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Radionuclide Monitoring

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Abstract

Monitoring of natural and anthropogenic radionuclides is important for providing baseline data on background radioactivity levels of environment, evaluating the impact of nuclear accidents and incidents, for emergency preparedness and radiation protection for humans and the environment. This article summarizes the major purposes of radionuclide monitoring and the processes for implementing of the monitoring program. An overall review and discussion on the techniques and methodologies for sampling, sample pre-treatment, radiochemical separation and measurement of various radionuclides in the monitoring program is presented.

Key words

Radionuclide, environmental monitoring, source monitoring, sampling, sample pre-treatment, chemical separation, radiometric method, mass spectrometric method

1 Sources of radionuclides

1.1 Natural radionuclides

Radionuclides occur naturally in the environment mainly from the substances of which the solar system and the Earth were originally formed, e.g., uranium (^{235}U , ^{238}U), thorium (^{232}Th) and potassium (^{40}K), and partly from interaction of high energy cosmic radiation with the Earth's atmosphere, e.g., tritium (^3H) and carbon-14 (^{14}C). The long-lived isotopes ^{235}U , ^{238}U and ^{232}Th are transformed by radioactive decay into series of decay products, e.g., ^{222}Rn , ^{226}Ra and ^{210}Po , which are also radioactive and contribute with additional radionuclides in the environment. A kilogramme of soil typically contains 400 Bq ^{40}K , 35 Bq ^{238}U and 30 Bq ^{232}Th and a cubic metre of seawater typically contains 1000 Bq ^3H , 4 Bq ^{14}C , 40 Bq ^{238}U , 4 Bq ^{226}Ra , 4 Bq ^{210}Po and 12000 Bq ^{40}K (National Academy of Sciences, 1971; UNSCEAR, 2000). A comprehensive summary of naturally occurring radionuclides and their nuclear properties can be found elsewhere (Valkovic, 2000).

1.2 Anthropogenic radionuclides

Development of nuclear power for military and peaceful uses has resulted in the production of a large amount of anthropogenic radionuclides. During 1950-1980, a number of atmospheric nuclear weapons tests were carried out, which peaked in the 1960s, causing radioactive global fallout. This is the primary source of anthropogenic radionuclides in the environment and is still noticeable in the seas and on land (UNSCEAR, 2000). The European facilities for reprocessing of spent nuclear fuel, Sellafield (UK) and La Hague (France) have discharged substantial amounts of radioactive effluents to sea which have dispersed in the North Atlantic Ocean (Aarkrog et al., 1985). Nuclear accidents such as Chernobyl in 1986 and Fukushima in 2011 caused heavy radioactive pollution near the power plants and fallout in the northern hemisphere. Other sources include operational releases from nuclear power plants, medical and industrial productions of radioactive materials and decommissioning of nuclear installations (Schupfner, 2003).

Radionuclides of concern

Natural radionuclides of special concern related to radiation protection are radon (mostly ^{222}Rn) and its decay products, as they are the most important sources of radiation exposure to the public, contributing about half of the total effective dose equivalent received from natural and anthropogenic radioactivity (Table 1). The radiation dose from ^{222}Rn and its progeny comes mainly from inhalation of the decay products of radon, which deposit within the respiratory tract and irradiate the bronchial epithelium. Drinking water should be analysed for its radon content according to a EURATOM Drinking Water Directive (EURATOM, 2013). Radium analysis is required under the Safe Drinking Water Act. The US EPA specifies that ^{226}Ra and ^{228}Ra should be detected at a concentration of 0.037 Bq/L. ^{210}Po and ^{210}Pb are decay products in the ^{238}U decay chain are important natural radionuclides due to their wide distribution and radiation exposure through ingestion and inhalation.

Anthropogenic radionuclides of particular concern are ^{90}Sr and ^{137}Cs . Both have half-lives of about 30 y and are readily transported through food chains due to their chemical similarities to calcium

and potassium. In the past years, increased and stricter environmental assessments for nuclear installations is required by the authorities. Radionuclides including ^3H , ^{14}C , ^{63}Ni , ^{59}Fe , ^{89}Sr and ^{90}Sr and actinides are listed in routine monitoring programs of nuclear power plants and research reactors in many European countries. ^{14}C released from nuclear power plants is an important contribution in terms of dose to man. During decommissioning of nuclear facilities, ^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{63}Ni , Pu isotopes, ^{241}Am and ^{244}Cm are required to be determined for waste characterization and management.

Table 1. Average individual radiation exposure from natural and anthropogenic sources (Valkovic, 2000)

	Radiation sources	Effective dose equivalent per year/mSv
Natural	Cosmic rays at sea level	0.37
	Radon (^{222}Rn and ^{220}Rn)	1.30
	Potassium (^{40}K)	0.30
	Other natural sources	0.40
Anthropogenic	Medical use of radiation	0.4-1.0
	Nuclear explosive testing	0.01
	Nuclear power production	0.002

2 Monitoring of radionuclides in the environment

The main purposes of any monitoring program for radiological protection of the public and the environment are 1) to verify compliance with regulatory requirements on e.g. discharge limits due to normal operation of nuclear and other industries involving radioactive materials, and 2) to provide data to assess the radiological exposure of populations due to the presence of radioactive materials in the environment from normal operation of nuclear and other industries, and from accidents or past activities (IAEA, 2010). In the present context, two types of monitoring may be considered: source monitoring and environmental monitoring.

2.1 Source monitoring

Source monitoring involves monitoring of the activity of radionuclides released to the environment from nuclear or non-nuclear installations focusing on points of releases, e.g. ventilation stacks and points of liquid release. Releases can be in the form of gases, aerosols or liquids. Monitoring programs should ensure that samples are representative and sufficient data is available to determine total discharges over the period given in the authorisation and trends over time. The radionuclide composition and activity concentration of discharges, particularly from nuclear facilities, may vary widely. Sampling programs should therefore be chosen based on a review of the anticipated radionuclide mixtures subject to the requirements specified by the regulatory body. In particular, source monitoring should focus on radionuclides that could lead to a significant fraction of the total dose to the representative person .

2.2 Environmental monitoring

Environmental monitoring involves measurement of radionuclide concentrations in environmental media and the main purpose is to ensure proper protection of the population. In 2000 the European Commission (EC) issued Recommendation 2000/473/Euratom, providing guidance to EU

countries on monitoring the levels of radioactivity in environment. EC recommendations on sample types and measurement categories are presented in Table 2. In general, environmental monitoring should cover all exposure pathways including the atmosphere, hydrosphere, terrestrial environment, marine environment and food chains. As an example, Table 3 shows the environmental monitoring program carried out in Denmark.

Table 2. EC Recommendation on sample types and measurements.

Media	Measurement category	
	Dense network	Sparse network
Airborne particulates	^{137}Cs , gross beta	^{137}Cs , ^7Be
Air	Ambient gamma dose rate	Ambient gamma dose rate
Surface water	^{137}Cs , residual beta	^{137}Cs
Drinking water	^3H , ^{90}Sr , ^{137}Cs	^3H , ^{90}Sr , ^{137}Cs
Milk	^{137}Cs , ^{90}Sr	^{137}Cs , ^{90}Sr , ^{40}K
Mixed diet	^{137}Cs , ^{90}Sr	^{137}Cs , ^{90}Sr , ^{14}C

3 Sampling and sample pre-treatment

Sampling is the first and important step for radionuclide monitoring. The sampling strategy should be adapted to the situation that is to be monitored and should be consistent with the objectives and purpose of the specific monitoring. Sampling theory has been widely discussed in the literature (Lehto and Hou, 2010). In the radionuclide monitoring, a large variety of samples needed to be collected including air (both gaseous and aerosol), deposition (dry and wet), surface water (seas, lakes, rivers) and depth profiles, soil and sediment (surface and cores), biological samples (vegetation, food, animal/human bones, tissues etc.), effluents (e.g., waste discharges) from nuclear facilities, operational and construction materials (e.g., concrete, graphite, steel, ion exchange resin and coolant from nuclear reactors). In the present context, aerosol, deposition and water sampling are briefly discussed.

3.1 Aerosol sampling

There are three types of aerosol particle sampling techniques: integral, size selective and passive sampling. Integral sampling is a simple and widely used technique for aerosol sampling, wherein air is pumped through a filter to collect the aerosol particle of a size bigger than the pore size of the filter. The size-selective sampler is used to separate and collect aerosol particles in different size fractions, using a multistage cascade impactor. Passive aerosol sampling is carried out with sticky foils.

3.2 Deposition sampling

For dry deposition, a high-walled pot collector is normally used. It is usually made of stainless steel with smooth surface and rounded corners, which do not adsorb radionuclides and allow for easy cleaning. Wet deposition can also be collected with a pot collector, but to avoid loss by evaporation, a funnel type collector is often used. In many cases, an ion exchange collector is used for wet deposition sampling, which consists of a funnel to collect precipitation on top of a mixed-bed ion exchange column through which the water passes into a container.

3.3 Water sampling

Small volume (< 20 L) surface water can be collected directly into a polyethylene bottle or barrel, while for large volume samples a submersible pump is often used. When the depth distribution of radionuclides is studied, water depth profiles need to be collected and a Nansen bottle is often used, especially for seawater collection to a depth up to 4000 m. Water samples are often acidified to pH 1-2 with HNO₃ to reduce adsorption of radionuclides on the container walls, except for analysis of certain radionuclides such as iodine.

Table 3. Environmental radioactivity monitoring program in Denmark carried out by DTU Nutech*

Sample	Station no.	Sampling frequency	Radionuclide measured
Airborne particulates	3	weekly	¹³⁷ Cs, ⁷ Be, ⁹⁰ Sr
Air	57	annually	Ambient gamma dose rate
Precipitation	11	monthly	¹³⁷ Cs, ⁹⁰ Sr, ³ H
Stream water	8	every second year	¹³⁷ Cs
Lake water	8	every second year	¹³⁷ Cs
Groundwater	11	annually	¹³⁷ Cs, ⁹⁰ Sr,
Soil	10	every fifth year	¹³⁷ Cs, ⁹⁰ Sr, Pu/Np
Grass	4	quarterly	¹³⁷ Cs, ⁹⁰ Sr
Vegetable, fruit and meat	1	annually	¹³⁷ Cs, ⁹⁰ Sr
Cereal	10	annually	¹³⁷ Cs, ⁹⁰ Sr
Milk	8	every second month	¹³⁷ Cs, ⁴⁰ K, ⁹⁰ Sr
Mixed diet	9	annually	¹³⁷ Cs, ⁹⁰ Sr
Imported food	1	every third year	¹³⁷ Cs, ⁹⁰ Sr
Seawater	14	annually	¹³⁷ Cs, ⁹⁰ Sr, ⁹⁹ Tc, Pu/Np, ³ H
Seaweed	5	quarterly	¹³⁷ Cs, ⁹⁹ Tc,
Sediment	1	annually	¹³⁷ Cs
Fish	3	annually	¹³⁷ Cs, ²¹⁰ Po
Lobster	1	annually	⁹⁹ Tc

3.4 Sample pre-treatment

After sampling, pre-treatment is necessary to ensure homogeneity and appropriate conditions for quantification. Drying, grinding, sieving and ashing are often sequentially performed for solid samples, such as soil/sediment, vegetation, foodstuffs, animal/human organs, bone and tissues. It should be noted drying and ashing should only be used for non-volatile radionuclides. Fresh samples should be processed without drying and ashing for volatile radionuclides such as ³H, ¹⁴C and high temperature ashing should be avoided for semi-volatile radionuclides, such as ²¹⁰Po.

For extraction of most non-volatile radionuclides from soil and sediment, acid digestion is commonly applied. It can be performed using a mixture of mineral acids (HCl, HF, HNO₃, HClO₄ and H₃PO₄) in open systems, pressure vessel or assisted with microwave (Qiao et al., 2009). For biological samples, H₂O₂ sometimes is added to acid digestion to prompt decomposition of organic matter in the samples.

For large volume water samples, pre-concentration is performed either in-situ or in the laboratory. Typically, evaporation, co-precipitation or chelation can be used. The evaporation involves reduction of sample volume by careful heating. The selection of co-precipitation approach depends on the chemical property of the targeted radionuclide and often employed co-precipitates are iron hydroxides, manganese oxide, and calcium phosphate/carbonate/oxalate (Chen et al., 2002). Some specific co-precipitation approaches have been developed for individual radionuclides, e.g., co-precipitation of ^{137}Cs with ammonium 12-molybdophosphate (AMP). Chelation is not as popular as co-precipitation, but mostly applied for specific radionuclides, e.g., insoluble cobalt-ammonium pyrrolidine dithiocarbamate (Co-APDC) chelate for ^{210}Po pre-concentration.

Fig. 1. General analytical process for radionuclide monitoring in the present context

4 Techniques and analytical methods for radionuclide monitoring

After sampling and sample pre-treatment, effective monitoring for radioactive substances is critically dependent on reliable, robust and focused analytical approach for various radionuclides and sample types. Herein we will discuss some technical and analytical details for determining radionuclides including gamma spectrometry, total alpha and beta, as well as radionuclide specific methods as illustrated in Fig. 1. The selection of specific radionuclides based on considerations related to their radiotoxicity, radiological impact and importance to different monitoring purposes as summarized in Table 4.

4.1 Gamma spectrometry

Gamma spectrometry is used to detect, identify and quantify gamma-emitting radionuclides (e.g., ^{131}I , ^{60}Co , ^{134}Cs and ^{137}Cs). It allows simultaneous analysis of multiple radionuclides, often with

little or no sample preparation, and is therefore a basic technique used for radionuclide monitoring. The equipment is based on solid-state detectors, typically germanium crystals cooled electrically or with liquid nitrogen, connected to electronics that process electrical pulses from the detected gamma rays. The size of the pulses correspond to the energies of the gamma rays and the accumulated data may be displayed in a gamma spectrum showing the detected gamma radiation as a function of energy. This allows identification of radionuclides by their characteristic gamma-ray energies.

Gamma spectrometry may be used in automatic setups for source monitoring purposes, e.g. continuous recording of discharges to air, or in laboratories for environmental monitoring purposes, e.g. analyses of individual samples. Quantitative gamma spectrometric analyses require calibration of the detector/sample configurations, i.e. establishing relations between gamma rays emitted from the sample and electric pulses/counts registered by the detector.

Table 4. Property and analytical techniques of some radionuclides selected in this work

Radionuclide	Half life	Radiation	Property	Typical sample type for monitoring
¹³¹ I	8.0 d	Gamma	Fission product, volatile, radiation dose to thyroid	Aerosol, grass
⁶⁰ Co	5.3 y	Gamma	Activation product	Soil, water, air
¹³⁴ Cs	2.1 y	Gamma	Fission product, volatile, radiation dose to tissue, transfer through food chains	Aerosol, grass and food
¹³⁷ Cs	30 y	Gamma	Fission product, volatile, radiation dose to tissue, transfer through food chains	Aerosol, grass and food
³ H	12.3 y	Beta	Naturally occurring, volatile, activation and fission product, radiation dose to soft tissue	Water, air and vegetation
¹⁴ C	5730 y	Beta	Naturally occurring and activation product, volatile, radiation dose to whole body,	Vegetation, air and water
⁸⁹ Sr	50 d	Beta	Fission product, transfer through food chains	Aerosol
⁹⁰ Sr	89.9 y	Beta	Fission product, radiation dose to bone, transfer through food chains	Aerosol, grass and food
²²² Rn	3.82 d	Alpha	Naturally occurring, radiation dose to lung	Air
²¹⁰ Pb	22.3 y	Beta	Naturally occurring, decays to ²¹⁰ Po	Aerosol
²¹⁰ Po	138 d	Alpha	Naturally occurring, volatile, accumulates in seafood, radiation dose to bone marrow, kidney and liver	Seafood
²²⁶ Ra	1600 y	Alpha	Naturally occurring, radiation dose to bone marrow	Drinking water
²²⁸ Ra	5.8 y	Beta	Naturally occurring, radiation dose to bone marrow	Drinking water

4.2 Gross alpha and beta

Gross alpha and beta analyses are used as screening tools for radiological characterization of drinking and waste waters from nuclear facilities. The World Health Organization recommends gross alpha-beta analyses in connection with a recommended reference dose level of 0.1 mSv/y due to consumption of drinking water. Screening levels are 0.5 Bq/L for gross alpha and 1 Bq/L for gross beta activity (World Health Organization (WHO), 2011). If the measured gross activity

concentrations are below the reference levels, the examined drinking water is considered acceptable for human consumption, otherwise, radionuclide-specific analyses are required.

The classical analytical methods for gross alpha and beta are based on counting dry residues of water samples by alpha/beta counters (Palomo et al., 2007). The water sample after filtration is acidified and evaporated onto a planchet for measurement with alpha/beta multi-counters or liquid scintillation counters. The gross alpha and beta method is relatively simple and fast, especially with the use of low-background scintillation counting coupled to alpha-beta discrimination allowing simultaneous determination of alpha and beta activities (Todorović et al., 2012). It is suitable for quick screening of a large number of samples. However, it may suffer from serious self-absorption of alpha emission which causes underestimation in the results.

4.3 Radionuclide specific methods

Herein we briefly discuss specific analytical methods for ^3H , ^{14}C , ^{89}Sr , ^{90}Sr , ^{210}Po , ^{210}Pb , ^{222}Rn , ^{226}Ra and ^{228}Ra . These radionuclides mostly are 'difficult-to-measure' radionuclides, which require thorough radiochemical separation as demonstrated in Fig. 2.

Fig. 2. Overview of radiochemical separation procedure for selected radionuclides in this context

4.3.1 ^3H and ^{14}C

^3H and ^{14}C are pure beta emitters with maximum beta energies of 18.6 keV and 156 keV, respectively. The commonly used measurement technique for ^3H and ^{14}C is liquid scintillation counting (LSC). Gas proportional counter (GPS) has been used for both ^3H and ^{14}C but with less

popularity than LSC (Gröning et al., 2009; Theodorsson, 1991). Accelerator mass spectrometry (AMS) measurement for ^{14}C is very widely applied for low-level environmental samples (Chung and Kim, 2013). Attempt has also been made for AMS measurement of ^3H based on the decay product ^3He , however, this method seems not to have won wide acceptance.

In most cases, chemical separation is necessary to enrich and purify ^3H and ^{14}C . For solid samples, oxidizing combustion using pyrolysis tube furnace or sample oxidizer is often used. The sample is combusted under O_2 flow with Pt or Cu catalyst, tritium is converted to water vapour and collected by a condenser or water/diluted acid trapping, while ^{14}C is converted to CO_2 and trapped in an alkaline solution such as CarboSorb or NaOH.

For liquid samples distillation is often used to purify ^3H and ^{14}C . After distillation, ^3H is collected as condensed tritiated water (THO) and measured by LSC. In ^{14}C analysis, Na_2CO_3 is added to the water sample to enrich ^{14}C by distilling the sample until near dryness (^3H is removed). Remaining Na_2CO_3 residue is further purified by oxidizing combustion as mentioned above. In case of low-level water samples, electrolysis can be used to enrich ^3H (Theodorsson, 1999). The enrichment factor for ^3H by using an electrolysis system can be reached up to 70 (Morgenstern and Taylor, 2009), thereby the ^3H detection limit can be reduced significantly.

For determination of ^3H and ^{14}C in air, specific sample collection systems should be used. In some systems, the air is first passed through a cooled condenser to collect THO, the dried air is then passed through a CarboSorb/NaOH solution to collect $^{14}\text{CO}_2$. In other systems, the air is pumped through a furnace with Pt as catalyst wherein all tritium is converted to THO and ^{14}C is converted to $^{14}\text{CO}_2$, following a molecular sieve to trap the HTO and $^{14}\text{CO}_2$. The collected THO and $^{14}\text{CO}_2$ is then released by heating and collected again using a condenser for THO and CarboSorb trap solution for $^{14}\text{CO}_2$.

4.3.2 ^{89}Sr and ^{90}Sr

^{89}Sr and ^{90}Sr are beta emitters with maximum beta energies of 1459 keV and 546 keV, respectively. Several review articles on the analytical methodology for determination of ^{89}Sr and ^{90}Sr have been published (Vajda and Kim, 2010).

For measurement of ^{89}Sr and ^{90}Sr , radiometric methods such as gas flow GM counting and LSC are normally used. Measurement of ^{90}Sr can also be done through measuring in-growth of its short-lived daughter ^{90}Y ($t_{1/2}=2.7$ d). Due to the much higher beta energy of ^{90}Y (max. 2280 keV), the ^{90}Y ingrowth approach is popularly used for ^{90}Sr determination especially for low-level environmental samples (Popov et al., 2006). With low-background gas flow GM counting, the detection limit for ^{90}Sr can be lower than for LSC, however, the former requires complicated source preparation and longer counting time compared to LSC. Another advantage of LSC is that ^{90}Sr and ^{89}Sr can be simultaneously measured via Cherenkov radiation (Tovedal et al., 2006), based on the fact that a very small fraction of ^{90}Sr beta particles gives rise to Cherenkov radiation due to the low beta energy of ^{90}Sr . In a newly separated Sr-sample, Cherenkov counts are mainly from ^{89}Sr , but with ingrowth of ^{90}Y via ^{90}Sr decay, the contribution from the ^{90}Y increases. By measuring the samples

two times, shortly after Sr separation and after 3 weeks when ^{90}Sr and ^{90}Y reached equilibrium, both ^{89}Sr and ^{90}Sr can be determined.

Several mass spectrometry techniques have also been used for ^{90}Sr analyses, e.g., AMS, and inductively coupled mass spectrometry (ICP-MS) (Vonderheide et al., 2004). Compared to radiometric methods, mass spectrometric methods allow much faster measurement for ^{90}Sr , but has relatively higher detection limits and are vulnerable to isobaric interferences (mostly from ^{90}Zr) (Feuerstein et al., 2008). In recent years, with the advance of triple quadrupole mass spectrometry (ICP-QQQ), the removal of ^{90}Zr by the coupled mass filters is improved.

Prior to measurement of ^{89}Sr and ^{90}Sr , chemical separation is necessary to remove interferences from matrix elements and other beta emitting radionuclides. Traditional methods for purifying Sr are based on the formation of Sr precipitate (e.g., $\text{Sr}(\text{NO}_3)_2$ in fuming nitric acid), liquid-liquid extraction (Vajda and Kim, 2010) or ion exchange chromatography (Stella et al., 1992). In recent years, extraction chromatography using Sr or DGA resin is getting popular (Maxwell et al., 2013; Qiao et al., 2017).

4.3.3 ^{210}Po and ^{210}Pb

^{210}Po is an alpha emitter with energy of 5.3 MeV, while ^{210}Pb is a beta emitter with maximum energy of 17.0 keV (84%) and 63.5 keV (16%) accompanied by emission of a 46.5 keV gamma-ray (4.25%). In many cases, ^{210}Po and ^{210}Pb are analysed together. Several review papers have summarized methodologies for ^{210}Po and ^{210}Pb assays (Baskaran, 2011; Matthews et al., 2007).

Quantification of ^{210}Po is relatively straightforward and mostly based on spontaneous deposition onto metal surfaces and measurement by alpha spectrometry. Many of the currently used detectors (such as PIPS detectors (Roos et al., 1994)) provide full absorption of alpha particles of up to 15 MeV with low background and high absolute efficiency (30%). Chemical separation for ^{210}Po is required in many cases before spontaneous deposition because sample matrices may result in a thick source with poor plating efficiency and low energy resolution. Depending on the deposition conditions, some ^{210}Pb and/or ^{210}Bi may also deposit and it can be especially problematic when the $^{210}\text{Pb}/^{210}\text{Po}$ and/or $^{210}\text{Bi}/^{210}\text{Po}$ ratios are high in the sample.

For chemical purification of ^{210}Po , solvent extraction, ion exchange chromatography and extraction chromatography have been used. Extractants such as isopropyl ether, methyl isobutyl ketone (MIBK), diisopropyl ketone, tributyl phosphate are effective in extracting Po from acid solution. DDTC, EDTA, TIOA, TOPO, TLA and Aliquot 336 have also been proven to obtain separation efficiency for Po. Although anion exchange (AG 1 $\times$ 4), cation exchange (AG 50W- $\times$ 8) resin and solid phase extraction resin e.g., Sr-resin (Bartusková et al., 2006) have been applied for Po purification, solvent extraction is still the most commonly used method.

^{210}Pb can be determined by alpha via its granddaughter ^{210}Po , beta or gamma spectrometric methods (Baskaran, 2011). The advantage of alpha spectrometry is the high energy resolution, low background in the energy range of 3-8 MeV (less than 0.05 counts/h/cm²). But it is critical to completely remove ^{210}Po from ^{210}Pb and then wait for at least 3 months to allow for ingrowth of ^{210}Po to be measured by alpha detector. ^{210}Pb measurements can also be made via the beta-

emitting daughter ^{210}Bi using, for example, gas flow anti-coincidence counter. Beta counting is not isotopic-specific and hence other beta emitting radionuclides can interfere.

Gamma ray spectrometry is utilized to measure ^{210}Pb using the 46.5 keV energy peak (Marković et al., 2017). The sensitivity by gamma counting is significantly lower than that of alpha and beta counting methods, mainly due to low branching (4.5%). The distinct advantage is that this method is non-destructive and thus there is no need for a spike. Attempts have been made to measure ^{210}Pb by ICP-MS, however, isobaric and molecular ionic interferences are major impediments that need to be overcome (Lariviere et al., 2005).

For alpha measurement of ^{210}Pb via ^{210}Po , the sample can be processed with the ^{210}Po chemical separation procedure as mentioned above. For beta and ICP-MS measurement of ^{210}Pb , separation of ^{210}Pb is necessary before detection, wherein solvent extraction, ion exchange chromatography and extraction chromatography (Pb-resin (Horwitz et al., 1994)) can be used.

4.3.4 ^{222}Rn

^{222}Rn is an alpha emitter with alpha energy of 6.3 MeV. The most common methods for determining radon are based on measuring its alpha radiation, using e.g., Lucas cells and ionization chambers (Ball et al., 1991). Gamma spectrometry via measurement of its daughter products ^{214}Bi and ^{214}Pb (Lucchetti et al., 2016) and LSC based on the extraction of ^{222}Rn into the immiscible scintillation cocktail (Fonollosa et al., 2016; Stojković et al., 2015), have also been used. Nowadays, many reliable radon measurement devices are available in the market with reasonably low detection limits, affordable price and simple operation (Todorovic et al., 2012).

Sample preparation for the water radon analysis is usually simple and does not need extensive chemical manipulations. This gives an advantage of much shorter turnaround time. However, many factors could affect the accuracy and precision of a radon water measurement, among which the most critical factor is the sampling technique (Todorovic et al., 2012). The water sample must be representative of the water being tested and such that it has never been in contact with air (Stojković et al., 2015). For measurement of radon in soil gas, extractive and passive methods have been used. In the extractive methods, usually a thin rigid tapered hollow tube is hammered into the ground to a convenient depth, causing minimum disturbance to the soil profile (Ball et al., 1991).

4.3.5 ^{226}Ra and ^{228}Ra

^{226}Ra decays by emitting alpha particles with energies of 4.60 MeV and 4.78 MeV to ^{222}Rn , accompanied with emission of 186.2 keV (3.59%) gamma-rays. ^{228}Ra is a pure beta emitter with the max. beta energy of 46 keV.

In earlier studies, emanation methods were developed, wherein ^{222}Rn is flushed out of a radium contained solution and counted to estimate the amount of ^{226}Ra (Curtiss and Davis, 1943). This technique is not often used nowadays due to its complicated set-up and risk of radon escape. Since the beta energy of ^{228}Ra is very low, ^{228}Ra measurement by counting its beta emission is very

difficult. ^{228}Ra is therefore often determined by LSC or a gas ionization detector via ingrowth of ^{228}Ac .

For ^{226}Ra measurement, alpha spectrometry, gamma spectrometry and LSC can be used. The most sensitive radiometric method for ^{226}Ra is alpha spectrometry (Fonollosa et al., 2016), due to the very low background. ^{226}Ra after chemical separation is co-precipitated with barium sulphate, which is collected on a filter and glued onto a sample disc for alpha counting. The main problem here is self-absorption and thus reduced energy resolution. ^{226}Ra can also be electrodeposited on a disk, however, a high Ba concentration in the Ra solution will significantly reduce the Ra chemical yield during electrodeposition and worsen the energy resolution of the alpha spectrum. Therefore, it is important to remove Ba from Ra before electrodeposition.

In other cases, ^{226}Ra is measured by LSC via counting the activity of its progeny radionuclide ^{214}Po with high alpha energy (7.687 MeV) or sum of Ra with all its alpha progeny (^{222}Rn , ^{218}Po and ^{214}Po) at equilibrium. The latter requires tight sealing of the separated ^{226}Ra solution to prevent radon escape, where Teflon-lined scintillation vials are recommended. ^{226}Ra emits gamma rays in the decay, however, the intensity of its gamma radiation is low (3.6%). Besides, the energy of the ^{226}Ra gamma radiation is overlapping with an intense gamma-ray emission of ^{235}U (185.7 keV, 57%). Therefore, direct measurement for ^{226}Ra using gamma spectrometry is not easily applicable. Mass spectrometric methods, e.g., ICP-MS, have been used for ^{226}Ra determination with the advantage of short analytical time. However, as radium is an alkaline earth element, high concentrations of barium, strontium and calcium may be expected to follow the separation and polyatomic interferences such as $^{88}\text{Sr}^{138}\text{Ba}$ and signal suppression due to matrix effect might appear.

In the radiochemical separation of radium, co-precipitation, ion exchange and solvent extraction are used. The most widely used co-precipitation method for radium is based on the formation of $\text{Ba}(\text{Ra})\text{SO}_4$ precipitation (Palomo et al., 2007). Other approaches using manganese oxides (MnO_x) (Andersen et al., 2003b) or hydrous titanium oxide (HTiO) (Andersen et al., 2003a) co-precipitation, as well as ion exchange chromatography (Aharmim et al., 2009) or extraction chromatography (Ln resin) have also been reported. Because radium has no stable isotopes, its nearest chemical analogue, barium is normally used as carrier and/or tracer for chemical yield monitoring. Gamma-emitting ^{133}Ba has also been used as a tracer for radium determination.

5. Quality assurance and quality control

Quality assurance and quality control are parts of good quality management, and should be integrated into all radionuclide monitoring programmes. For quality assurance and control in radio-analytical procedure, an effective laboratory quality management system would incorporate the aspects including proficiency tests and laboratory inter-comparisons; blank samples to ensure that there is no unexpected source of activity in reagents or cross-contamination of samples proceeded in parallel; analysis of reference materials; analysis of duplicate samples and accreditation by an appropriate accreditation body. Accreditation bodies recognize competence of testing and calibration laboratories based on e.g., ISO/IEC 17025:2017 standard.

6. References

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