion exchange resin** from 6M HF. Zr is eluted with 22M HF, Nb with 7M HNO_3 or 2M HBr/0.5M HF. Sb remains on the resin and is detected directly by γ spectrometry. Sb could not be eluted quantitatively with <0.2M HCl from the resin.

For the determination of the Sb chemical recovery, the 603 keV (98%) and 1691 keV (50%) γ lines of ^{124}Sb tracer or the amount of stable Sb (+carrier) are measured.

3.3 Major radionuclides of contamination origin in nuclear waste and destructive methods for their determination

3.3.1 Fission products

3.3.1.1 ^{90}Sr

It is a pure β^- emitting isotope of maximum β energy in the medium energy range (β_{Max} 546 keV). Its short-lived decay product is ^{90}Y that gets in secular equilibrium with the parent in a couple of weeks. ^{90}Y is also a pure β^- emitting isotope, of maximum β energy in the high energy range (β_{Max} 2270 keV). Due to its high fission yield, long half-life (28 y), high energy β radiation of its daughter, and its bone seeking nature ^{90}Sr is a radiologically very important fission product on medium time scale for waste management.

Sr is a DTM isotope, for its determination by LSC, other β counting techniques, or recently by means of MS (TIMS, AMS) radiochemical separation is required. When β counting techniques are used, the sample matrix has to be removed including all other alkaline earth metals. Till the recent times the major issue was the separation of Sr from the typically much bigger amount of Ca, but this difficulty has been overcome by the use of Sr specific crown ether extractant (Sr resin). ^{89}Sr, a pure β^- emitting isotope of 50 d half-life might also cause interference if samples are not “old”. By repeated β counting the interference can be eliminated. If ^{90}Sr is detected by ICP-MS, the major interference in the Sr source is stable ^{90}Zr, chemical separation has to assure the efficient removal of matrix to get low salt content in the measuring source.

For the selective separation of Sr several procedures have been developed and are in use in waste characterization. The **conventional method** is based on a series of precipitations: pre-concentration of alkaline earth metals as carbonate or oxalate precipitates, purification with Fe hydroxide scavenge, separation of Sr and Ca as nitrate precipitate with or without the use of fuming nitric acid, separation of Sr and Ba as chromate precipitate. This method is still useful when big amounts of Sr have to be separated, e.g., when more than 100 L of sea water is analysed for ^{90}Sr.

Later certain steps of the procedure were replaced by more efficient chromatographic separation. Cation exchange resins were used in presence of specific complexing agents (e.g., EDTA) for the separation of Sr, but cation exchangers are not highly selective for Sr against Ca and Ba.

^{90}Sr can be determined via the measurement of its ^{90}Y daughter. **Liquid-liquid extraction of Y with TBP or HDEHP** and back-extraction with acids provides a higher selectivity for Y and therefore a faster procedure, but in this case the short-lived ^{90}Y is detected, what reduces the measurement sensitivity. Recently the use of the diglycolamide based **DGA resin** for selective Y separation has been reported.

The big break-through in the analysis of ^{90}Sr came with the discovery and the commercial availability of the Sr selective extraction chromatographic resin, the 4,4’(5’)-di-t-butylcyclohexano-18-crown-6 containing **Sr resin**. After pre-concentration of alkaline earth metals with a precipitate, Sr is separated by ECh on Sr resin. The Sr source for measurement is the eluate of the resin (ICP-MS) or a precipitate of the purified Sr (β counting) that can be easily dissolved and mixed with an LS cocktail (LSC).

There are various options for the determination of the chemical recovery depending on the actual measurement method. If the final Sr source for the measurement is a Sr precipitate of stoichiometric composition (and the Sr content of the sample is neglectable) then gravimetric yield determination of the Sr (or Y) source is adequate. The mass of stable Sr (in the sample, the carrier and the Sr source) can be determined by AAS, ICP-OES, ICP-MS. The Sr recovery can also be obtained by the measurement of ^{85}Sr tracer using γ spectrometry or direct LSC counting.

ISO issued a standard for ^{90}Sr determination. According to ISO 18589-2:2009 three procedures were recommended, the conventional Sr procedure based on precipitations, the Y extraction procedure using HDEHP and the extraction chromatography of Sr using Sr resin.

A review paper about the various methods for ^{90}Sr determination was published in 2010 [33].

3.3.1.2 ^{99}Tc

It is an almost pure β$^-$ emitting isotope of maximum β energy in the medium energy range (β$_{Max}$ 294 keV). It is produced by high fission yield (6%), and is also an activation product of ^{98}Mo, therefore it has relatively high activity concentration in radioactive waste. Due to its very long half-life ($T_{1/2}$=2.11*10^5 y) and high mobility it represents on long term a high radiation risk.

It is a DTM nuclide, for its determination by LSC, other β counting techniques, or by means of ICP-MS radiochemical separation is required to remove the matrix components and interfering radionuclides/elements including the chemically similar Ru isotopes (^{106}Ru with half-life of 374 d) and stable Ru containing ^{99}Ru (abundance 12.7%) and ^{100}Ru (abundance 12.6%). The latter isotopes are responsible for isobar interference and abundance sensitivity, respectively in ICP-MS. Typical detection limits in β and LSC measurement are 1-100 mBq/sample. ICP-MS is more sensitive allowing measurements at detection limit of 1 µBq/sample.

Tc has no stable isotope, therefore, it has no isotopic carrier, but Re is often used as non-isotopic carrier. In solutions Tc forms basically pertechnetate TcO_4^- anions, that are responsible for the high mobility of Tc in nature, however it can be reduced readily to Tc(IV), e.g. at pH 4 with potassium pyrosulfite ($K_2S_2O_5$) and Fe^{2+}.

Tc can be pre-concentrated **by co-precipitation with Fe(OH)$_2$ as TcO$_2$** when pH is 9 or higher. TcO_2 can be dissolved with HCl and oxidized back to TcO_4^- with H_2O_2. Tc can also be concentrated on an **anion exchange resin** from low acidity solutions. $RuCl_4^-$ also retained on the resin can be selectively removed by oxidation with NaOCl.

Tc can be separated by LLE, anion exchange and ECh. The principle of most procedures is the formation of strong complexes of TcO_4^- with quaternary amines, e.g., in the form TOA that is extracted with xylene or strong basic anion exchange resins, or TEVA resin. TcO_4^- anions are strongly bound from dilute acid and can be stripped/eluted with more concentrated acids or NaOH. With this procedure a good separation from tetravalent actinides is achieved. Examples for the separation are the following: TcO_4^- is extracted with **TOA/xylene** from sulfuric acid and back extracted with 2M NaOH. TcO_4^- is retained from 0.1M nitric acid (containing H_2O_2) on **TEVA resin**, it is stripped with 12M HNO_3. Recently a TOA impregnated membrane, the **TK201 disc** has been prepared for the rapid concentration and separation of Tc from water samples where sample is loaded from 0.01M HNO_3 containing H_2O_2 and Tc is stripped with 2M NH_4OH. The new ECh material containing polyethyleneglycol coated resin, the **TK202 resin** can retain Tc from 5M NaOH solution and Tc is stripped with distilled water.

The complete separation methods usually contain pre-concentration, separation, and purification steps together with source preparation.

To determine the chemical recovery the short-lived ($T_{1/2}$= 6 h) ^{99m}Tc tracer emitting 140 keV (89%) γ radiation can be used. If the sample is measured by LSC a longer cooling time is needed before measurement for the decay of the tracer. The non-isotopic Re carrier is also often measured by ICP-MS.

3.3.1.3 ^{129}I

It is a very long-lived ($T_{1/2}$=1.57*10^7 years) β$^-$ decaying isotope of maximum β energy in the low energy range (β$_{Max}$ 154 keV). Its daughter nuclide ^{129m}Xe decays by internal conversion to ^{129}Xe and emits low energy, low intensity γ radiation (40 keV, 7.5%) and conversion and Auger electrons. ^{129}I is a fission product of fission yield of 0.84%. Due to its long half-life and high mobility, it is radiologically very important radionuclide in waste samples in the long term.

It is a DTM nuclide that can be measured by low energy γ spectrometry, LSC, NAA, ICP-MS, and AMS. For sensitive measurements radiochemical separations are required for each measurement method. Detection limits vary in the wide range of 100 mBq/sample (γ spectrometry) and nBq/sample (AMS). High sensitivities of about 1 μBq/sample are achieved with RNAA where ^{130}I is produced by neutron absorption and detected via its γ radiation (536 keV, 99%; 668 keV, 96%). ICP-MS is less sensitive. The major interferences in the radiometric methods are other radioactive nuclides, in ICP-MS and AMS stable iodine (^{127}I). The sample matrix has to be removed in all DA techniques.

The same radiochemical separation procedures can be applied for all measurement techniques, but the final measurement sources are different. In γ spectrometry, it can be PdI_2 precipitate, in LSC and ICP-MS the source is iodide in liquid that is mixed with scintillation cocktail for LSC, in RNAA the source can be MgI_2or PbI_2, and in AMS the source is AgI.

Iodine can be separated from solid samples as I_2 using oxidizing agents such as H_2SO_4/HNO_3 or by combustion. The evaporated I_2 can be trapped in NaOH solution containing a reducing agent, e.g., $NaNO_2$ that turns iodine to iodide ions I^-. Iodide can be obtained from solid samples by leaching.

Iodide ions form insoluble **AgI precipitate**.

Iodine has to be separated before measurements. The separation is most frequently performed by selective oxidation and reduction cycles in combination with extraction. **Iodide can be oxidized** selectively to I_2 with H_2O_2 or $NaNO_2$, followed by the **extraction of I_2** with CCl_4. Iodide can be back-extracted in aqueous phase with a reducing agent such as $NaHSO_3$. This procedure will separate Cl- ions, as well.

Iodide and chloride can be separated using the **CL resin** that is a Pd and Ag selective resin retaining these noble metals partially irreversible. The sample is loaded from 1M H_2SO_4 on the Ag treated CL resin. Chloride is eluted with 0.1M NH_4SCN and iodide is stripped with 0.35M Na_2S.

Iodide can be purified on **anion exchange resin**. Sample is loaded from 0.01M HNO_3 on the column. Iodide ions are eluted with 2M $NaNO_3$.

The chemical recovery can be determined by measuring ^{125}I tracer that is an EC nuclide with half-life of 59 days. It emits low energy γ radiation (35.5 keV, 6.7%) and several X-rays. Stable iodine (^{127}I) as a carrier can also be measured by ICP-MS. From stable iodine ^{126}I is produced in (n,2n) reaction that can be measured together with ^{130}I in RNAA.

3.3.1.4 ^{135}Cs

It is a pure β^- emitting isotope of maximum β energy in the medium energy range (β_{Max} 270 keV). Its short lived (29 h) daughter ^{135m}Ba emits γ line at 268 keV (16%). Due to its high fission yield (from ^{235}U 6.5%), very long half-life ($2.3*10^6$ y) and the high mobility it is a radiologically important fission product on long term for radioactive waste and the environment of nuclear facilities.

^{135}Cs is a DTM isotope, for its sensitive determination neutron activation analysis (NAA) and ICP-MS can be applied. The γ spectrometric measurement via its ^{135m}Ba daughter is usually not sensitive because samples containing ^{135}Cs also contain ^{137}Cs and most likely ^{134}Cs of much higher activity than that of ^{135}Cs. On the big Compton background the 268 keV line is not detectable. When ^{135}Cs is irradiated by neutrons the short lived ($T_{1/2}$=13 d) ^{136}Cs is produced that emits easy to measure γ radiation at 818, 1048, 1235 keV. The major interference in this method comes from the radioactivity of ^{137}Cs and ^{134}Cs. The latter one is produced as a result of neutron irradiation of stable Cs besides ^{134}Cs present in the sample originally. ^{135}Cs can be determined by ICP-MS. Main interferences originate from abundance sensitivity due to stable ^{133}Cs, and isobaric nuclide ^{135}Ba. Spectrometric corrections for both interferences are possible but the accuracy of the results will be reduced. MS measurements by TIMS and especially RIMS have higher sensitivity than ICP-MS.

For the chemical separation of Cs a few inorganic ion exchangers are available: ammonium molybdophosphate (AMP) retains Cs by ion exchange from 0.1M HCl, the precipitate is dissolved with 10M NaOH. Cs can also be concentrated on copper ferrocyanide (CFC), potassium cobalt hexacyanoferrate, or zirconium phosphate inorganic ion exchanger. Recently AMP is available in the form of a resin: AMP-PAN.

Caesium can be purified by cation exchange chromatography. Alkali metals with Cs are retained on the resin from 2% EDTA-0.75M NaOH solution. Ba as EDTA complex gets in the effluent. Alkali metal ions are sequentially eluted with water and dilute HCl. Separated Cs is eluted with 3M HCl.

Sensitivities of NAA and ICP-MS are comparable.

3.3.2 Actinides

3.3.2.1 Plutonium nuclides: ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu

Long-lived Pu nuclides – with the exception of ^{241}Pu - are α emitters. The main α lines of ^{239}Pu and ^{240}Pu cannot be resolved with standard α spectrometers where the FWHM is 20-40 keV, the peaks can only be resolved if high resolution α spectrometer and appropriate spectrum fitting software are applied. The α peak of ^{238}Pu is generally well separated from those of ^{239,240}Pu.

^{241}Pu is β- decaying isotope emitting low energy β electrons (β_{Max} 20.8 keV). Its long-lived decay product is ^{241}Am. Due to the long half-lives, emission of highly ionizing α particles, and the bone seeking nature Pu nuclides are radiologically very important on medium-long time scale for waste management.

Plutonium isotopes are all DTM nuclides, for the α emitters α spectrometry is the standard measuring technique. From the α spectra the activities of ^{238}Pu-238 and ^{239,240}Pu can be calculated. Because of the long and similar half-lives of the latter ones ($2.41*10^4$ y and $6.56*10^3$ y) the usual practice is to determine their gross activities. Activities of ^{239}Pu and ^{240}Pu can be determined separately by ICP-MS. The detection limits in case of α spectrometry and ICP-MS are comparable. Unfortunately, ^{238}Pu cannot be determined accurately by ICP-MS due to the isobaric interference from ^{238}U that usually has significantly higher (massif) concentration than ^{238}Pu in waste samples. Recently other mass spectrometric techniques (TIMS, AMS, RIMS) have also been used. For the detection of the low energy β particles emitted by ^{241}Pu LSC is the standard counting technique.

Radiochemical separations are needed for the determination of all Pu isotopes to remove the matrix and the possible interferences (^{241}Am in α spectrometry, ^{238}U in ICP-MS, ^{3}H, ^{55}Fe, ^{63}Ni etc. in low energy LSC counting).

For the separation of Pu several procedures based on solvent extraction (LLE), anion exchange chromatography (AEC), extraction chromatography (ECh) has been developed and are in use.

- The well-known PUREX procedure for the separation of U and Pu is known from nuclear technology. Tributylphosphate can extract Pu(IV) and U(VI) species as $Pu(NO_3)_4(TBP)_2$ and $UO_2(NO_3)2(TBP)_2$ from nitric acid solution (3M-4M). Pu is stripped after reduction with 9M HCl selectively as Pu(III) followed by stripping of U(VI) with dilute acid. This procedure could be adopted for analytical purposes but distribution coefficients and selectivity is moderate compared to other up-to-date reagents. TBP is available as ECh resin as well. Beside TBP other procedures based on liquid-liquid extraction (LLE) are used for Pu separation. Neutral ion association complexes are formed with t-octylphosphine oxide (TOPO), anionic complexes are formed with t-octylamine (TOA) in nitric or hydrochloric acid solutions of medium or high concentrations, and chelate extractants such as ethylhexylphosphoric acid (HDEHP), thenoyltrifluoroacetone (TTA) are used in less moderated acid solutions after oxidation state adjustment of Pu(IV).
- In analytical practice the most frequently used procedure is based on AEC where anionic Pu(IV) species such as $[Pu(NO_3)_6]^{2-}$ and $[PuCl_6]^{2-}$ are formed and retained on the resin from concentrated nitric and hydrochloric acid solutions. This procedure is a solid phase analogue of the LLE with TOA. The oxidation state of Pu(IV) is adjusted with $NaNO_2$ or H_2O_2. In nitric acid solutions similar anionic species of Th are formed and retained while in hydrochloric acid U species are retained. The eluate of 8M HNO_3 is used for Am/Cm determination. The retained plutonium is selectively stripped as Pu(III) with HCl containing a reducing agent (NH_4I or $TiCl_3$). This procedure is highly selective, does not necessarily require pre-concentration, it is robust, but time consuming.
- Many efforts have been done to speed up the separation, increase the selectivity, the efficiency and the robustness and develop combined procedures for various actinides while preserving the selectivity for the individual ones. By the production and commercial availability extraction chromatography (ECh) was introduced in the analytical practice and started to replace the conventional procedures. In ECh the organic extractant is fixed on more or less inert support (most likely porous polymer resins). The extraction process takes place in the thin organic layer thus speeding up the reaction rate, and keeping the chromatographic technique the separation factor is high. Several ECh materials have been developed basically from those extractants that were superior for actinides. Plutonium (actinide) selective ECh materials are TEVA, UTEVA, TRU, DGA resins. **TEVA resin** containing Aliquat 336 is

specific for tetravalent actinides (Pu, Th, Np), **UTEVA resin** containing organic phosphate is specific for tetra- and hexa-valent actinides (Pu, Th, Np, U), **TRU resin** containing TBP and CMPO and **DGA resin** containing diglycolamide can retain tetra-, hexa- and tri-valent actinides (Pu, Th, Np, U, Am/Cm) as well. Actinides are usually retained on the resins from nitric or hydrochloric acid solutions of moderate or high concentrations after oxidation state adjustment and are sequentially eluted from the resins with dilute acids, or complexing agents (e.g., oxalate), or redox reagents and if necessary further chromatographic purification is performed.

In many cases the pre-concentration of actinides is performed before chromatographic separation with co-precipitation, e.g., using Fe (ferrous or ferric) hydroxide using Fe as a carrier, with Mn dioxide, Ca phosphate, lanthanide fluorides. Resins of very high distribution ratio (DIPHONIX resin, DIPEX resin) can also be used for actinide pre-concentration.

TEVA resin is an ECh analogue of anion exchangers or TOA. It is frequently used both as the main separation agent or as purifying agent for the selective separation of Pu(IV) due to its high distribution ratio and selectivity for Pu(IV).

When the simultaneous determination of Pu and Am is required, the best choice is TRU or DGA resins because they are the only options for the retention of trivalent Am species as well. Although TRU or DGA resins are usually applied for Am (Cm) separation after the removal of Pu(IV) species by one of the described procedures, there are attempts for their mutual separation on single TRU or DGA columns.

There are various options for the determination of the chemical recovery depending on the actual measurement method. In α spectrometry samples are spiked with known activities of ^{236}Pu or ^{242}Pu standard reference material. The tracer activity is measured directly in the source by α spectrometry. In ICP-MS ^{242}Pu tracer is used for chemical yield determination.

For LSC of ^{241}Pu the chemical recovery has to be determined indirectly, either by α spectrometry or ICP-MS. Chemical yield can be estimated from the difference of gross α activities after and before extraction of Pu/U. (^{241}Am activity is determined by γ spectrometry and subtracted from the gross alpha determination before extraction.)

Several standards for the determination of Pu isotopes by α spectrometry were developed and issued. According to ISO 18589-4 standard three methods were recommended, extraction with HDEHP, anion exchange chromatography, extraction chromatography with TRU resin. The American standards ASTM C 1001-05 (2005) and ASTM D3865-02 (2002) recommended the use of anion exchange chromatography (see Table 4).

The recommended procedure of IAEA for the rapid determination of Pu and Am uses TRU resin (IAEA Analytical Quality in Nuclear Applications Series No. 11: IAEA/AQ/11, 2009). In the recommended procedure of IAEA for sequential determination of Sr-90, Am-241 and Pu radioisotopes Pu is separated by anion exchange chromatography (IAEA/AQ/37, 2014) (see Table 4).

A review paper about the various methods for Pu isotopes determination was published in 2010 [34].

3.3.2.2 Americium and curium nuclides: ^{241}Am, ^{243}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm

The long-lived Am and Cm nuclides, i.e., ^{241}Am, ^{243}Am, ^{242}Cm, ^{243}Cm, ^{244}Cm belong to minor actinides according to the terminology in nuclear industry. They are all α emitters. The half-life of ^{242}Cm is 163 d therefore it is not relevant for characterization of “old” radioactive waste. The most sensitive technique for their determination is α spectrometry. The radiologically most important nuclide is ^{241}Am ($T_{1/2}$=432 y) that is formed by the β decay of the parent ^{241}Pu. Its main α line (5486 keV) overlaps with that of ^{238}Pu (5499 keV) therefore a good separation of Am from Pu is necessary. The production rate of ^{243}Am in the actinides transmutation is much smaller than that of ^{241}Am, therefore it is often used as a radionuclide tracer for Am, Cm determination. The α energies of ^{241}Am (5486 keV) and ^{243}Am (5275 keV) are relatively close to each other, for this reason also a good quality (thin) α source is needed, and an Am-lanthanide separation is often required to avoid source thickening. The α energies of ^{243}Cm (5785 keV) and ^{244}Cm (5805 keV) are close to each other, they cannot be resolved by standard α spectrometry, high resolution α spectrometry provides the best chance for their spectrometric resolution. Due to their comparable half-lives (29 and 18 y, respectively) and the much lower production rate of ^{243}Cm, their gross activities are usually calculated or the activity of ^{243}Cm is simply neglected.

^{241}Am and ^{243}Am can be measured by γ spectrometry at the 59 keV and 75 keV γ lines, respectively with low energy γ spectrometer, but the sensitivity is much lower than that in α spectrometry. To increase the sensitivity chemical concentration/separation is desirable also for γ spectrometry.

^{241}Am and ^{243}Am can be measured by ICP-MS; the major interference is ^{241}Pu. ^{241}Am can be detected by other powerful MS techniques, e.g., TIMS, AMS, RIMS, but these techniques cannot be regarded as routine ones in waste characterization. A review about the mass spectrometric determination of ^{241}Am has been prepared by S. K. Aggarwal [35].

Americium and Cm nuclides are all DTM nuclides, for their determination radiochemical separations are needed. Am and Cm due to their chemical similarities are usually processed together. Both form trivalent actinide species in most of the aqueous solutions. Am(III) can be oxidized with very strong oxidizing agent such as $K_2S_2O_8$ together with Ag^+ catalyst to Am(V) while Cm remains still trivalent but traces of reducing agent will reverse the reaction. The trivalent species are similar to lanthanides (Ln's) therefore separation of Am, Cm from Ln's is a challenging job that is unavoidable if samples like soils contain Ln's in mg amounts or more.

Am, Cm can be pre-concentrated with many precipitates such as ferrous or ferric hydroxides, Ca oxalate, Ca fluoride, lanthanide fluorides and hydroxides, MnO_2, $BaSO_4$, Ca phosphate, Ca/Mg carbonate. The classical procedure to separate Am, Cm after removal of other actinides (e.g., by anion exchange chromatography) was based on their repeated co-precipitations with ferric hydroxide and Ca oxalate. Am, Cm are also pre-concentrated by ECh with resins of extremely high distribution coefficient, e.g., with Diphonix and Dipex resins from big volumes of water samples.

Am, Cm (and lanthanides) can be separated with LLE, ion exchange and ECh. Trivalent actinides are not retained by many of the usual extractants, anion exchangers and ECh resins that can retain tetra- and/or hexavalent actinides (AEC, TBP, TOA, TOPO, TEVA, UTEVA), therefore tetra and hexavalent actinides are often preliminary separated before processing Am, Cm. When Pu and Th are retained on AEC from 8M HNO_3 Am gets in the effluent. (See other options for Pu and U removal in the relevant paragraphs.)

- Efficient retention of Am, Cm (and Ln's) is performed by **cation exchange chromatography** or by LLE using **chelating extractants**, e.g., HDEHP or TTA or the phenyl-methyl-benzoyl-pyrazolone containing PMBP from dilute acid solutions, but the selectivity of these procedures is limited.
- There are a few extractants of high selectivity for Am, Cm. **CMPO** was one of the first molecules that extracted trivalent actinides selectively. The CMPO and TBP containing ECh resin, the TRU resin was prepared by Horwitz et al. for analytical applications. TRU resin has a widespread use in Am, Cm (and Ln's) separation. Fe^{3+} is a major interference for Am, Cm retention. Resin combinations such as TEVA-TRU, UTEVA-TRU are used for actinide separations where Am, Cm are retained on TRU resin after Pu, Th and/or U removal.
- **Malonamides and diglycolamides** showed stronger Am, Cm retention than CMPO. Later a diglycolamide coated ECh resin called DGA resin was prepared that proved to be superior to TRU resin for Am, Cm separation because much higher distribution coefficients for Am, Cm were achieved than in case of TRU resin. DGA resin can retain Am, Cm (and Ln's) from 3-4M HNO_3 or HCl solutions even in the presence of Fe^{3+} ions, and they can be stripped together with dilute acids.

There are a few methods for the **separation of Am, Cm from Ln's.** The classical solution is cation exchange chromatography with gradient elution using α-HIBA (after removal of the matrix and Pu with anion exchange). The other procedure (also applicable after matrix and Pu removal) is based on the retention of Am, Cm and Ln's on anion exchange resin from 1 M HNO_3 – 93% methanol, Ln's are removed with dilute HCl – NH_4SCN –

methanol solution, and Am, Cm are stripped with 1.5 M HCl – 80 % methanol. The ECh version of the latter procedure uses TEVA resin, (the analogue to anion exchange resin), where samples are loaded in a 2 M NH_4SCN – 0.1 M formic acid solution followed by the elution of lanthanides with 1 M NH_4SCN – 0.1 M HCOOH and stripping Am, Cm with 0.25 – 2 M HCl. Am, Cm can be separated by anion exchange chromatography using 8M LiCl in 40% methanol for elution.

Separation of Am from Cm is usually not necessary, but it can be performed by co-precipitation of Cm with Ln fluoride after selective oxidation of Am.

Am/Cm α sources can be prepared by electroplating or micro-co-precipitation. The previous one is favoured for better resolution. For chemical recovery determination of Am in α spectrometry and ICP-MS samples are spiked with ^{243}Am standard of known activity. Isotope dilution technique is used to calculate the activity of ^{241}Am. It is often assumed that the chemical recovery of Cm is the same as that of Am.

In the standard test method **ASTM C 1205-07** (see Table 4) for "The Radiochemical Determination of Americium-241 in Soil by Alpha Spectrometry" Am-241 is determined in soil samples up to 10 g. The soil is completely dissolved by the use of pyrosulfate fusion. After the initial separation on barium sulphate Am together with other actinides and lanthanides is extracted from concentrated $HClO_4$ solution with 15 % HDEHP in n-heptane and back-extracted with 5 M HNO_3. Americium is separated from other trivalent actinides and lanthanides by oxidation of Am and precipitation of the interferences with LaF_3.

The recommended procedure of IAEA for the rapid determination of Pu and Am uses a single TRU resin. Pu(IV) and Am are retained from 2M HNO_3, Am is stripped with 4M HCl and Pu is stripped after reduction with $TiCl_3$ with 4M HCl (IAEA Analytical Quality in Nuclear Applications Series No. 11: **IAEA/AQ/11, 2009**). In the recommended procedure of IAEA for sequential determination of ^{90}Sr, ^{241}Am and Pu radioisotopes Am, Cm are separated by ECh using TRU resin after the removal of Pu and Th by anion exchange chromatography. Am, Cm separation from Ln's is performed (**IAEA/AQ/37, 2014**) (see Table 4).

A **review paper** about the various methods for ^{241}Am isotope determination was published in 2010 [36].

3.3.2.3 Uranium nuclides: ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U

Uranium is regarded as major actinide according to the terminology in nuclear industry. ^{234}U, ^{235}U, and ^{238}U are natural radionuclides, the latter two isotopes are the parents of the two natural decay series with half-lives of billion years. ^{235}U is a fissile isotope, one of the nuclides responsible for energy production in thermal nuclear reactors operated by U based fuel. It is the major component of some atomic bombs. ^{233}U is fissile isotope produced by thermal neutron capture of ^{232}Th, it is responsible for energy production in the nuclear reactors operated by Th based fuel. The long-lived U nuclides, i.e., ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U are all α emitters. ^{236}U is produced in the burn out process of ^{235}U, its presence indicates that the sample originates from nuclear fuel or atomic bomb. These isotopes are not only radiologically important, but they are important in provenance revealing the origin of the sample. Their mass or activity ratios are used in safeguards analysis.

The most sensitive technique for the determination of ^{234}U is α spectrometry, but all U nuclides can be measured by α spectrometry. The highest sensitivity for the measurement the other U nuclides is achieved by mass spectrometric techniques, such as ICP-MS. For the measurement of isotope ratios, various MS techniques can be applied. The natural ^{234}U, ^{235}U, and ^{238}U isotopes can be easily determined by α spectrometry because the α lines (including those of ^{232}U tracer) are well separated. The major α lines of ^{233}U (4824 keV) and ^{234}U (4777 keV) and those of ^{235}U (4397 keV) and ^{236}U (4494 keV) are partially overlapping they cannot be completely resolved in standard α spectrometry, for the accurate determination ICP-MS is used. The amount of ^{233}U is usually very small in samples from the U fuel cycle, therefore ^{233}U can be used as radioactive tracer in ICP-MS measurements for U yield determination. ^{232}U nuclide is an excellent tracer in α spectrometry but not detectable in ICP-MS due to its small specific mass as a result of its short half-life (72 y). Gamma spectrometry can be used in two different ways to detect U isotopes: i) The low energy γ and X-rays can be detected with low energy γ detector, ii) The high energy γ radiation emitted by the isotopes themselves or by daughter nuclides can be detected by γ spectrometry using standard HPGe detectors. Secular equilibrium within the decay series is supposed to exist in the latter technique what is not always attained. ^{238}U can be detected via short-lived progeny nuclides ^{234}Th (63,3 and 92,5 keV) and ^{234m}Pa (1001 keV). ^{235}U can be detected via its 186 keV γ line (54%) but it overlaps with the γ line of ^{226}Ra. These methods are orders of magnitude less sensitive than α spectrometry or ICP-MS. Occasionally U isotopes are detected by LSC most likely by PERALS spectrometry. It has to be mentioned that there are other spectroscopic techniques (AAS, OES, XRF etc.) to detect the element uranium, but here no information about the isotope composition is obtained.

Uranium is radiochemically separated before measurement by α spectrometry and occasionally by ICP-MS. From a destructed/dissolved sample U can be pre-concentrated by co-precipitation together with other actinides. It is necessary/recommended to reduce U(VI) to U(IV) before co-precipitation with Fe hydroxide, Ca oxalate, Ca fluoride, lanthanide fluorides and hydroxides, MnO_2, $BaSO_4$, Ca phosphate, Ca/Mg carbonate.

Uranium can be separated by LLE with many extractants (TBP, MIBK, TOPO, HDEHP, CMPO). E.g., Pu, Th, U were extracted from 4 M-6 M HNO_3 to **TOPO**, and back-extracted with less concentrated acids. Chelating extractants were also used for U separation. According to the standard test method ASTM **D6239-09,** uranium is separated from drinking water with an extractive scintillator that contains **HDEHP** as extractant. Uranium is extracted from a 0.01 M DTPA solution that masks the extraction of undesired ions.

More selective separation can be achieved with chromatographic technique. **Anion exchange resins** can retain U from concentrated HCl solution together with Pu. According to the ASTM standard test methods **D3972-09, C1473-11 and C1000-11**, uranium is retained on a strong basic anion exchanger from 8 M–9 M HCl after sample destruction and pre-concentration with ferrous hydroxide precipitate. Uranium is stripped from the column with 0.1 M–1 M HCl. Fe interfering with U retention is removed preliminary by extraction with di-i-propylether.

Higher selectivity is obtained with more specific extractants in ECh. Although supported TOPO and HDEHP were used successfully for U separation the dipentylpentyl phosphonate containing **UTEVA resin** proved to be superior to other resins developed so far for U and tetravalent actinides (Th, Np, Pu). They were retained both from 2-8M HNO_3 or 4-9M HCl. U was stripped with dilute acid. Uranium (together with Th, Np(IV), Pu(IV)) is even stronger retained from 8M HNO_3 or 9M HCl on **TRU resin**, and can be stripped with 0.1M ammonium bioxalate. Recently tandem columns (e.g., UTEVA-TRU, TEVA-TRU) have been used for the sequential separation of the individual actinides.

α sources can be prepared by electroplating or micro-co-precipitation with Ln fluoride from reducing media.

The most sensitive measurement technique for the determination of U isotopes, especially the isotope ratios is MS. With ICP-MS all isotopes – with and without ^{233}U tracer - can be measured. The most accurate method to measure isotope ratios is TIMS. For measurements of high sensitivity and accuracy radiochemical U separation with high decontamination factors for isotopes causing abundance sensitivity (^{239}Pu) and polyatomic interferences is unavoidable. For the less sensitive measurement simple sample preparation (destruction, dissolution) is sufficient.

A **review** about analytical methodology for ND determination of U isotopes is given in Chapter 5 of the Handbook of Radioactivity Analysis [37].

3.3.2.4 ^{237}Np

Neptunium is a minor actinide in the terminology of nuclear industry. The most important long-lived ($2.14*10^6$ y) isotope of Np is ^{237}Np, it is the only relevant Np isotope of significance in radioactive waste. It is produced by consecutive n reactions, i.e. (n,γ), (n,2n) and radioactive decay from ^{235}U and ^{238}U in nuclear reactors and explosions. (The primordial ^{237}Np has already decayed.) Although the activity of ^{237}Np is much less than that of ^{239}Pu, and its mass is much smaller than that of ^{238}U, it is of big importance in radioactive waste due to its relatively high mobility.

^{237}Np is an α emitter with main α particle energy at 4788 keV (51%). It is a DTM nuclide. ^{237}Np can be measured by α spectrometry, but the main α line overlaps with that of ^{234}U (4777 keV). Therefore, it can be measured by α spectrometry after separation of the sample matrix and the “complete” removal of U. Much higher sensitivity can be achieved by MS techniques, especially by SF-ICP-MS. The major interference in ICP-MS measurements is the abundance sensitivity due to ^{238}U, therefore high decontamination factors against U have to be assured. AMS is also used for Np measurement because of its ultra-high sensitivity. ^{237}Np can be detected by NAA via ^{238}Np.

The short-lived ($T_{1/2}$=2.4 d) γ emitter ^{239}Np is a good tracer to be followed by γ spectrometry for chemical recovery determination. It can be produced by n irradiation of ^{238}U or by milking from ^{243}Am tracer. The long-lived ($T_{1/2}$=150000 y) electron capture ^{236}Np is a good tracer in ICP-MS measurements.

In aqueous solutions Np exists in 3 oxidation states, Np(IV), Np(V) and Np(VI) where typically Np(V) is the most stable. The stability of the Np complexes like those of other actinides increases in the Np(V)<Np(VI)<Np(IV). Using a reducing agent Np species are converted to Np(IV) that makes strong complexes and can be extracted with many neutral (ion association) extractants, as Np^{4+} cation it is bound to cation exchangers and many chelates, and as anionic $[Np(NO_3)_6]^{2-}$ or $[NpCl_6]^{2-}$ species it is bound to anion exchangers, amine extractants. If Np and Pu are separated in the same procedure, the major issue is the mutual adjustment of the oxidation states of both actinides to the tetravalent form. This situation was achieved by the combination of redox reagent, e.g., after a strong reduction where Np(IV) and Pu(III) are formed a slight oxidation is performed to keep Np as tetravalent while Pu is oxidized to Pu(IV): $Fe^{2+}/NaNO_2$ or (Fe^{2+}, ascorbic acid, sulfamic acid)/$NaNO_2$.

Np after reduction to Np(IV) can be pre-concentrated with all precipitates used in case of tetravalent actinides (see the paragraph on Pu isotopes).

Np(IV) can be extracted with chelate extractants such as **TTA in toluene** from 1M HNO_3 or HCl, and back-extracted with more concentrated (8M-10M) HNO_3. A good separation from Pu(III) is achieved. **HDEHP** was also used for the retention of Np, Pu and Am from 0.1M HNO_3. Np was stripped with 1M HNO_3/hydroxyl amine.

Among the extractants forming ion association complexes with actinides **TOPO** was used to extract Pu and Np from 5M HCl, where Pu(III) was back-extracted with 1M HCl/ascorbic acid. Np remained in the TOPO.

Np(IV) as anionic nitrate or chloride complex is retained on anion exchange resin from 8M HNO_3 or 9M HCl. It can be stripped with dilute acid or by changing its oxidation state. Np can be extracted with TOA, as well.

The most common method of selective ^{237}Np separation is based on **anion exchange** chromatography. Np(IV), Pu(IV) and Th were retained from 8 M HNO_3 followed by the selective stripping of the actinides. Th and Pu are stripped selectively with 9–10 M HCl, 9–10 M HCl/0.1M NH4I followed by stripping of Np with more dilute 1–4 M HCl.

Recently more ECh procedures have been developed. **TEVA resin** containing quaternary amine extractant retains Np selectively from 2-3M HNO_3 after reduction with Fe(II) sulfamate and ascorbic acid. Pu gets in the effluent. After removal of Th with 6M HCl, Np(IV) is stripped with dilute HNO_3/HF mixture. The standard procedure **ASTM C 1475-05** for the determination of ^{237}Np in soil is based on the use of TEVA column (see Table 4). The Np(IV) oxidation state is adjusted using ferrous sulfamate and $NaNO_2$. Sample is loaded from 2.5 M HNO_3/0.5 M $Al(NO_3)_3$ and Np is stripped with 0.02 M HNO_3/0.02 M HF.

Np(IV) was retained on **UTEVA** resin from 8M HNO_3 together with Pu(IV) and Th, and it was stripped with 4M HCl together with Th.

Np was separated from uranyl nitrate solution using HDEHP containing **Ln resin** column. Np and Pu species were retained from 10 M HCl load while U entered into the effluent.

In the **ASTM standard guide C1561-10** (see Table 4) for the determination of Pu and Np in uranium hexafluoride and U-rich matrix, two **TRU resin** columns are used. U is separated by retention on the 1st column from a 0.1 M oxalic acid–2 M HNO_3 solution, then other actinides are retained on the 2nd column from 3 M HNO_3 and stripped sequentially.

On **DGA resin** Np(IV), Th(IV), UIV) as well as Pu(III), Am(III) are retained from 4M HCl in presence of Na_2SO_3 reducing agent. Actinides can be stripped sequentially, where Np+Th (+Zr) are stripped with 0.5% oxalic acid/0.5M HNO_3.

To increase the decontamination factor for U repeated ECh separations are performed, e.g., with UTEVA-UTEVA, DGA-TEVA systems.

A **review** about analytical methodology for ND determination of U isotopes is given in Chapter 5 of the Handbook of Radioactivity Analysis [37].

Table 4: List of ISO and ASTM Standards and IAEA Procedures for the Separation and/or Determination of Th, U, Np, Pu, Am, Cm, Po, Ra and Sr Radionuclides

Standard	Title
ISO 18589-4 (2007)	Measurement of Radioactivity in the Environment. Soil. Part 4. Measurement of Pu Isotopes by α-Spectrometry
ISO 11483 (2005)	Nuclear fuel technology – Preparation of plutonium sources and determination of ^{238}Pu/^{239}Pu isotope ratio by alpha spectrometry
ASTM C 1001-05 (2005)	Standard Test Method for Radiochemical Determination of Plutonium in Soil by Alpha Spectroscopy
ASTM D 3865-02 (2002)	Standard Test Method for Pu in Water
ASTM C 1205-07	The Radiochemical Determination of Americium-241 in Soil by Alpha Spectrometry
ASTM C 1475-05 (2010)	Standard Guide for the Determination of ^{237}Np in Soil
ASTM D 3972-09	Standard Test Method for Isotopic Uranium in Water by Radiochemistry
ASTM D 6239-09	Standard Test Method for Uranium in Drinking Water by High-Resolution Alpha-Liquid-Scintillation Spectrometry
ASTM C 1284-10	Standard Practice for Electrodeposition of the Actinides for Alpha Spectrometry
ASTM C 1163-08	Standard Practice for Mounting Actinides for Alpha Spectrometry using Neodymium Fluoride
ASTM D 3084—05	Standard Practice for Alpha-Particle Spectrometry of Water
ASTM C 1561-10	Standard Guide for the Determination of Plutonium and Neptunium in Uranium Hexafluoride and U-rich Matrix by Alpha Spectrometry
IAEA/AQ/11 (2009)	A Procedure for the Rapid Determination of Pu Isotopes and Am-241 in Soil and Sediment Samples by Alpha Spectrometry
IAEA/AQ/12 (2009)	A Procedure for the Determination of Po-210 in Water Samples by Alpha Spectrometry
IAEA/AQ/34 (2014)	A Procedure for the Sequential Determination of Radionuclides in Phosphogypsum: Liquid Scintillation Counting and Alpha Spectrometry for ^{210}Po, ^{210}Pb, ^{226}Ra, Th and U Radioisotopes.
IAEA/AQ/37 (2014)	A Procedure for the Sequential Determination of Radionuclides in Environmental Samples: Liquid Scintillation Counting and Alpha Spectrometry for ^{90}Sr, ^{241}Am and Pu Radioisotopes.
ISO 18589-2:2009	Measurement of radioactivity in the environment-Soil- Part 5: Measurement of Sr 90
IAEA/AQ/27 (2013)	Rapid Simultaneous Determination of 89Sr and 90Sr in Milk:a Procedure Using Cerenkov and Scintillation Counting, IAEA Analytical Quality in Nuclear Applications

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