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Analytical Methodology for the Determination of Radium Isotopes in Environmental Samples

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Analytical Methodology for the Determination of Radium Isotopes in Environmental Samples

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Sales and Promotion, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
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For further information on this publication, please contact:

Chemistry Unit, Agency’s Laboratories, Seibersdorf
International Atomic Energy Agency
2444 Seibersdorf
Austria

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FOREWORD

Reliable, comparable and ‘fit for purpose’ results are an essential requirement for any decision based on analytical measurements. For the analyst, the availability of tested and validated analytical procedures is an extremely important tool for production of such analytical measurements. For maximum utility, such procedures should be comprehensive, clearly formulated, and readily available to both the analyst and the customer for reference.

Since 2004, the environment programme of the IAEA has included activities aimed at the development of a set of procedures for the determination of radionuclides in terrestrial environmental samples. Measurements of radium isotopes are important for radiological and environmental protection, geochemical and geo-chronological investigations, hydrology, etc. The suite of isotopes creates and stimulates continuing interest in the development of new methods for determination of radium in various media. In this publication, the four most routinely used analytical methods for radium determination in biological and environmental samples, i.e. alpha spectrometry, gamma spectrometry, liquid scintillation spectrometry and mass spectrometry, are reviewed.

The IAEA wishes to thank all the participants for their valuable contributions to development and review of the report. The IAEA officer responsible for this publication was Chang Kyu Kim of the Terrestrial Environment Laboratory, IAEA Environment Laboratories, Department of Nuclear Sciences and Applications.

CONTENTS

1. INTRODUCTION

1.1. History and radiochemistry

Radium is an alkaline earth metal with the atomic number 88, belonging to Group IIA in the Periodic Table. It has more than 20 isotopes, all of them radioactive. Two radium isotopes, ^{226}Ra and ^{228}Ra are very significant from a radiological protection viewpoint due to their relatively long half-lives, presence in nature, and high dose conversion factors.

Radium was discovered in 1898 by Marie and Pierre Curie. Initially radium was not considered as a possible hazard for workers or the general public, and in fact was commonly used for diagnostic and therapeutic medical purposes. In the 1950s radium was identified as a pollutant of the environment, caused by uranium mining and milling in the USA, later similar reports have been published in Europe. Other, non-nuclear branches of industry – oil and gas exploitation, phosphate fertilizer production, underground mining of different raw materials (coal, heavy sands, gold etc.) – have also been identified as significant sources of environmental pollution due to radium release.

The natural abundance of radium in environmental waters is invariably too low for the solubility product of radium sulphate, or any other radium compound, to be exceeded. Therefore adsorption and co-precipitation (with barium and calcium) play the most important role in forming radium-bearing deposits. A very good overview of radium properties, behavior in the environment, and methods of detection is given in IAEA Technical Reports Series No. 310 The Environmental Behavior of Radium, which was published in 1990 [1]. Despite the many publications since that time on radium behavior, the technical report of IAEA [1] may still be considered as a comprehensive source of information. The present review will only be focused on the methods of radium determination.

1.2. Decay data for radium isotopes

Radium is a radioactive element from which no stable isotope is known. The mass numbers of the known isotopes range from 206 to 230 and their half-lives ($T_{1/2}$) span from 182 ns for ^{216}Ra to 1600 years for ^{226}Ra. The four radium isotopes ^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra occur naturally and are members of the three decay chains which are depicted in Figure 1, Figure 2 and Figure 3: ^{223}Ra ($T_{1/2}$ = 11.4 days) is part of the actinium series with ^{235}U as parent nuclide, ^{224}Ra ($T_{1/2}$ = 3.7 days) and ^{228}Ra ($T_{1/2}$ = 5.75 years) are both members of the thorium series parented by ^{232}Th, and ^{226}Ra ($T_{1/2}$ = 1600 years) belongs to the uranium series headed with ^{238}U. The neptunium series shown in Figure 4, beginning with ^{237}Np, includes the radium isotope ^{225}Ra ($T_{1/2}$ = 14.9 days) which is utilized in some procedures as a suitable yield tracer for the radium determination. The radium isotopes ^{223}Ra, ^{224}Ra and ^{226}Ra are alpha-particle emitters, whilst ^{228}Ra and ^{225}Ra are beta-particle emitters.

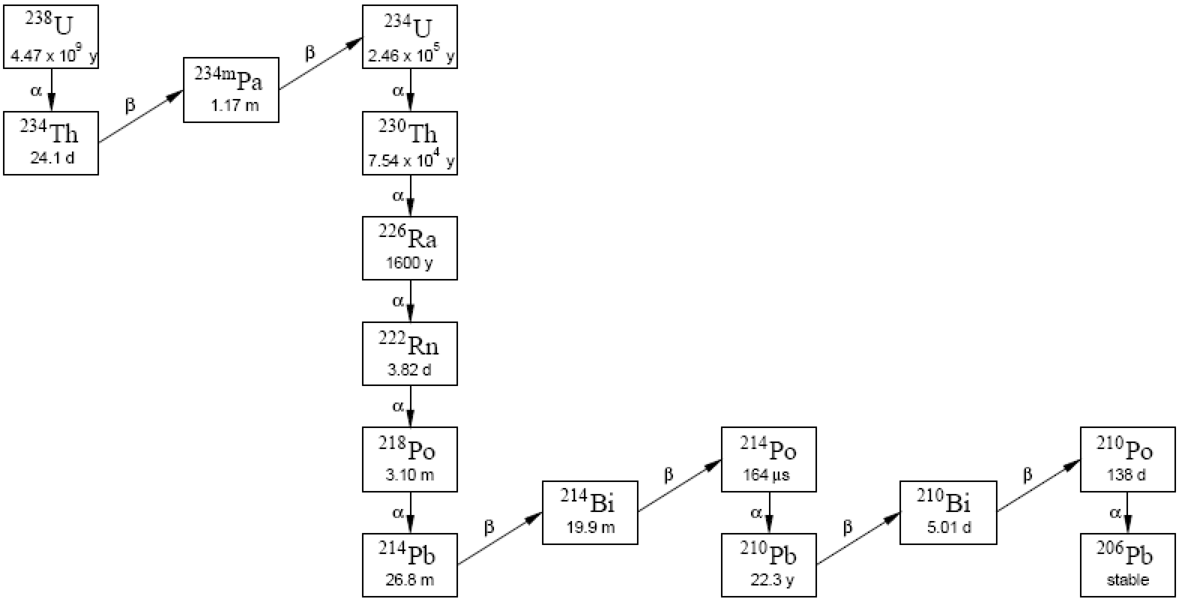

FIG. 1. ^{226}Ra is a member of the uranium (^{238}U) decay series [2].

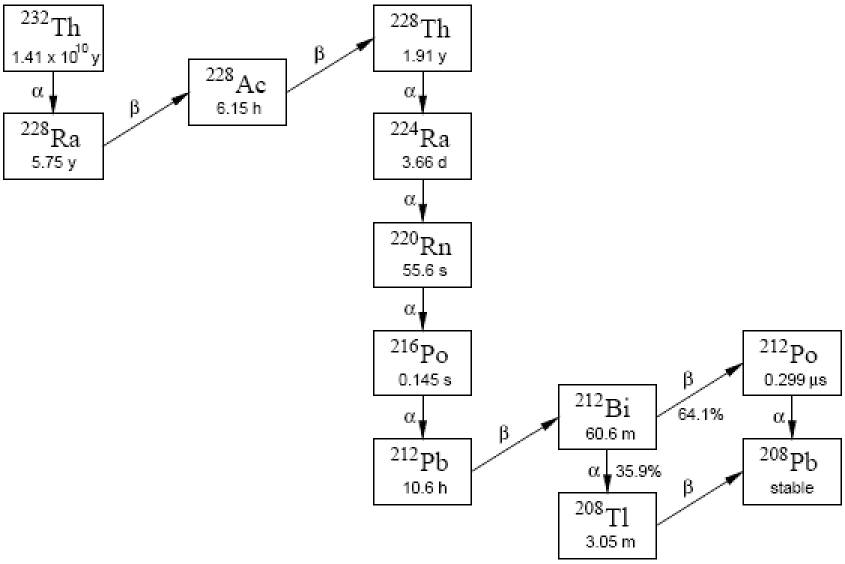

FIG. 2. ^{228}Ra and ^{224}Ra are members of the thorium (^{232}Th) decay series [2].

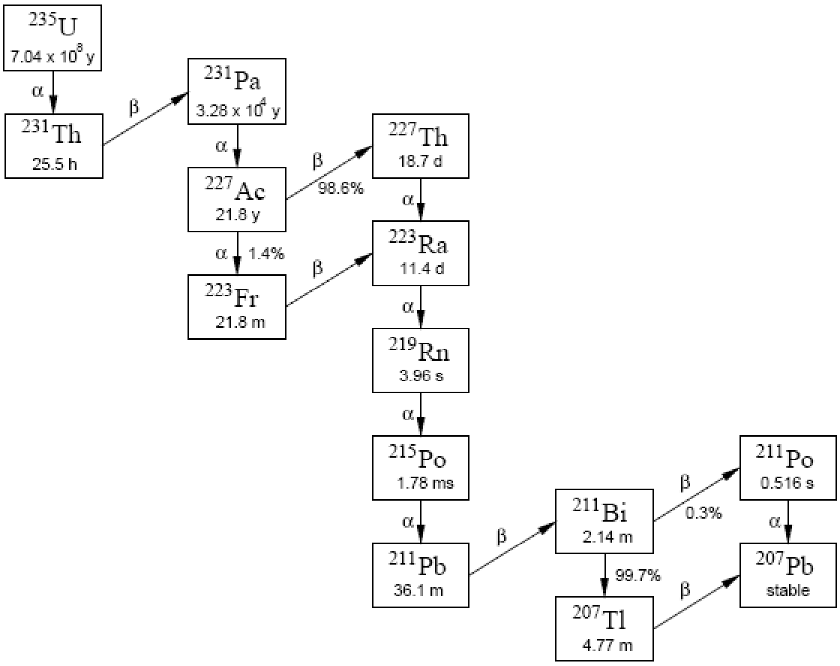

FIG. 3. ^{223}Ra is a member of the actinium series within the ^{235}U decay series [2].

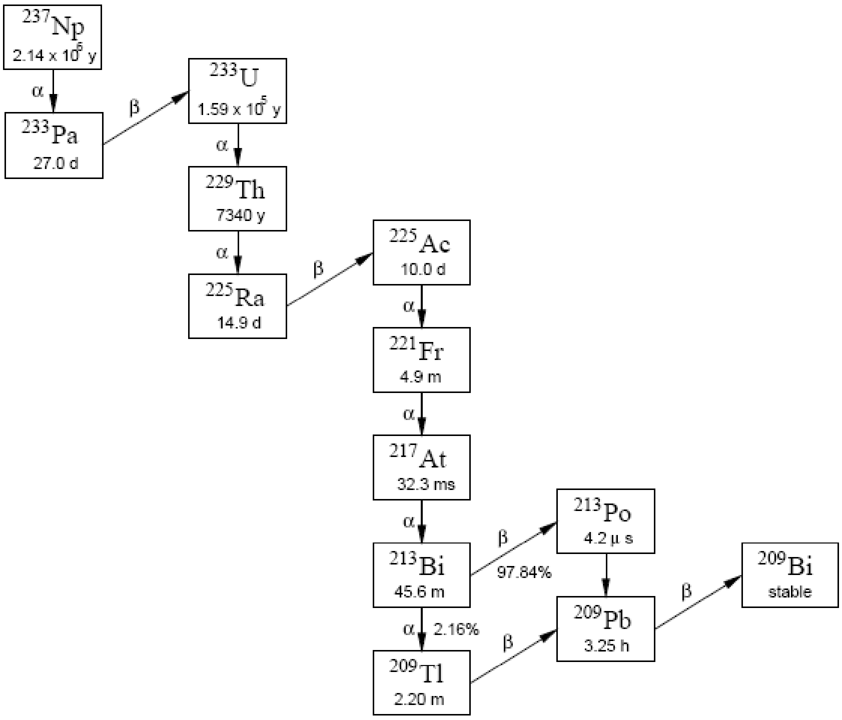

FIG. 4. ^{225}Ra is a member of the neptunium (^{237}Np) series [2].

Detailed decay data for radium isotopes considered in this review may be found in the recommended data of LNHB (laboratoire national henri becquerel) [3] and the nuclear data of the IAEA [4].

1.3. Why is the measurement of radium required?

Radium has in the past, and continues to be, used in numerous applications including medical diagnosis and therapy, industrial applications such as self-luminous dials on clocks and instruments and is a waste product of uranium mining, and other natural resource exploitation processes: NORM (naturally occurring radioactive material).

Considering the radiotoxicity of different radionuclides, radium isotopes are important because they can be easily incorporated into bones due to having similar properties to other elements from Group II (i.e. calcium) and produce short living radionuclides of high specific activity. For the general public, the consumption of food and water containing radium may lead to the accumulation of these nuclides, contributing to radiological dose.

National and international regulators have shown an increasing interest in regulating radium levels in most industries and consumer products. The US Environmental Protection Agency (EPA) has released national drinking water regulations which limit the concentration of various contaminants to defined levels and set the maximum contaminant level for the sum of ^{226}Ra and ^{228}Ra to 185 mBq L^{-1} (5 pCi L^{-1}) and for ^{224}Ra to 555 mBq L^{-1} (15 pCi L^{-1}) [5]. The European Commission Drinking Water Directive 98/83/EC gives an indicative effective dose of 0.1 mSv a^{-1} from ingestion of radioactive substances in tap water (TID – Total Indicative Dose), but does not define maximum activity concentrations for individual radionuclides [6]. The implementation of this Directive should be performed in all EU (european union) Member States. For instance in Germany, the Mineral and Table Water Regulation restricts the activity concentration of ^{226}Ra and ^{228}Ra in table, well and packaged drinking water which is marked as suitable for the preparation of baby nutrition to maximum values of 125 mBq L^{-1} and 20 mBq L^{-1}, respectively [7].

In geographical regions with naturally elevated concentrations of radionuclides in the surrounding soil and rocks the risk of their ingestion may be higher as a result of consumption of plants, animals and animal products which may include several radionuclides [8].

Radium isotopes are often present in industrial waste products, referred to as NORM.

It encompasses substances with enhanced concentrations of natural radionuclides, which are occurring at production sites and in the environment as a result of industrial or mining activities. They may cause enhanced exposure to both workers and members of the public. NORM is characterized by an enrichment or translocation of natural radionuclides. A translocation is only considered as a NORM generating process, if the availability of radionuclides to exposure pathways is increased. Both the enrichment and the translocation are due to physical or chemical processes taking place in industry or mining. Radium isotopes are often significant contaminants for NORM industries.

NORM may be associated with the following materials or activities [9]:

- Materials (products, by-products, residues, waste) with enhanced concentration of natural radionuclides which are resulting from technological processes in non-nuclear industries. The processing of raw material, such as chemical separation, metallurgical smelting or physical screening, had enhanced the concentration of individual or several natural radionuclides.

- Raw materials or waste rock with natural elevated concentrations of natural radionuclides which are not processed as mentioned under a), but are heaped up or reused, e.g. as construction material or for backfilling of mines.
- Processes of treatment of drinking water or waste water (e.g. surface water, pit water, seepage water) can lead to waste (sludge) with enhanced concentrations of natural radionuclides
- Mining or industrial processes which release solid or dissolved natural radionuclides (other than ^{222}Rn or ^{220}Rn) to surface water, seepage water or ground water. Such discharge may lead to an accumulation of natural radionuclides in environmental media, like river bed or bank sediments, soils or sewage sludge.

For EU member states, the following processes are considered as possible sources of NORM material [9]: phosphate industry, mining and processing of metal ores, tin, niobium, aluminium, iron and steel, zinc, copper, molybdenum, vanadium, hafnium and lead, mining and processing of mineral sands, zirconium and rare earth elements, manufacture and use of thorium compounds, titanium dioxide pigment industry, oil and gas extraction, coal mining and combustion, and waterworks and waste water treatment plants.

In most of these processes radium isotopes are concentrated in waste or by-products, as in the phosphate industry, where phosphogypsum is created. Phosphogypsum is a waste by-product from the production of phosphoric acid and is produced by precipitation as calcium sulphate during the leaching of phosphate containing rocks with sulphuric acid. The commercial use of this gypsum may be restricted because of elevated concentrations of radionuclides, including ^{226}Ra. The accrued stacks of gypsum have the additional problem of leaching out the radionuclides by rain or drainage water and distribution to the environment [10]. Hence, phosphate fertilizers can possess traces of ^{226}Ra which might cause increased concentrations in watersheds of predominantly agriculturally used land [11].

For the assessment whether natural levels are exceeded or not comprehensive investigations of the occurrence and the (radio)chemical behavior of natural radionuclides in numerous matrices of environmental samples have been carried out and revealed not only large differences within similar sample matrices all over the world, but also the potential for scientific applications in the direction of dating methods in the half-life range of the employed radionuclide (e.g. ^{14}C, ^{238}U, ^{226}Ra, ^{228}Ra), studies of geochemical processes and of dynamics in aqueous systems and the possibility of risk estimation for radioactive wastes and in geographical regions with higher radionuclide concentrations in the surroundings [12–14].

The composition of volcanic rocks, fault gouges and sediments can give insights into the age, the kind and the duration of geochemical formation, dissolving, depositing and rearrangement processes via the disequilibria between parent and progeny nuclides, e.g. by the determination of excesses and deficiencies of ^{226}Ra in comparison to its parent nuclide ^{230}Th [15–16]. Geochronological studies of sedimentation rates determining the ^{210}Pb activity can be rendered more precisely by taking the partial contribution of ^{226}Ra to the ^{210}Pb concentration into account [17]. The ^{226}Ra concentration — directly measured — can shed light on oceanographic deep water movements and — in relation to its daughter ^{210}Pb — the residence time of water layers. The ^{228}Ra concentration can be consulted to assess oceanographic superficial water movements in the range of 3–30 years and can support the ^{232}Th/^{228}Th geochronology explaining the imbalance of both thorium nuclides because of the higher mobility of ^{228}Ra, the parent of ^{228}Th [18].

1.4. Measurement techniques

1.4.1. Alpha spectrometry

Alpha spectrometry can be described as recording the energy of the emitted alpha particles in the form of a pulse height distribution. The pulses are created in a sensitive detector volume which can be gaseous, liquid or solid, and registered after electronic amplification. Although the alpha radiation exhibits discrete energies the interaction between alpha particle and detector is subjected to statistical variations which cause the emergence of a broadened peak instead of a discrete line. Commonly used detector types are ionization chambers, proportional counters, semi-conductors and scintillation counters.

An alpha particle spectrometer can be assessed by several parameters as the detector type, detector performance, the quality of the source, and the source/detector geometry all influence the counting efficiency, the background, and thus the detection limit, the possible contamination and the quality of the measured spectra, including energy resolution and peak tailing [19–28].

The energy of alpha particles emitted by the known radionuclides ranges in a narrow region of 4 to 9 MeV. Hence, spectrometers with a high energy resolution are required for the analysis of mixtures of alpha emitting radionuclides. Solid scintillators (e. g. crystals of CsI (Tl) or thin layers of ZnS (Ag) can have an energy resolution down to 8%. Liquid scintillators have often a sensitivity of nearly 100% and benefit from the 4π arrangement (the analyte is completely surrounded by the scintillator), but their energy resolution reaches only values of about 20%. Semi-conductor detectors are used with the greatest success due to their strict energy linearity (i.e. the same energy calibration for all types of particles) and their very good energy resolution of 0.5–1%. The strong interactions among alpha particles and air components cause a significant energy loss which complicates spectral analysis. Thus, the measurements are carried out under vacuum in the case of solid detector types (i. e. scintillator crystals, semi-conductors). Further optimization is achieved by adequate arrangement of source and detector to each other.

The measurement of the absolute activity of a source demands a high expenditure in equipment and comprehensive corrections of the obtained values. Therefore, the activity of the unknown radionuclides is generally determined in relation to a standard with a known activity. For the determination of the detector efficiency a standard should be preferably prepared from the same radionuclide preferably prepared and measured under the same geometrical and instrumental conditions. An alternative is the use of another isotope of the same element as internal tracer which is added to the sample prior to radiochemical separations. In the literature, the latter method is sometimes called ‘isotopic dilution alpha spectrometry’.

A recent review paper [28] gives an overview of the status quo of the technical development between the years 1984 and 2006 and comprises numerous references describing practical experiences, new instrumental developments and theoretical models or simulations.

1.4.2. Gamma spectrometry

Gamma spectrometry is a useful non-destructive method that permits the simultaneous determination of many radionuclides in a bulk sample [29–36], without the need for complicated and time consuming radiochemical separations as undertaken for alpha spectrometry. However, it is limited by the weak emission probabilities of many potentially useful emission lines, the relatively poor efficiency of the High Purity Germanium (HPGe) detectors over a wide range of energy, the difficult task of precisely calibrating the efficiency of the detector, and the need to evaluate self-absorption effects [37].

Gamma spectrometry relies on the generation of an electronic pulse, proportional in magnitude to the gamma ray emissions produced from the radioactive decay of a radioactive material being measured. Each radioactive material that emits gamma radiation has a characteristic 'finger print' that can be used to both qualitatively identify the radionuclide present, and quantitatively establish the activity concentration of the material (there are a number of decay processes where gamma radiation is not produced, these radionuclides cannot be measured directly by gamma spectrometry).

Typical gamma ray spectrometry systems generally fall into two categories relying on either the generation of a light pulse in a scintillating inorganic or organic material, and subsequent collection of the generated photon by a photomultiplier tube or photodiode, or a high purity germanium or silicon crystal that generates electrical pulses directly proportional to the energy of the gamma photons striking the detector element. Traditionally, thallium doped sodium iodide (NaI) were, and are still, used extensively as the industry standard scintillation gamma spectrometer, but suffer from poor spectral resolution. Newer materials including Cesium Iodide (CsI), Bismuth Germanate (BGO), Lanthanum Bromide (LaBr) and a number of organic scintillators have been developed and provide significantly enhanced robustness, resolution and efficiency over NaI detectors.

For the purpose of this review, discussion on high resolution gamma spectrometry detectors will be limited to HPGe (high purity germanium) systems. High resolution gamma ray spectrometry allows for the separation of close photopeaks that may not have been able to be resolved using scintillation detectors. Modern germanium detectors are typically available with a Full Width half Maximum (FWHM) resolution of approximately 2 keV at the 1332 keV photopeak of cobalt-60, and a few hundred eV at lower energies. Germanium detectors have a useful energy range from around 5 keV to several MeV, and may have a relative detection efficiency, compared to the industry standard 3” x 3” diameter NaI detector, of greater than 100%. The basic high resolution gamma spectrometry system consists of the detector crystal, mounted in a cryostat (maintained at approximately -190^{o}C by either liquid nitrogen or a mechanical refrigeration system) to reduce electronic noise, an integral preamplifier, a high voltage supply, amplifier and multichannel analyzer (MCA). Modern systems tend to incorporate the high voltage supply, a digital amplifier and MCA in a single component that is operated via an external computer system. The detector element in a basic system is enclosed by a passive environmental radiation shield to decrease interference from external radiation sources (natural background radiation). The shield is made from low background lead (~ 100 mm thick) and may include an additional internal graded shield of tin and copper to attenuate the respective lead and tin fluorescent x-rays produced within the shield. Active shields incorporating Compton suppression and veto shields may also be used to further reduce Compton scattering and background radiation effects in the detector. Selected ultra low background construction materials for the detector housing and preamplifier, and low background environments (e.g. under dam walls, underground) may also be used to further increase the sensitivity of the gamma spectrometry system. Gilmore [38] provides a detailed review of gamma spectrometry, covering theory and practical applications.

1.4.3. Liquid scintillation spectrometry (LSS)

The history of LSS (liquid scintillation spectrometry) initiated in the 1950s, when the technique was used for studying scintillation properties of various liquids [39]. Initially, LSS methods have been applied for measurements of soft beta emitters like ^{3}H and ^{14}C [40, 41].

Horrocks [42] applied the technique for alpha emitter measurements, and Cerenkov counting was introduced for high energy beta particle counting, [43, 44], predominantly for ^{32}P. Measurements of radium with application of this technique started in the 1960s [45]. Al-Masri and Blackburn [46] applied Cerenkov counting technique to measure ^{226}Ra in narural water samples.

The main reason for the rapid development of LSS applications is due to the ability to undertake the counting of alpha and beta particles with high efficiency and accuracy [47–51], this fact being important for low energy beta emitters (^{3}H, ^{14}C) as well as for isotopes decaying with the emission of alpha particles. Counting efficiency for alpha particles can reach 100%, and is higher for beta particles in comparison with other methods, primarily due to the 4π counting geometry typical of modern LSS instrumentation [52]. The precision and accuracy of methods applying LSS technique are very good for numerous radionuclides, but due to poor energy resolution it can only be achieved by chemical preparation and separation of samples prior to measurements [48, 53–63].

There are a number of disadvantages in LSS including quenching (caused by chemicals in, or color of, the sample), poor energy resolution and relatively high background, especially in comparison with alpha particle spectrometry [56, 64–68].

The LSS technique is often used for the determination of radium isotopes in environmental samples, especially in liquids [68, 69]. LSS methods can provide high sample throughput, and acceptable detection limits for several radium isotopes [65, 70, 71]. Various methods of sample preparation and different cocktails can be applied, enabling analyses of a variety of samples. The LSS methods for radium determination can be divided into procedures where either no sample preparation is undertaken (Cerenkov counting, where no scintillation cocktail is added), or the sample is simply mixed with a water immiscible cocktail (as a two-phase sample, usually only ^{226}Ra can be measured via ^{222}Rn and its progeny), or with a water miscible cocktail (as a homogeneous or semi-homogeneous sample for ^{226}Ra and ^{228}Ra). Such methods can be used only for samples with relatively high activity or the counting time must be rather long.

Pre-concentration with use of radiochemical methods, followed by measurement with a low background spectrometer allows for measurement of low ^{226}Ra, ^{228}Ra and ^{224}Ra concentrations, bearing in mind that detection limits are strongly dependent on the sample volume and the background of the LS spectrometer.

An important factor in LSS is the selection of a suitable spectrometer. To meet the low detection limits required in most applications, the LS spectrometer should provide for alpha / beta separation, and incorporate passive and/or active shielding systems to ensure optimal background radiation reduction [47, 71, 72].

1.4.4. Mass spectrometry

In mass spectrometry, decomposed and ionized species of the sample are dispensed by means of electric and / or magnetic fields in the electrostatic and magnetic analyzers according to their specific ion masses (Mass/charge). Mass spectra are obtained by detecting the ion beams at different positions (or at the same position but different magnetic fields) corresponding to different ionic masses. The major parts of mass spectrometers are the ion sources for the excitation and ionization of the sample, the single or double focusing analyzers for dispersion of the ion beam and the recording device for detection of the mass distribution.

Mass spectrometric methods, which are used for the determination of isotopes of elements, have also been developed for the determination of relatively long-lived radionuclides (generally $T_{1/2}$ more than 25 years) [73]. In these methods, the atoms of the radionuclide of interest are directly detected.

Among the different isotopes of Ra, the longest-lived ^{226}Ra (1600 years) has been determined by various mass spectrometric methods. Although ^{228}Ra has a relatively short half-life (5.75 years) its mass spectrometric determination has also occasionally been reported.

Thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS) have been used for the determination of ^{226}Ra and ^{228}Ra. An excellent review about the critical evaluation of radiometric and mass spectrometric methods for the determination of long-lived radionuclides has been published by Hou and Ross [74]. Performance parameters including detection limit and separation time have been compared. Resolution and sensitivity of MS determinations are highly dependent on the type of the ion source and the analyzer. The sensitivity of mass spectrometric methods for ^{226}Ra analysis was found to be comparable to those of LSS and alpha spectrometry, and the analytical time was much shorter than using radiometric methods. Nevertheless, radiometric methods are more suitable for the determination of ^{228}Ra.

The main advantages of mass spectrometric methods are high sensitivity and short analytical times, typically only some minutes. Radiochemical pre-concentration and separation procedures are usually unavoidable, but process times are typically shorter than is the case for radiometric methods due to the small sample sizes.

The major problems in mass spectrometric analysis relate to the formation of isobaric (e.g. ^{228}Th isobaric with ^{228}Ra) and polyatomic interferences (e.g. ^{88}Sr^{138}Ba, ^{87}Sr^{139}La, ^{86}Sr^{140}Ce, ^{40}Ar^{40}Ar^{146}Nd, ^{18}O^{208}Pb and several combinations of molybdenum isotopes with xenon isotope), the formation of multiple charged ions, the abundance sensitivity (or tailing) of neighboring atoms, matrix effects and mass fractionation during detection [75].

To eliminate or suppress the effect of interferences, radium has to be radiochemically separated from the interfering elements and the matrix components, and requirements for purity of the source are usually very high. Instrumental techniques can also help reduce the deleterious effects of the interferences and increase the sensitivity and the accuracy of the method.

1.5. Criteria for method selection

The selection of the method for the analysis of environmental samples must be done in consideration of the requirements of the user and/or requirements of legal acts regulating the content of radium isotopes. The most important task for every analyst is to choose the most appropriate and suitable analytical procedures for the analysis [76]. The determination method must be chosen taking into account following parameters:

- the goal of the analysis;
- the type of the sample, including the matrix of the sample;
- radium isotopes to be determined;
- predicted concentration of particular radium isotopes;
- costs.

When a determination is undertaken to assess the radiation hazard of workers or members of the general public, the reliability of results and analysis of all important nuclides is of importance. It is also important to ensure that a suitable validation of the method has been conducted, and where appropriate in many countries, a requirement of the certification of the method to international quality standards should be fulfilled. When measurements are performed for research purposes only, then the choice may be based according to the needs of the user.

Typically the radium concentrations in environmental samples are very low and therefore pre-concentration and chemical preparation for such samples is necessary, and despite that, sometimes measurements are done very close to the detection limit(s).

It is evident that there are a number of techniques available for the determination of radium isotopes in environmental samples. While several of the described methods are primarily aimed at measurement in a liquid matrix (e.g. potable water), it is possible, using the sample preparation and separation procedures summarized within this review, to adapt all of the methods to applications covering water, solid and sediment samples, biota and even air samples collected on filters.

2. SAMPLE PREPARATION

According to the aim of the radionuclide analysis (e.g. nuclear decay data, radionuclide concentrations in environmental samples for scientific or commercial purposes) and the selected measurement technique the preceding treatment consists of various steps adjusted to the respective requirements: sampling, preservation, pre-treatment, separation, source preparation, measurement and evaluation.

Sample collection and preservation are not included in this review, but are described elsewhere, e.g. Koide and Bruland [77], Sidle et al. [11], Martin and Hancock [2].

Water samples are generally acidified after collection. Solid materials (e.g. soil, sediment and biota) are usually dried at 80–110°C in 12–48 hours and ashed in a temperature range of 450–800°C over a period of 12–48 hours to destroy the organic matter which can complex radionuclides to a not negligible extent.

2.1. Digestion of solid materials

To break up the matrix and provide complete or partial access to the radionuclide the samples have to be decomposed by ashing, wet techniques under exposure of various acid combinations or fusion techniques via melting with different salt mixtures.

For the complete or nearly complete dissolution by a wet digestion strong oxidizing acids at raised temperatures are used, such as concentrated or fuming nitric acid, Aqua Regia, sulphuric acid or mixtures of concentrated nitric acid with perchloric acid or hydrofluoric acid. For accelerating the wet digestion the leaching and decomposition can be supported by applying high pressure in an autoclave system, and in recent years the advantages of the microwave technology are more and more discovered. [77, 78]

A fusion technique with a suitable fluxing base or salt and optional additives is used for the destruction of refractive material. The various procedures derived from developments for analyzing the composition of geological samples [79–81] and adjusted to the demands of the radiochemical analyst can apply hydroxides [82], peroxides [83], fluorides, pyrosulphates [12, 79, 84, 85], carbonates [79, 82, 83, 86], or borates [80, 81, 87–93] as fluxes, alone or in mixtures. The methods are usually very fast with time lengths of 5–60 minutes. The automation of the fusion combined with the simultaneous treatment of more than one sample offers a high sample throughput in the laboratory. The fusion technique can be transferred to other solid materials not containing refractory silicates or oxides like fertilizer [82], pine needles or oysters [88], washing powder [90], coal [91, 93], and food [92].

Jia et al. [83] tested a 1:1 mixture of sodium carbonate and sodium peroxide for the determination of radium in reference soils with accurate and reproducible results. For the radium analysis in soil, uranium ore and mill tailing Percival and Martin [12] and Sill [85] combined a fluoride fusion with a pyrosulphate fusion. The solid material is heated with anhydrous potassium fluoride until a clear melt is obtained. Intermittently warming and cooling the melt with concentrated sulphuric acid volatilize the silicon tetrafluoride. With addition of sodium sulphate the melting process is transferred to a pyrosulphate fusion. The cake is solubilised by boiling in dilute hydrochloric or sulphuric acid with or without addition of little hydrogen peroxide. The sample size manageable with this method ranges from 0.1 to 5 g.

The Lithium metaborate fusion [80, 81, 87–93] works effectively on a wide range of diverse sample matrices and breaks up the most silicates, oxides, sulphates, and carbonates in short heating times of 5–20 minutes. In the course of the reaction no hydrogen fluoride or sulphuric acid fumes are developed. The sample size digested by a lithium metaborate fusion usually ranges from 0.1 to 5 g. Unavoidably, considerable amounts of boric acid and silica gel (dependent on the material) are present in the digestion cake which precipitate from acidic solutions and have to be removed prior to further treatment, above all chromatographic procedures. The coagulation can be assisted by a flocculating agent (e.g. polyethylene glycol) supporting the precipitation of colloidal silica gel [81].

Bojanowski et al [89] developed a rapid method for the determination of ^{226}Ra in soil and sediment applying a lithium metaborate fusion with sodium iodide or bromide as non-wetting reagents followed by transfer of the melt into an acidic sodium sulphate solution, immediate barium sulphate co-precipitation and subsequent alpha-particle spectrometry.

2.2. Pre-concentration and separation

The following section describes the treatment of liquid samples, i. e. different types of water and of solutions obtained from the digestion of solid samples. A clear differentiation between pre-concentration and separation is not always given in practice. The most frequently applied pre-concentration method is co-precipitation. Typical methods for separation are co-precipitation, ion exchange chromatography, extraction chromatography (solid phase extraction), and solvent extraction. Hence, the diverse methods presented here can partially be applied in all three steps.

2.2.1. Evaporation

Samples of water with a low total quantity of dissolved substances (e.g. potable, mineral, ground, rain water) can be pre-concentrated by evaporation without any selectivity regarding the enrichment of radium. Evaporation is a common source preparation method for determination of radium by gamma spectrometry. The evaporation to dryness is often applied for the determination of gross alpha and beta activities in drinking water by LSS or gas proportional counting. Handled sample volumes range from < 0.1 L up to 20 L and are processed at 70–100°C and atmospheric pressure or at lower temperatures under vacuum conditions in less than one hour or in 2–3 days [94, 95]. For digestion solutions of solid materials a volume reduction by evaporation is also practicable.

2.2.2. Co-precipitation

Co-precipitation is practicable for the pre-concentration of the analyte from large water samples and for the separation of the analyte from matrix components and other radionuclides.

For radium no stable nuclide is known, thus, a chemically very similar carrier must be selected. Barium is often the element of choice as the predecessor of radium in Group II, but strontium and calcium are also suitable.

The co-precipitation with barium sulphate is most often employed as pre-concentration step which is simultaneously associated with separation and purification. Other specific co-precipitations can be carried out with barium chromate or oxalate, calcium or aluminium phosphate [77] and strontium sulphate [99].

(a) Barium and lead sulphate

Within the alkaline earth metals, the sulphates are increasingly poorly soluble in water at acidic, neutral and alkaline pH going from magnesium through calcium and strontium to barium and radium. In most cases the reaction is combined with a parallel lead sulphate co-precipitation. Therefore, the specificity of the barium sulphate co-precipitation is somewhat reduced as the lead sulphate takes along other radionuclides such as thorium, actinium, polonium and uranium. Depending on the source preparation technique, the kind of measurement (i.e. alpha spectrometry, gamma spectrometry, LSS) and the statistical requirements, the basically similar method is carried out with minor variations sometimes decisive for the final results. [2, 85, 95–98, 100–104].

Sill [85] published a very thorough and detailed study about the application of a lead sulphate co-precipitation for enrichment and separation of radium and a barium sulphate co-precipitation for purification in combination with a micro-filtration as source preparation method for the alpha spectrometry of radium from water and soil samples. Solid samples are digested by two succeeding fusions with potassium fluoride and pyrosulphate and the fusion cake is dissolved in dilute hydrochloric acid. Sulphuric acid, potassium sulphate, and sodium sulphate are added to the solutions as precipitation agents. The crystallization of lead sulphate carrying radium as well as barium is accomplished by the stepwise addition of lead carrier [12]. The precipitate is dissolved into alkaline diethylenetriaminepentaacetic acid (DTPA).

The adjacent barium sulphate co-precipitation as source preparation for alpha spectrometry is done by adding an appropriate amount of barium carrier, adjusting the pH of > 9 to 4.8 with 50% acetic acid and filtering through a 0.1 μm membrane. The total amount of barium has to be kept in the range from 75 μg to 525 μg. The crystallization process can be initiated by addition of a seeding solution of $BaSO_4$. Barium sulphate exhibits the property of adsorbing radium from solutions initially only on the surface of the crystals, but on standing for some minutes the radium is built into the crystal lattice. [85, 105] The most accompanying elements co-precipitated with lead sulphate as lead, calcium, strontium, thorium, or polonium [2, 84, 95 are not precipitated from the alkaline complex solution as their complexes with DTPA are much stronger than those of barium and radium [85]. The performance of the lead and barium sulphate co-precipitation steps can be examined by the addition of ^{133}Ba as yield tracer [85, 101].

Bojanowski et al. [98] followed in the most steps the procedure of Sill [85], but slightly varied the conditions for source preparation as 2-propanol was added prior to adding barium carrier, sodium sulphate and $BaSO_4$ seeding suspension. The 2-propanol acts as surfactant to minimize the adhering properties of the barium sulphate precipitate.

Other precipitating reagents are potassium persulphate which slowly releases sulphate ions entailing the formation of large crystals [106], sulphuric acid alone [95] or in combination with ammonium sulphate [83, 97] or sodium sulphate [85]. The complexing reagent DTPA is interchangeable by alkaline ethylenediaminetetraacetic acid (EDTA) [57, 86, 98, 101] or 1,2-cyclohexylenedinitrilotetraacetic acid (CyDTA) [83, 97] or DTPA [107]. Goldin [86] tested citric acid at alkaline pH as masking reagent to prevent the precipitation of lead and barium sulphate prior to the addition of the precipitating reagent by sulphate or carbonate ions present in the sample in order to get good recoveries of ^{226}Ra after lowering the pH with sulphuric acid. The reported decontamination factors for lead, thorium, and uranium reached values of 10^3 to 10^4.

Sill [84] reported that virtually all alpha-emitting radionuclides from radium to californium can effectively be co-precipitated with barium sulphate from acidic solutions in presence of a large excess of potassium sulphate directly after the potassium fluoride-pyrosulphate fusion without a previous lead sulphate co-precipitation. After fusing the barium sulphate with a large amount of Aluminium nitrate further separation and purification steps can be started, e.g. solvent extraction with Aliquat 336 in xylene.

Percival and Martin [12] developed a procedure for the determination of ^{226}Ra and ^{228}Ra as well as thorium, actinium and protactinium in different sample types of uranium mining using a very similar procedure as described by Sill [85], but by measuring with gross alpha counting or emanation instead of alpha spectrometry. Zikovsky [95] investigated the co-precipitation of radium, polonium, thorium, and uranium with barium sulphate recovering 13% polonium, 18% thorium and less than 3% uranium together with 88% radium. In most methods using lead and barium sulphate co-precipitation, uranium stays in solution in the hexavalent state [2, 84]. Rodriguez-Alvarez and Sanchez [108] combined the barium sulphate co-precipitation of radium with a subsequent ferric hydroxide co-precipitation of thorium and uranium in the filtrate. After dissolving the barium sulphate the co-precipitated thorium is separated from the radium and combined with the thorium fraction of the second co-precipitation. Jia et al. [97] also combined barium sulphate and ferric hydroxide co-precipitation, but without removal of the barium sulphate prior to formation of the ferric hydroxide obtaining a pre-concentration of radium, thorium and uranium as high as possible.

The reported recoveries of ^{226}Ra (radium) by the above outlined methods can achieve 75–97% [85, 95, 101, 107, 108].

Following chemical and radioactive interferences are briefly compiled:

- High concentrations of calcium disturb the precipitation of lead sulphate because the element is readily emplaced into the crystal lattice.
- Thorium is carried in the lead sulphate precipitate, but the complex of thorium with DTPA is very stable and does not re-precipitate by addition of acetic acid.
- Nitrate anions should only be present in small amounts as they interfere with the sulphate precipitation [84, 85].
- Condensed phosphates form very stable complexes with barium and radium and have to be hydrolyzed to orthophosphates prior the co-precipitation step.
- Lanthanum, cerium, and calcium precipitating with excess of alkali sulphates increase the recovery of barium and radium, but also increase the needed amount of DTPA.
- Hydrochloric acid keeps the calcium in solution, hydrolyses the condensed phosphates, and prevents the precipitation of lead, bismuth, and polonium, and decreases the barium and radium recovery, above all at elevated temperatures as lead and barium sulphate exhibit an increased solubility.
- The amount of barium used as carrier depends on the procedure steps following the barium sulphate co-precipitation, the expected barium content of the sample, the available measurement technique and the necessary source preparation technique. If the barium is completely separated from the radium during the subsequent chemical steps, quantities ranging from 75 μg to 110 mg Ba^{2+} can be added. Moreover, the measurement is virtually possible by alpha spectrometry, liquid scintillation counting

and gamma spectrometry after suitable source preparation. If the barium sulphate co-precipitation is used as final source preparation technique barium amounts greater than 0.5 mg per sample severely reduce the resolution in alpha spectrometry. If radium is electrodeposited for the alpha spectrometric determination, the residual quantity of barium should not exceed 10–100 µg in dependence of an aqueous or an organic electrolyte.

- Barium reagents can contain trace contaminations of radium (above all ^{226}Ra) increasing the procedure blank and thus, adversely affecting the achievable detection limit [97, 115, 123].

(b) Miscellaneous co-precipitation methods

Manganese dioxide

Manganese dioxide (MnO_2) freshly precipitated from large volumes of water up to 10 litre effectively encloses a variety of radionuclides (e.g. radium, thorium, uranium, polonium, actinium and lead) which are assumed to be dissolved. Potassium permanganate and manganese dichloride are added to the acidified water which was previously spiked with an appropriate yield tracer and degassed to remove CO_2. Then, the formation of MnO_2 is initiated by raising the pH to 8–9 [2, 98, 108, 109].

Beside the complete dissolution of manganese dioxide into dilute hydrochloric acid with a little hydrogen peroxide [2], acidic hydroxylamine hydrochloride [103, 108], or a mixture of ascorbic and acetic acid [98], the radionuclides can also be obtained without complete MnO_2 dissolution by leaching with cold nitric acid accepting a lower recovery [110].

Rodriguez-Alvarez and Sanchez [108] compared the co-precipitation of radium with barium sulphate and manganese dioxide from water samples and obtained very similar recoveries in the range of 72–90% for both methods. The barium sulphate co-precipitation was recommended if only radium has to be analyzed.

Bojanowski et al. [98] investigated the influence of high salt concentrations on the MnO_2 co-precipitation efficiency and found out that sodium chloride concentrations up to 100 g L^{-1} do not affect the recovery of barium, radium or uranium. The effect of calcium and magnesium ions is much stronger as concentrations of 0.2 g L^{-1} to 1 g L^{-1} or higher made a second or third repetition of the precipitation procedure necessary in the filtrate of the foregone precipitation to attain high recoveries. Moreover, barium is not precipitated with the same efficiency as radium which could cause erroneous recovery corrections if ^{133}Ba is used as yield tracer.

Aluminium orthophosphate and lead nitrate

Koide and Bruland [77] carried out radium analyses in seawater up to 20 L and marine sediments up to 5 g by co-precipitation with aluminium orthophosphate $AlPO_4$. Because the alkaline earth metals form also insoluble phosphates calcium, strontium, and barium are co-precipitated as well. Lead and radium are separated from thorium and uranium by lead nitrate co-precipitation after addition of 90% fuming nitric acid [105]. The precipitate is washed with ice-cold 75% nitric acid, whereat the main part of accompanying calcium and strontium contaminations are removed, and dissolved in water or dilute hydrochloric or nitric acid for further purification steps, e.g. ion exchange chromatography (see section 2.2.4). The alpha spectrometric measurement was carried out after electrodeposition of radium. The effectiveness of the radium co-precipitation with aluminium orthophosphate was determined to 90%.

Calcium carbonate and phosphate

Some references mention the co-precipitation of radium with calcium or barium carbonate or calcium phosphate, but these methods for pre-concentration are not very common, because the recovery of radium drops fast with increasing volumes of water due to the better solubility in comparison to calcium or barium sulphate [77, 98, 111].

2.2.3. Adsorption

In oceanographic investigations the enrichment of radium from low concentrations in sea water was executed already since the 1970s with filtering or adsorbing acrylic fibers coated with a thin layer of manganese dioxide [11, 102, 110].

Manganese fibers (Mn-fibers) are prepared from cartridges made of acrylic fiber tissue which are immerged into a potassium permanganate solution, whereas manganese dioxide is deposited. The water sample is passed through the cartridge at a constant flow rate (5–10 L min^{-1}). The adsorbed radium is removed from the fiber either by the complete dissolution of the manganese dioxide with hot hydrochloric acid and few hydrogen peroxide (recovery > 90%) or by leaching the MnO_2 layer with cold nitric acid (recovery 35–60%). With this technique moderate to very large volumes of 1–2000 L are handled [110].

Sidle et al. [11] made use of the radium pre-concentration with MnO_2 fibers from samples of ground water aquifers and drainage ponds for the investigation of a possible radium entry from ammonium phosphate fertilizer over the drainage ponds and agricultural land into the ground water. After dissolution into hydrochloric acid the radium was co-precipitated with barium sulphate and mounted on an appropriate filter for gamma spectrometry.

The coating of polyamide disks with manganese dioxide is a further approach to use the selective adsorption of radium from water volumes of 1–2 L. The simultaneous use of the pre-concentration equipment (disks) as finished measurement source for the alpha spectrometry is a trial to develop a very time saving and effective determination method for radium (and polonium). The MnO_2 layer is deposited on only one side of the disk. To collect the radium from the sample the disk is positioned with only the coated side contacting the water at pH 7–8. A recovery of 75–90% was achieved after a contact time of 150–445 hours. Immediately after drying the disk is immediately counted in an alpha spectrometer for the determination of ^{226}Ra, ^{224}Ra, and ^{228}Ra (via ^{228}Th) [102, 112, 113].

In an acidic milieu of pH < 3 and after longer contact time the MnO_2 layer is damaged resulting in poor resolution in alpha spectrometry. Salt concentrations of higher than 2 mmol L^{-1} Ca^{2+} as representative for the competing alkaline earth metals cause a severe decline of radium recovery [112, 114].

Bayes et al [103] prepared MnO_2-impregnated cotton filters similar to the Mn-fibres and MnO_2 disks. Small volumes of 100 mL were filtered for the determination of radium in mineral waters with a low flow rate of 3 mL min^{-1} compared to 5–10 L min^{-1} for pre-concentrating radium from large volumes of sea water (100–1000 L) [110]. The radium (and the manganese dioxide) was extracted from the filter with a solution of hydroxylamine hydrochloride in hydrochloric acid.

Koulouris [113] investigated the principal sorption characteristics of radium on manganese dioxide. In the batch tests, the ^{226}Ra is adsorbed to 40% in 15 minutes and to 75–80% after 15 hours reaching the equilibrium. Barium showed faster kinetics. The adsorption increases with the temperature suggesting an endothermic nature of sorption process, but the increase is limited by the mechanical damage of the manganese dioxide. The column tests exhibit higher radium recoveries up to 90%. In the pH range of 4–12 no changes in the radium recovery were observed maintaining a constant level which declines dramatically below pH 4. The author explained these facts with a positive surface charge at low pH and the existence of a zero point charge corresponding to a certain pH value above that no variation of the adsorption takes place because the surface charge remained negative. The composition and the amount of the dissolved matrix substances showed no influence on the radium adsorption efficiency which is possibly due to the large quantity of MnO_2 used in the several trials (10-15 g).

2.2.4. Ion exchange chromatography

The methods described in the following section can only represent a small extract of the numerous variants reported in the literature. For concentrating radium strong acidic cation exchange resins are frequently used loading the samples dissolved in dilute acids (HCl or HNO_3) and eluting the less retained components with HCl or HNO_3 of increasing concentrations, finally stripping Ra with 4-9 M HCl or 4–5 M HNO_3. By this procedure, Mg and Ca are removed effectively, but the Ra fraction is contaminated with Ba, Sr [16, 99, 111, 115–117], and lanthanide impurities [16]. The batch method was applied to a large water volumes [115, 118, 120]. The separation of Ra from Ba which is a crucial interference in mass spectrometry [119] and source preparation by electrolysis for alpha spectrometry can also be accomplished by cation exchange chromatography. In combination with complexing agents, e.g. EDTA, Ra (Ba) concentration and separation is carried out [121]. Volpe [119] eluted Ba before Ra from a strong acidic cation exchanger with 0.01 M ammonium EDTA (pH 8.94). Frequently used cation exchange resins are BioRad AG50WX8 or Dowex 50WX8.

Strong basic anion exchange resins do not retain radium but can efficiently scavenge other interfering radionuclides like thorium, actinium, or uranium from concentrated acid solutions (8 M HNO_3, 9 M HCl) [111].

In the 1970s, Gleason [122] developed one of the first successful approaches for the separation of radium and barium using CyDTA as selective eluent. This method was adopted by several investigators and used with only minor variations [83, 97, 108, 123]. After pre-treatment of the sample Rodriguez-Alvarez et al. [108] dissolved the residue in CyDTA. After adjusting the cation exchange resin to pH 5 by washing with boric acid the CyDTA solution is passed through whereat radium and barium are retained on the column. The barium is removed with CyDTA at pH 8.5 and then the radium is eluted with nitric acid. Jia et al. [97] dissolved the barium sulphate co-precipitate directly in the alkaline CyDTA solution; otherwise the employed procedure was the same. Yamamoto et al [123] pointed out that for the separation of radium and barium the best complexing agent is CyDTA in the case of high barium to radium ratios.

Volpe et al. [119] applied a cation resin in a pressurized quartz capillary column that was washed with diammonium EDTA solution at pH 9 to eliminate actinium, lead, calcium, strontium and barium. Radium was eluted with EDTA at pH 10. The EDTA was removed using a further cation-exchange column by washing with dilute HCl, and eluted radium with concentrated HCl.

Hancock and Martin [124] and Purkl and Eisenhauer [121] reported a procedure in which the lead sulphate co-precipitate was dissolved in ammoniacal EDTA at pH 10. The solution was passed through an anion exchange column retaining thorium and actinium, and radium and barium were eluted with EDTA at pH 10. After adjusting the pH of the combined effluents to 4.5 with nitric acid and adding ammonium acetate the solution is passed through a cation-exchange column that was washed with ammonium acetate and dilute nitric acid to eliminate lead, and the remaining thorium, actinium, polonium and uranium. Barium was eliminated with 2.5 M hydrochloric acid [121, 125]. Radium was then eluted with 6 M nitric acid. The decontamination factors of the radium separation procedure are > 10^4 for thorium, actinium, polonium, uranium and lead, but only > 200 for barium.

Lawrie et al. [78] applied cation exchange chromatography to separate radium in water samples from magnesium, calcium, uranium, and thorium and used Sr Resin for further purification. Andrews et al [126] carried out three subsequent separation steps by two cation exchange columns to concentrate radium with barium and one Sr Resin column to separate them. Crespo [127] also described a procedure comprising two anion and one cation exchange chromatography steps. The latter was used to remove barium from radium washing out barium with 2.5 M hydrochloric acid and extracting radium with 6 M hydrochloric acid. Thakkar et al [128] subsequently used cation exchange resin and Ln resin to separate ^{226}Ra and ^{228}Ra from water samples.

2.2.5. Extraction chromatography (solid phase extraction)

The basis of a solid phase extraction is the selective recognition/retention of charged or neutral species by organic molecules supported on inert solid carriers [129, 130].

(a) Manganese dioxide Resin

The MnO_2 resin consists of an inert macroporous carrier substrate on which the manganese dioxide is precipitated in finely divided form by reduction. For the retention of radium from de-ionized water and low-salinity water the optimal pH ranges from 4–8 where recoveries of > 90% are achieved [102]. The explanation for this fact is the same one as given by Koulouris [113] based on the surface charge of MnO_2, which is positive at low pH preventing the adsorption of Ba^{2+} and Ra^{2+} and becomes increasingly negative with higher pH providing more free hydroxide functions for the adsorption of Ba^{2+} and Ra^{2+}. Additionally, the slow dissolution on MnO_2 at low pH and the precipitation of carbonates and hydroxides at pH > 10 could possibly be responsible for the recovery decreases [112, 113].

The kinetic tests show a distinct dependence on the salt concentration. With increasing salinity the time necessary for reaching the distribution equilibrium is longer ranging from 10 min for de-ionized water to 90 minutes for sea water. The barium quantity absorbed in 15 min decreases from 100% from de-ionized water to 35% from sea. These results are most likely ascribed to the higher concentrations of alkaline earth metal ions (Mg^{2+}, Ca^{2+}, Sr^{2+}) in sea water competing with the binding sites on the resin [102].

In dynamic column experiments at gravity flow (about 1 mL min^{-1}) the recoveries for radium and barium achieved 91–96% independent of the salinity. Measurements at different flow rates revealed that radium is favoured over barium implying the failure of ^{133}Ba as yield tracer at flow rates higher than 20 mL min^{-1} [102].

Maxwell [131] reported lower recoveries of only 60% for ^{133}Ba from low salt content water and added calcium to improve the recovery.

(b) Strontium (Sr) Resin

Recently, a more specific material, the Sr resin, has had wide-spread application for the removal of Ba and Pb from Ra. Sr resin is the trade name of an extraction chromatographic (EC) material containing 4,4’(5’)-di-t-butylcyclohexano-18-crown-6 ether as an extractant [132]. In 3 M HNO_3 solution the nitrate complexes of Ba, Sr and Pb are retained with increasing distribution coefficients. Radium is collected in the effluent. Examples are given in the chapter on mass spectrometry measurements.

(c) 3M™ Empore™ Radium Rad Disk

The Radium Rad Disks from 3M™ are filter-like membranes that consist of an inert polymer matrix of polytetrafluoroethylene fibrils in which particles of radium ion selective organic compound (a crown ether) is embedded [133–135].

The Radium Rad Disks are mainly dedicated for the rapid determination of the longer-living radium isotopes ^{226}Ra and ^{228}Ra in environmental water samples or similar aqueous solutions up to a volume of 4 L.

Following an appropriate treatment of the disk the radium can be measured by gamma spectrometry, with a proportional counter, via radon emanation, by LSS or alpha spectrometry [100].

For example, after drying the disk ^{226}Ra can immediately be measured by gamma spectrometry [134]. ^{228}Ra can indirectly be measured with a gas proportional counter via its progeny ^{228}Ac. After a storage time of 1.5–3 days, the ingrown ^{228}Ac is eluted to about 90% with highly diluted diammonium hydrogen citrate solution (DHC, 0.0006 M) [134]. Another possibility is given by eluting the radium from the disk with alkaline EDTA, adding lead and yttrium carrier, and storing the eluate for 1.5–3 days. The separation of ingrown ^{228}Ac from radium is achieved by consecutive lead sulphide precipitation for removal of radium and yttrium hydroxide precipitation for isolation of ^{228}Ac. In both cases, the ^{228}Ac fraction is purified by re-precipitation as oxalate which is transferred to a stainless steel planchet representing the source for the gas proportional counter [134].

The emanation technique is applicable for the indirect determination of ^{226}Ra by its gaseous daughter ^{222}Rn. For it, the radium is eluted from the disk with alkaline EDTA solution which is filled into a radon bubbler, degassed with helium and stored gas-tight for several days for in-growth of ^{222}Rn. The ^{222}Rn is transferred to a radon counter where the alpha scintillations from ^{222}Rn and its daughters are registered.

The simultaneous measurement of ^{226}Ra and ^{228}Ra by alpha / beta separating LSS can be performed immediately on the alkaline EDTA eluate which is reduced to a small volume and mixed with a water-miscible liquid scintillator.

^{226}Ra can be determined by alpha spectrometric determination after elution from the disk with alkaline EDTA and preparation of an alpha-source. The recoveries are 90–93% [100].

Interferences during the extraction of radium from the water sample may occur by other bivalent ions like Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} or Pb^{2+}, and monovalent ions like Na^{+}, K^{+} or NH_4^{+}. According to the manufacturer the Radium Rad Disk can tolerate the alkaline earth metal ions Mg^{2+} and Ca^{2+} with smaller ion radii up to a concentration of 10 g L^{-1} without disturbance of the radium extraction. Metal ions with ion radii similar to radium like Sr^{2+}, Ba^{2+}, and Pb^{2+} can remarkably impede the radium up-take in the range of 0.5 mg l^{-1} for Ba^{2+} to 2.0 mg L^{-1} for Sr^{2+} and Pb^{2+}. The monovalent ions Na^{+}, K^{+}, and NH_4^{+} can interfere at concentrations of 10 g L^{-1}.

Ďurecová [134] investigated the elution behavior of radium, barium, strontium, bismuth, and lead towards different molarities and volumes of diammonium hydrogen citrate (DHC). An elution of actinium was achieved to nearly 90% by highly diluted DHC (0.0006 M) whereas radium (and barium) remains on the disk (to 99%). But a separation of strontium and lead from actinium could not be achieved, so these elements have to be washed from the disk before the in-growth of ^{228}Ac. Radium and barium are completely eluted from the disk with 0.2 M DHC.

Purkl and Eisenhauer [121] started their purification procedure with a solution from the pre-concentration of radium with an Empore Rad Disk obtained by extracting the disks with EDTA and ammonium acetate.

(d) Miscellaneous

For the purification from possible interferences several other chromatographic procedures have been used where the resins are specific for the interferences but radium is not retained. UTEVA resin containing diamylamyl-phosphonate and removing thorium and uranium from 3–8 M HNO_3 [136], TRU resin containing octylphenyl-i-butylcarbamoylmethylphosphine oxide and t-butylphosphate and retaining lanthanides and actinides from 1.5–3 M HNO_3 [100, 117], Ln resin containing bis(2-ethylhexyl)-phosphoric acid and extracting lanthanides from dilute acid solutions (0.01 M HNO_3) [131, 136] have been used.

A resin self made by impregnation of microthene (a microporous polyethylene powder) with trioctyl phosphineoxide (TOPO) effectively retains thorium and uranium from concentrated hydrochloric acid and let pass radium and barium [83, 97, 137–140].

For the determination of ^{228}Ra via its daughter ^{228}Ac Diphonix Resin (a polystyrene scaffold functionalized with diphosphonic and sulphonic acid groups) or DGA Resin (containing N,N,N',N'-tetraoctyl-diglycolamide) are applicable which retain actinium whilst radium is eluted [102, 131]. Barium and radium are not hold back and can be determined from the eluate which has a sufficient purity for several source preparation techniques, e.g. barium sulphate co-precipitation according to Sill's procedure [85] or reducing to a defined volume and mixing with an appropriate scintillation cocktail [99]. The elution of actinium is brought about with hydroxyethane-1,1-diphosphonic acid (HEDPA) at usage of Diphonix Resin [102, 141, 142] and with diluted hydrochloric acid in the case of DGA Resin [131]. The obtained actinium fraction is pure enough to directly carry out the source preparation, e.g. the co-precipitation with cerium fluoride and micro-filtration for the measurement in a proportional counter [134] or mixing with scintillation cocktail for liquid scintillation counting [102].

3. SOURCE PREPARATION

3.1. Alpha spectrometry

An ideal source has to be indefinitely thin, weightless, perfectly even, and contains, if possible, only the radionuclide of desire to avoid self-absorption, backscattering, and spectral interferences during the measurement. Fulfilling these pre-requisites for a real sample means separating the radionuclide from most of the sample matrix by a sometimes time-consuming and elaborate chemical procedure, concentrating it to a small volume and bringing it into a layer as thin as possible on a suitable substrate. As the alpha spectrometer counts under vacuum conditions all volatile residues have to be removed from the source prior measuring to avoid contamination or damage of the detector [21].

Well-known techniques are electrodeposition, vacuum sublimation, direct evaporation, electro-spraying, and precipitation which differ in quality and quantity of the deposited material and have to be carefully chosen according to the measurement aim [21, 22, 28, 143]. For the material of the substrate, on which the analyte layer is formed, most frequently stainless steel, but also tantalum, platinum, silver, nickel, optically flat glass, ceramics, or polymers (e.g. VYNS, Mylar) are used as thin polished disks in various diameters, as squares or films/foils [21].

The direct precipitation method combined with a micro-filtration increasingly gains in popularity. Theoretically, every insoluble compound can be used if its formation is fast in a moderate temperature range, the co-precipitation of the analyte is nearly quantitative and reproducible, the precipitate sufficiently adheres on the substrate, and the crystals are small, equal in size and regularly distributed on the substrate [21, 144]. Different attempts are described in the literature among them the co-precipitation of the actinides (and lanthanides) with cerium hydroxide or cerium fluoride [144], and the co-precipitation of radium with barium sulphate [20, 85] are well-elaborated by various other investigators. Sill [85] presented resolutions between 65 and 100 keV (FWHM) for sources from the cerium hydroxide and cerium fluoride precipitation, respectively, and for the barium sulphate precipitation resolutions down to about 50 keV.

Surely the best known and thoroughly investigated method for preparation of sources for alpha spectrometry is the electrodeposition on to a metal surface from aqueous or organic solutions (the latter one is also called molecular plating). In general, pure solutions give a nearly quantitative deposition yield which drops with increasing content of impurities. This problem can be overcome to a certain extent by adjusting the pH value and by the addition of complexing agents like EDTA [21, 28, 145]. The resolution can achieve FWHM values of about 15-17 keV [145].

3.1.1. Electrodeposition

One of the first investigations on the subject was published in 1937 about the electrodeposition of radium containing barium salts from a non-aqueous solution in acetone. As Sill et al. [84, 85] recognized the deposition of ^{224}Ra during the electroplating of ^{228}Th from an aqueous acidic solution, deeper examinations were carried out in the 1970s and 1980s by a few investigators as Koide and Bruland [77], Roman [146] or Short [147].

An often made assumption was the restricted possibility to electrodeposit radium with satisfactory yields from aqueous solutions because this element reacts readily with water and also its oxide and hydroxide are very soluble in water [148]. Thus, the first investigations were carried out about the so-called molecular plating – the electrodeposition from organic solutions.

(a) Electrodeposition from organic solutions

Soret and Tauveron [148] selected a method which was originally developed for the electrodeposition of plutonium from propan-2-ol containing hydrochloric acid on a platinum disk. A very similar method was used by Koide and Bruland [77]. The radium fraction is electrolyzed from a solution composed of 90% propan-2-ol and 10% 0.05 M hydrochloric acid. The deposition is done on a stationary platinum disk cathode and a platinum wire anode applying a current of 100–150 mA and a voltage of 40 V. After about 20 minutes the electrolysis achieved nearly 100%, but the main part of the radium (90%) is already deposited in the first 5 min. To stabilize the deposited layer some drops of ammonia are added before switching off the current. Flaming the disk volatilizes the gaseous radon daughters, but can further improve the stability of the deposit. The organic solvent is replaceable by ethanol and the molarity of the hydrochloric acid can be increased by a factor of two without significant drop in the recovery. The texture of the platinum anode must not be too close-meshed, because trapped gas bubbles formed during the electrolysis lead to a noticeable radium loss [77].

Whitehead et al. [149] executed a detailed work based upon the method of Koide and Bruland [77]. The stainless steel disk used as cathode was vertically rotatable, and the platinum anode was fixed. The achieved resolution of the alpha spectra was 75 keV FWHM. Nitric and hydrochloric acid are interchangeable without significant differences in the electrodeposition behavior. Instead, with perchloric acid the current rises strongly causing an overheating of the medium and degradation of the organic solvent which could also take place in the system propan-2-ol/nitric acid at elevated temperatures. Sulphuric acid let rise the deposition time about the factor 25. Using cation exchange resins the eluates often contain traces of the sulphonic acid exchange groups washed out from the resin which are oxidized to sulphate during treatment with nitric acid and/or hydrogen peroxide.

(b) Electrodeposition from aqueous solution

Roman [146] worked out a widely applicable procedure for the electrodeposition of radium from an aqueous ammonium acetate solution at pH 9. Platinum as cathode material mostly used at molecular plating techniques was replaced by a stainless steel disk, but as anode material platinum was maintained. The electrolyte solution was made up of 0.35 M ammonium acetate in 0.1 M nitric acid resulting in a pH value of 5 from which a total volume of 10 mL was taken. Applied current and voltage were 400–600 mA and 10–14 V, respectively. In the first hour only 5% of the radium activity was found on the plate, but in the second hour the deposition jumped up to 75–80% to reach 90–100% after 3–4 hours [149, 150]. The achieved resolution of the alpha spectra was 40–45 keV in terms of FWHM [146, 147]. The use of sulphuric and perchloric acid instead of hydrochloric acid reduces the electrodeposition recovery of radium [147, 149].

The deposition is accompanied by the appearance of a brown color on the cathode surface with proceeding electrolysis. Measurements delayed by 20 days [146], 3 months, and one year [150] revealed the almost complete retention of radon on the disk. The secular equilibrium is reached after the theoretical time (about 20 days). In dependence of the deposited radium activity the disk is storable for a longer time (3–12 months) without significant activity losses of radon and its daughters. At higher activities radon escaped from the disk at longer storage times presumably due to the radiolysis of the layer [146].

Short [147] adopted the method of Roman [146] and ascertained the robustness of the technique towards some contaminant ions as sodium, potassium, calcium, aluminium, or silica against the previous assumption of very pure radium solutions being necessary for the electrodeposition.

Garcia-Tenorio and Garcia-Leon [150] investigated the behavior of the actinides at the electrodeposition of radium with the method of Roman and selected ^{239}Pu as representative. While the achieved radium yields of 70–95% confirm the applicability of Roman’s technique ^{239}Pu was deposited to 35–45%. Hence, if actinides are present in the raw sample a separation is indispensable to avoid spectrometric interferences.

Orlandini et al [151] tried several electrolytes finding that 0.17 M ammonium oxalate in 0.14 M hydrochloric acid at pH 3 gives higher electrodeposition yields and is robust towards traces of barium (5–10 µg), and firstly examined the positive effect of deliberately added platinum in dissolved form on the electrodeposition from aqueous medium. .

Alvarado et al [152] simulated matrix effects with different elements like magnesium, calcium, barium, and iron in the range of 10, 50 and 100 µg using the electrolyte solution of 0.17 M ammonium oxalate in 0.14 M hydrochloric acid. As magnesium, calcium and iron showed only a slight decrease in the radium recovery, barium caused a severe drop to 50% yield at amounts of only 10 µg.

Crespo [127] examined the behavior of actinium during the electrodeposition of radium with regard to the use of ^{225}Ra as yield tracer. If the source preparation is delayed after the chemical separation the daughter ^{225}Ac ($T_{1/2}$ = 10.0 d) grows in to some extent and could possibly deposited at the electrolysis of the radium fraction up to 17%.

The presence of platinum in the deposited layer from the aqueous electrolyte composed by 0.35 M ammonium acetate in 0.1 M nitric acid recognized in preliminary examinations by

Roman [146] was confirmed by Hamilton et al. [153] with X-ray fluorescence spectrometric measurements, but the amount varied in every trial presumably dependent on the occurrence of oxidized platinum on the anode surface.

Moreover, the recovery of radium and the deposition time seemed to be related to the quantity of platinum in the layer: Hamilton et al [153] investigated the effect of the deliberate addition of platinum comparing the electrodeposition techniques from aqueous and organic medium. The platinum was added as a solution of sodium hexachloroplatinate (Na_2PtCl_6) taking amounts corresponding to 195 µg Pt. In the case of using the aqueous electrolyte the platinum caused a considerable acceleration of the radium deposition achieving more than 80% after only 1 h in contrast to Roman [146]. With the organic electrolyte, radium yields of more than 90% were achieved after 30 minutes which seemed to be a slight retardation comparing the results from Koide and Bruland [77] and Whitehead [149] which showed 20 minutes to be more than sufficient to deposit almost 100% of the radium [151, 153]. The aqueous electrolyte consists of ammonium oxalate and hydrochloric acid, but the added quantity of 20 µg of platinum did not significantly change the characteristics of the electrolysis after 1 hour only a small radium activity was found on the disk, reaching 85% after 2 hours and nearly 100% after 3–4 hours. The alpha-spectrometric resolution changed from 40 keV FWHM without added platinum to 50–60 keV FWHM with 100–300 µg platinum [97].

Alvarado et al [152] were looking for another element supporting the electrodeposition in the same way as platinum selecting palladium, gold, silver, copper, nickel, and iron, but platinum remained the only element with that outstanding positive effect.

(c) Influence of barium on the electrodeposition

Vargas and de Soto [154] carried out several electrodeposition trials comparing two methods belonging to molecular plating, both basing upon the procedures described by Koide and Bruland [77], Whitehead et al. [149], or Martin and Hancock [2] using 90% ethanol and 10% dilute nitric acid alone or in mixture with hydrochloric acid. In the result, the methods tolerate barium up to 100–150 µg yielding 75–90% of the radium activity with only a slight decrease in resolution from 25–30 keV to 35–40 keV FWHM [154].

Martin and Hancock [2] tested the influence of barium on the electrodeposition of radium from aqueous medium applying 0.35 M ammonium acetate in 0.1 M nitric acid, 600 mA over 3 hours. The addition of only 1 µg barium to the electrolyte brought about a large drop in the yield from 93% down to 63%, 9 and 60 µg barium resulted into 31% and 10%, respectively. By use of ammonium oxalate in hydrochloric acid the tolerance against barium increases only slightly up to 5 µg [152].

3.1.2. Co-precipitation with barium sulphate

The elaborate study of Sill [85] provides the analyst a detailed working instruction for the co-precipitation of radium with barium sulphate and the subsequent micro-filtration. This type of source preparation is directly carried out following the co-precipitation of radium with lead and/or barium sulphate from an acidic solution and the dissolution of the precipitate in 0.1 M DTPA or EDTA. The volume of the complex solution should be maintained as small as possible.

If the sample contains marginal amounts of barium less than 50 µg [98] like potable water, blanks or standards, and the previous co-precipitation was carried out only with lead, barium carrier is added in the range of 75–175 µg. The precipitation reagent is a solution of 40% anhydrous sodium sulphate in water. The adjustment of the pH value from > 9 to 4.8 by few drops of 50% acetic acid starts the formation of barium sulphate. A barium sulphate seeding suspension was added immediately after the acetic acid supporting the crystallization. After 30 min the precipitation was complete and the precipitate was mounted on a 0.1 µm membrane filter, washed with little 80% ethanol and dried. The average yield obtained from test solutions spiked with ^{226}Ra and ^{133}Ba is 92–100 % measured by alpha spectrometry and gamma spectrometry, respectively. All reagents employed in the precipitation procedure except the seeding suspension should be filtered through a 0.45 µm membrane after preparation and stored rather in plastic bottles than in glass ware to avoid the formation of insoluble materials [98, 101, 103].

With a resolution ranging from 50–60 keV FWHM achieved for sources prepared from pyrosulphate cakes and 65–80 keV FWHM for sources prepared from alkaline DTPA solutions, the simultaneous measurement of ^{226}Ra, ^{224}Ra, and ^{223}Ra is possible using either ^{133}Ba or ^{225}Ra as yield tracer. Also, the determination of ^{228}Ra can be carried out via alpha-spectrometry after a suitably long in-growth period for ^{228}Th (about 6 months), but it could also be done by gamma spectrometry of the source [85].

In two examples, Sill [85] reported 56% retention with a resolution of 52 keV FWHM after an in-growth period of 29 days and 71% retention with a resolution of 58 keV FWHM after an in-growth period of 78 days.

3.2. Gamma spectrometry

An attractive feature of gamma spectrometry is the ability to use bulk samples that often require little, or no, radiochemical preparation. For solid materials including soils and sediments, the sample can often be directly placed into the sample holder or container after only very basic preparation (e.g. drying, ashing, sieving etc.). Sample homogeneity is also more easily attained with the larger sample sizes typically used.

The Marinelli beaker, a reverse entry container typically available in volumes ranging from 100 mL to 4 L, is designed to enhance detection efficiency by encompassing the detector element. For smaller samples, of the order of 10s of grams, the well geometry detector allows the sample to be introduced to the detector element approaching a 4π geometry. Plastic Marinelli beakers are readily available, but consideration should be given to the impact of radon permeability of the chosen materials. This is addressed at greater length in Section 4.

It is important that all prepared samples should closely match the physical geometry of reference materials used to calibrate the gamma spectrometer, parameters of sample diameter, height, chemical composition and density all being of importance.

Radiochemical sample preparation techniques, as described in Section 2 of this review, are still applied in gamma spectrometry sample preparation to increase sensitivity, particularly for liquid samples, and in situations where the removal of interfering radionuclides is advantageous (e.g. removal of ^{235}U to reduce interference with direct ^{226}Ra measurements). The final, prepared sample is transferred to a sample container for measurement. More detailed information on interference effects is provided in Section 4.

3.3. Liquid scintillation spectrometry

LSS measurement methods for radium determination can be divided into two general groups: where no sample preparation is required, and alternatively where radiochemical methods may be used prior to measurement.

Measurements in the first category are done either without a cocktail (Cerenkov counting), with a water immiscible cocktail (as a two-phase sample, usually only ^{226}Ra can be measured via ^{222}Rn), or as a homogeneous or semi-homogeneous sample (for ^{226}Ra and ^{228}Ra, but suffers from problems with interfering radionuclides). Such methods can be used only for samples with relatively high activity or the counting time must be rather long.

By use of radiochemical sample preparation it is possible to measure ^{226}Ra, ^{228}Ra and ^{224}Ra concentrations, although detection limits are strongly dependent on the sample volume and the background of the LS spectrometer.

The application of Cerenkov counting for the determination of radium (mostly ^{226}Ra) has been reported several times [155]. The most significant problem is that this method is not specific for radium isotopes, for instance the spectra for ^{226}Ra (as measured from the decay progeny) and ^{40}K are similar, and the presence of interfering radionuclides in natural waters cannot be precluded. Therefore this method can be used only for the very rough estimation of radium levels at relatively high concentration. Without a pre-concentration step the method cannot be adequately used for measurement of environmental samples, containing a mixture of natural radionuclides, often including the prevailing ^{40}K radionuclide.

The extraction of ^{222}Rn into LS cocktail (traditionally toluene based or mineral oil) for determination of either ^{222}Rn directly, or ^{226}Ra indirectly, was introduced in early 1970s [57, 59]. It is still a very popular technique due to its simplicity. Two versions of this method are usually used for the measurement of radon concentration in water samples:

- The extraction of radon from larger volume of water (for instance 500 mL of water with 25 mL of water immiscible scintillator) in the extraction bulb, followed by the removal of water and transfer of 20 mL of the scintillator into LS vial to be measured.
- Sampling of water into a syringe (10 mL) followed by transfer of the sample into LS vial, under the scintillator (volume of the scintillator 10 mL).

When the first method is used, the detection limit can be lower, as the extraction is done from a larger volume of water, but there is the possibility of radon loss during sampling, which is often the most important source of uncertainty of produced results. It is much easier to avoid this problem when the second method is applied and detection limit is still good enough for radon-in-water measurements.

The second method can be applied not only for the determination of ^{222}Rn but also for the determination of ^{226}Ra in water samples [61, 62]. In this method radon is extracted from the water phase into an organic phase (containing the scintillation cocktail, leaving Ra and other interfering radionuclides in the water. Despite the fact that the aqueous phase is still in the vial, interaction of radionuclides remaining in the aqueous phase is negligible. An initial count should be made to establish the radon concentration in the sample. The sample is then retained for a minimum of 20 days for ingrowth of ^{222}Rn from ^{226}Ra in the sample, and ‘unsupported’ ^{222}Rn decays away. The detection limit of this method is mostly dependent on the counting time and, on the LS spectrometer used for the measurement. An alpha / beta separation LS spectrometer has been used by many authors to decrease the background in the alpha counting window as the calculation of results is determined from the alpha spectrum channel alone. This process both improves the detection limit as well as shortens the counting time. Publications relating to this methods are numerous [60–62, 96], and detection limits, where quoted, are typically within the range 0.05–0.20 Bq L^{-1}.

The latter values are related not only to the LS spectrometer and scintillation cocktail to water ratio, but are also dependent on the type of vials used for measurements. For instance, polyethylene vials used for different applications in LSS are not suitable for long term storage of samples, due to escape of radon and scintillator from the vial. Low diffusion polyethylene vials (Teflon coated - PTFE) are available and overcome these problems as the escape of radon from the sample during long storage is negligible. Low background glass vials can also be used for the method, although background is always higher than for the Teflon lined vials.

Another method of direct radium determination is a simple mixing of the water sample with a water-miscible cocktail. In this method, the cocktail forms a homogeneous mixture with the sample [61]. The interference of other radionuclides is, however, a limiting factor for the determination of radium isotopes. Typical tritium concentrations in water of at least 2–3 Bq L^{-1} directly interfere with measurement of ^{228}Ra. Additionally, determination of ^{226}Ra can be difficult due to presence of interfering radionuclides, as the energy resolution in LS spectrometry is poor for samples containing water. Successful application of this method requires the use of a low background, alpha / beta separation LSS. Several authors reported such applications, often expanding counting time to achieve good LLD value. Another possibility is to use only a part of resulting alpha spectrum, to reduce the background significantly and to achieve a lower detection limit for ^{226}Ra. In this method a narrow window corresponding to the alpha peak of ^{214}Po (7.7 MeV) is used [156]. With a combination of the optimal setting of alpha/beta discrimination levels, choice of vial and scintillation cocktail, in conjunction with extended counting times, a useful LLD value can be achieved.

The best results in radium determination can be achieved with application of sample pre-concentration and chemical preparation prior to counting. There are various methods of chemical preparation of aqueous samples for radium measurements, based mostly on co-precipitation of radium with barium carrier as sulphates, and subsequent steps of purification are applied to receive at the final step a precipitate of radium/barium sulphates or a solution containing soluble barium and radium salts [13, 65, 70, 86, 157, 158]. The precipitate is mixed with water and gelling liquid scintillator, or the resulting solution is mixed with water miscible cocktail. Such samples can be measured for radium determination, with or without alpha/beta separation features of the LS spectrometer [50]. Different methods are used to calculate the yield of the preparation technique as it is not possible to use a radium isotope as a spike, however ^{133}Ba may be used for this purpose [159]. The determination of the yield of the method can be done by gamma spectrometry of the sample prior to, or after measurement for radium. Another possibility is to measure ^{133}Ba in the LS spectrometer in the beta spectrum of the sample, but there are some interferences possible, especially with ^{228}Ra, which cannot be measured directly, or not at all when ^{133}Ba is added to the sample.

Co-precipitation with a barium carrier is the most popular technique of radium pre-concentration and purification for LSS applications as the sample volume can be reduced substantially, most of the interfering radionuclides are eliminated, in this way the selectivity of the method is improved substantially, the preparation is not dependent on the chemical matrix and can be applied for a wide variety of the aqueous samples, much better sensitivity can be reached due to relatively simple sample treatment, and a very simple method of yield calculation, based on gravimetric methods, can be applied.

An overview of the methods, which can be applied for the preparation of water and aqueous samples is provided in Section 2 of this review. Most of them have been, or can be adopted for the use in LS spectrometry rather easily, to produce final composition of the sample suitable for LSS.

The classical method of radium separation from aqueous solutions in form of barium/radium sulphate is based on the technique, developed by Goldin [86] for alpha spectrometry. The application of this method for LS spectrometry can be done in two different ways – by finally mixing the precipitate with gelling scintillator to obtain a semi- homogeneous sample, or by dissolving the precipitate again and mixing the aliquot of the solution with a water miscible scintillator. This method has a good selectivity for removal of other naturally occurring radionuclides, like uranium, thorium or polonium.

To establish the radiochemical yield, samples were often spiked with ^{133}Ba [159, 160]. Based on the measurement of the beta counts of ^{133}Ba activity recovered in the vial in the low energy window of the beta spectrum of the LSS, the radiochemical yield is calculated from the count rate ratio between sample and standard source measurement.

The advantage of using the LSS method is that no additional instrumentation or measurement is needed to evaluate the yield. However, the ^{133}Ba activity added to the sample must be adequately high (~ 5 Bq) to make sure that the counting rate of ^{133}Ba conversion electrons is high compared to the counting rate contribution from ^{228}Ra and ^{226}Ra-progeny in the low energy part of the β-spectrum.

Alternatively, an accurate value of radiochemical yield can also be obtained by gamma spectrometry using an HPGe gamma detector. Villa et al. [159] compared the two methods, and concluded that the radiochemical yields by gamma spectrometry are similar to that obtained by LSC (liquid scintillation counter).

Another method of calculation of the yield for radium is based on gravimetric methods. By knowing the amount of barium added as a carrier at the beginning of the chemical preparation, and weighing the precipitate after the preparation, but before mixing with the scintillator, it is possible to assess the recovery of barium, and hence radium.

3.4. Mass spectrometry

In mass spectrometry source preparation depends on the type of the ionization source of the mass spectrometer. In thermal ionization mass spectrometry, a small volume (down to 1 μl) of aqueous solution containing the analyte in nanogram to microgram amounts is deposited on a filament surface. In inductively coupled plasma mass spectrometry liquid samples after a chemical separation procedure are introduced into the plasma using an evaporation system. One of the advantages of ICP-MS over other techniques if the radiochemical separation is not regarded is the relatively simple source preparation method.

4. MEASUREMENT AND QUALITY ASSURANCE

4.1. Measurement, activity calculation and interpretation of results

4.1.1. Alpha spectrometry

The radium isotopes ^{226}Ra, ^{223}Ra and ^{224}Ra are alpha-particle emitters and can directly be measured by alpha spectrometry. The beta-emitting radium isotope ^{228}Ra can indirectly be measured by alpha spectrometry via its progeny ^{228}Th or ^{224}Ra. But because of the long half-life of ^{228}Th ($T_{1/2}$ = 1.9 a), the in-growth period ranges between 3 and 18 months (depending on the ^{228}Ra activity and required sensitivity), and hence for routine analysis of ^{228}Ra alpha spectrometry is not an adequate measurement method.

(a) Tracer for the determination of radium

According to the radium isotope which shall be analyzed, the nuclides ^{223}Ra, ^{224}Ra and ^{225}Ra are usually applied as tracers. These nuclides are suitable either for electrodeposition or for co-precipitation with barium sulphate and micro-filtration as the technique of source preparation. The use of ^{223}Ra or ^{224}Ra is only suitable for the determination of ^{226}Ra and ^{228}Ra, but their possible occurrence in the sample has to be considered by addition of a quantity large in comparison to the present activity. The determination of ^{223}Ra with ^{224}Ra and vice versa is not recommendable because the main alpha-peaks of both nuclides overlap with each other.

The isotope ^{225}Ra is an ideal tracer for the following reasons: [2, 83, 97, 127]

- It does not occur naturally.
- ^{225}Ra progeny ^{225}Ac, ^{221}Fr and ^{217}At are alpha-particle emitters and become detectable in the spectrum after a short in-growth period (1–4 days).
- The alpha-peak of ^{217}At at 7.067 MeV shows no interferences with the alpha-peaks of the radium isotopes ^{226}Ra, ^{224}Ra and ^{223}Ra or of their progeny and is the basis of the calculation of the chemical recovery of ^{225}Ra.
- In the decay chain from ^{225}Ra to ^{217}At no gaseous radon isotope is formed which could escape from the source causing an in-growth delay or a contamination of detector and chamber.
- Although ^{225}Ra has a short half-life ($T_{1/2}$ = 14.8 d), it is easily available from a solution of its parent ^{229}Th ($T_{1/2}$ = 7340 a).

For the sole determination of ^{226}Ra the quantity of the ^{225}Ra spike depends only on the statistical error required and the counting time disposable. For the additional determination of ^{223}Ra and ^{224}Ra the amount of the ^{225}Ra spike is limited because the in-growing ^{225}Ac slowly extends into the energy region of ^{223}Ra and ^{224}Ra. In the case of the determination of ^{226}Ra, the in-growth of its direct progeny ^{222}Rn has to be considered because of interferences with the energy region of ^{225}Ac, ^{223}Ra, and ^{224}Ra.

The use of the non-isotopic tracer ^{133}Ba entails some weak points. Although the elements are chemically very similar the small differences can bring about significant deviations in the recovery of radium and barium during the individual working steps [85, 98].

(b) Measuring conditions and spectrum appearance

At use of ^{225}Ra as yield tracer the source should be measured immediately after its preparation to obtain the maximal count rate for the radium nuclides ^{226}Ra, ^{223}Ra and ^{224}Ra. After a suitable period for in-growth of ^{225}Ac and ^{217}At, respectively, the source is counted a second time for an accurate calculation of the ^{225}Ra recovery [97, 124, 127].

Using ^{133}Ba as yield tracer, an immediate measurement after source preparation is only necessary if ^{223}Ra and ^{224}Ra have to be determined due to their short half-lives. As ^{133}Ba is no alpha-particle emitter, interferences between tracer and analyzed radionuclides are not created in the alpha spectrum.

The determination of ^{228}Ra from the same source as the alpha-particle emitting radium nuclides is possible via the beta-decay of its progeny ^{228}Ac measured immediately after the electrodeposition by counting the disk in a proportional counter [149]. Another possibility is to store the disk for about 20 days for the decay of the short living radium isotopes ^{223}Ra and ^{224}Ra and their fast developing and decaying β-emitting progeny, to heat the disk at 800°C to volatilize radon, lead and bismuth, and then to β-count ^{228}Ac which is in equilibrium with ^{228}Ra. [147].

Figure 5 shows three radium alpha spectra obtained from samples of groundwater. The resolution expressed by the FWHM values is 38 keV for the ^{226}Ra main. The alpha peaks of ^{226}Ra at 4.684 MeV (5.95%) and 4.871 MeV (94.04%) are well resolved. The overlapping of ^{225}Ac with the energy region of ^{223}Ra and ^{224}Ra and the extension of the growing ^{225}Ac peak into the ^{222}Rn peak are well visible. The three spectra are a good example for the time course of decay and formation of the different radionuclides. The only constant is the ^{226}Ra peak. At the measurement 20 days and 6 months after electrodeposition, theoretically, ^{222}Rn shall be almost in equilibrium with ^{226}Ra, but in the middle and lower spectrum it turns out to be not the case which suggests a loss of radon gas to a significant extent during storage. This fact is confirmed by the descendents ^{218}Po and ^{214}Po which are in equilibrium with ^{222}Rn, but not with ^{226}Ra. [2].

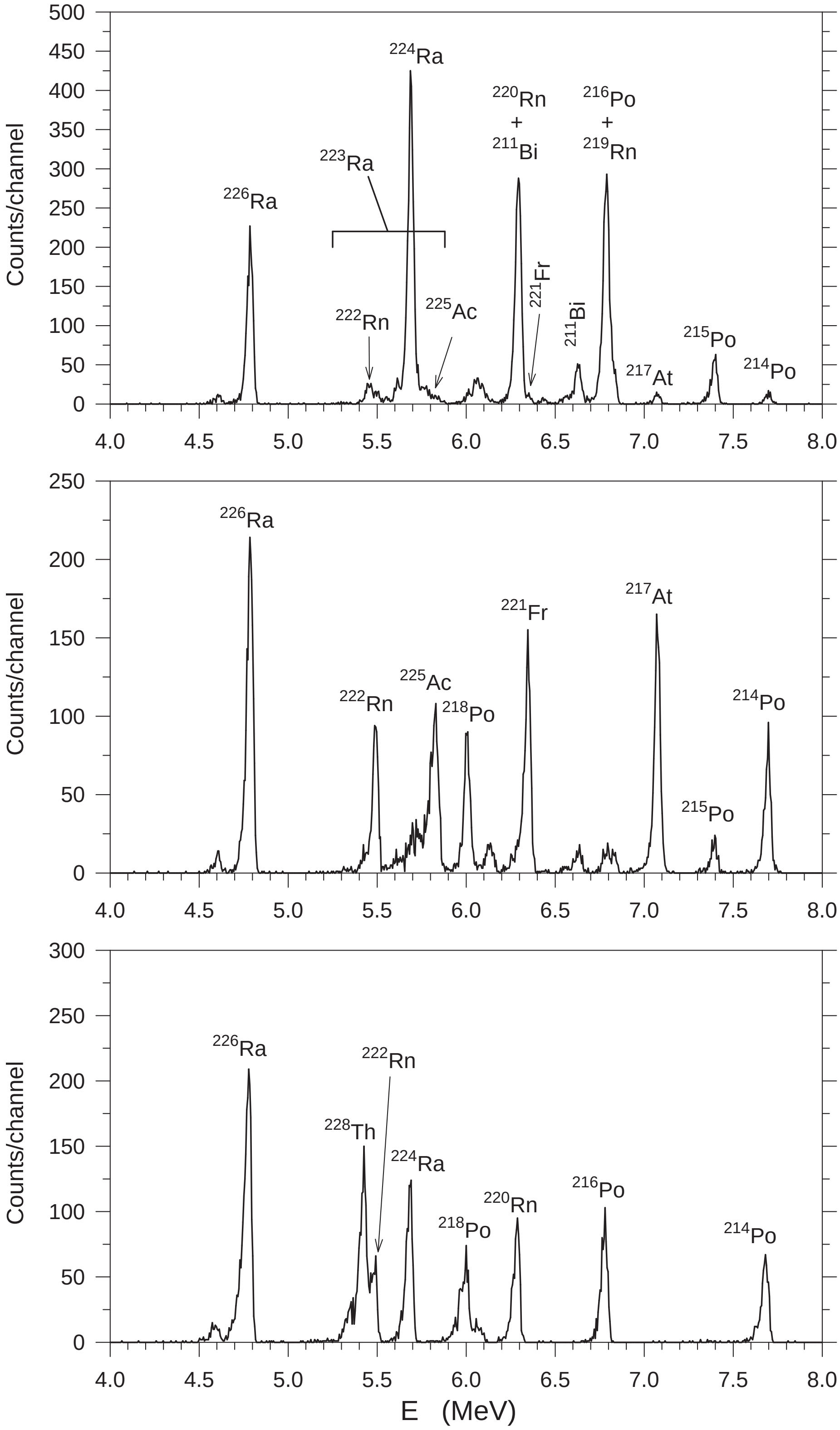

FIG. 5. Alpha spectra of radium in a groundwater sample using ^{225}Ra as yield tracer. Above: counted immediately after electrodeposition. Middle: recounted 20 days after electrodeposition. Below: recounted 6 months after electrodeposition [2].

Figure 6 depicts an alpha spectrum of a source prepared by co-precipitation of radium with barium sulphate [107].

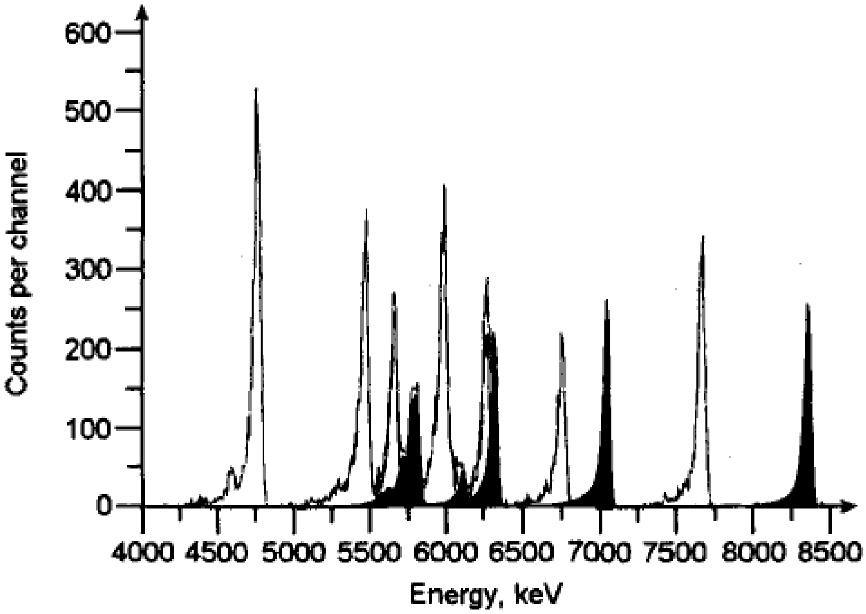

FIG. 6. Alpha spectrum of a real sample containing ^{226}Ra and ^{224}Ra and their ingrown descendents and a simulated spectrum of the ^{225}Ra tracer descendents (shadowed peaks, assuming the same peak shape); source preparation by barium sulphate co-precipitation; the average resolution is 62 keV FWHM for the real spectrum [107].

(c) Interfering radionuclides in the spectrum

Radionuclides other than radium can be present in the sample matrix and can disturb the alpha spectrometric determination of the radium nuclides when they are not separated completely. Interferences with the alpha energy of ^{226}Ra could be caused by e.g. ^{230}Th, ^{229}Th, ^{231}Pa, and ^{234}U. Interferences with the alpha energies of ^{223}Ra and ^{224}Ra can occur by $^{243+244}$Cm, ^{241}Am, ^{238}Pu, ^{228}Th, ^{227}Th, ^{225}Ac, ^{222}Rn, ^{218}Po, ^{213}Bi, and ^{210}Po, but the overlapping of the alpha peaks is only partially, thus, a mathematical correction is possible in the most cases. The determination of ^{228}Ra via its alpha-particle emitting progeny ^{228}Th can be interfered by the presence of ^{241}Am, ^{238}Pu, ^{222}Rn, or ^{210}Po. Hence, the spectrum evaluation is mostly done for the progeny ^{224}Ra.

However, because of the preceding chemical separations, the number of radionuclides possibly emerging at the measurement is rather limited, and such interferences are unusual. A more common difficulty arises from separation of the contributions to various peaks due to the complexity of the radium alpha spectrum (Figures 5 and 6). Commonly, the counts of a well-resolved peak are summed over a so-called region of interest (ROI) giving an accurate value for the area beneath the peak. For overlapping peaks or peak tailing into another peak, the spectrum analysis could be carried out by consulting a library or a user-defined search programme [2]. Alternatively, a mathematical code can be used for unfolding the peaks [28].

4.1.2. Gamma spectrometry

Modern gamma spectrometry systems are typically operated via computer software applications. The advantage of these systems is that the package provides for the system control (high voltage and amplifier settings and monitoring), multichannel analyzer energy and efficiency calibration, photopeak detection (including multiplet deconvolution), integration and identification, provision of activity concentration and uncertainty calculations.

Methods for the determination of radium isotopes in environmental solids by gamma spectrometry can be obtained by two means, the direct measurement of the principal photopeaks (186 keV in the case of ^{226}Ra), and indirect measurement using the gamma radiation emitting progeny.

The advantage of using the direct measurement method, particularly for ^{226}Ra, is that the sample can be prepared and measured immediately without the need for progeny ingrowth. The disadvantages of this method relate primarily in that the emission probability of this gamma photopeak is quite weak (3.28%), and furthermore by the presence of the interfering primary gamma emission of ^{235}U at 185.7 keV that has a higher photon emission probability of 57.24%. While ^{235}U generally presents at a much lower activity concentration than ^{226}Ra in environmental samples, it has an effective photon emission of ~ 2.6% at this energy (assuming a natural U isotopic ratio). The energy resolution of currently available HPGe spectrometers is generally considered insufficient to separate the two peaks (Figure 7). If no chemical separation is carried out initially, quantification of ^{226}Ra via the 186 keV gamma line must be conducted by attempting to quantify the contribution of the ^{235}U isotope to the doublet peak. This may be achieved using the ^{234}Th emissions (as a surrogate for ^{238}U, and then using the natural isotopic abundance ratio to calculate the ^{235}U activity concentration) or one of the low intensity emissions of ^{235}U, e.g. at 143.8 keV with a probability of 11.0%. Sample matrix effects, including self attenuation need to be considered when conducting these calculations [161–163]. Alternatively, sophisticated deconvolution algorithms [164] may be utilized to determine the respective contributions from each radionuclide. These interference issues may be resolved using one of the suggested radiochemical purification procedures detailed in earlier sections.

The indirect measurement method using progeny radionuclides is commonly applied for ^{224}Ra, ^{226}Ra and ^{228}Ra isotopes.

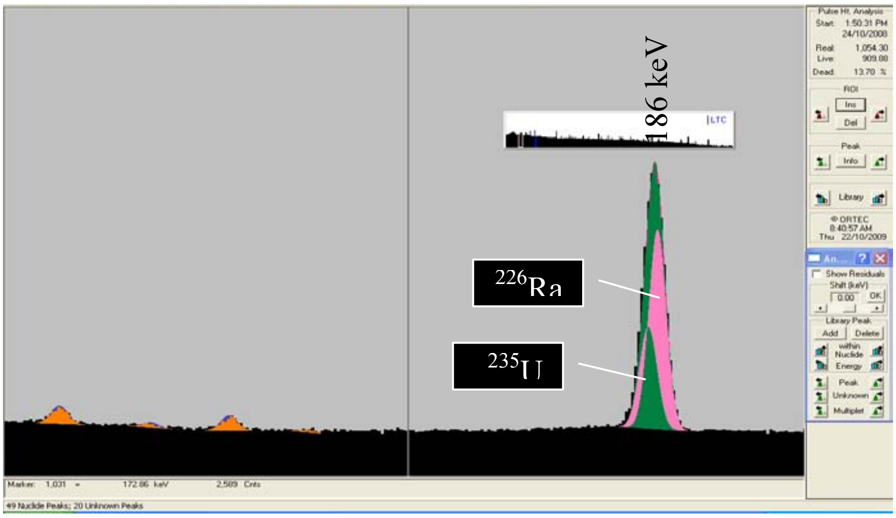

FIG. 7. Deconvolution of ^{235}U and ^{226}Ra photopeaks (EG&G GAMMA-X™ Detector, ~18 % relative efficiency).

The determination of ^{226}Ra in environmental solids by gamma spectrometry has long been based on the detection of emissions of the radon progeny (^{222}Rn) nuclides, i.e. ^{214}Pb and ^{214}Bi after an ingrowth period of at least 20 days, during which the sample has been hermetically sealed to ensure secular equilibrium between ^{226}Ra and its progeny [165–167]. ^{228}Ra is measured indirectly through its progeny, ^{228}Ac in equilibrium, generally by the 911 keV gamma line. When undertaking combined ^{226}Ra and ^{228}Ra measurements, the ingrowth period for ^{226}Ra adequately covers the ^{228}Ra progeny ingrowth as well (Figure 8) The determination of ^{224}Ra in environmental solids by gamma spectrometry has long been based on the detection of the gamma emissions of ^{220}Rn progeny, i.e. ^{212}Pb and ^{212}Bi, after an equilibrium period of ~ 80 hours. It is necessary to undertake the ^{224}Ra measurement not long after equilibrium has been achieved due to the isotope's short half-life of 3.7 days.

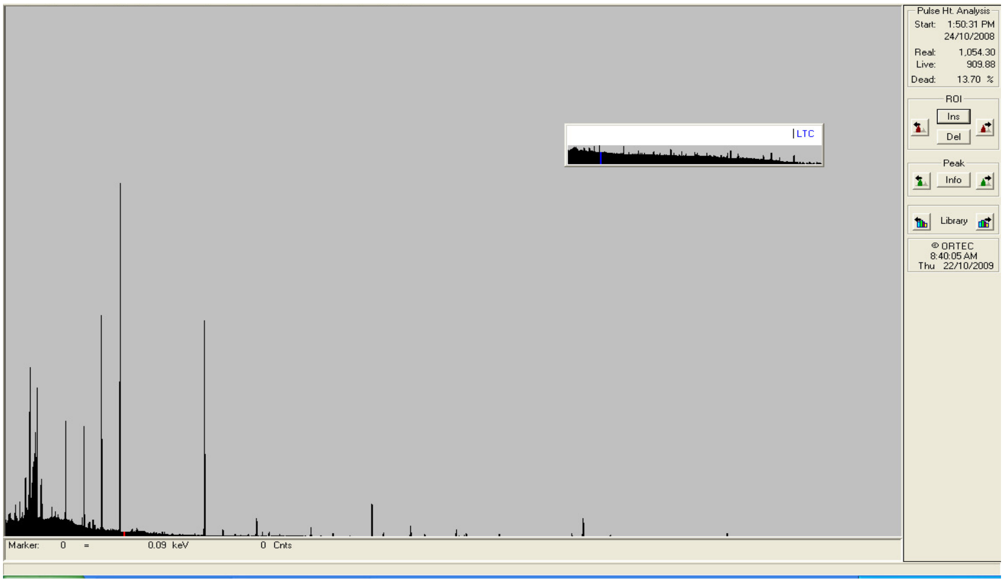
Pulse Ht. Analysis
Start: 1:50:31 PM 24/10/2008
Real: 1,054.30
Live: 909.88
Dead: 13.70 %
Marker: 0 = 0.09 keV 0 Cnts
© ORTEC 8:40:05 AM Thu 22/10/2009

FIG. 8. Typical gamma spectrum for sample containing ^{226}Ra in secular equilibrium with decay progeny (EG&G GAMMA-X™ Detector, ~18 % relative efficiency).

Other than photopeak resolution interference effects (which are common to most spectrometry techniques), the attainment and maintenance of secular equilibrium of progeny activity concentration in the sample for the indirect measurement method, and sample self-attenuation, applicable to both direct and indirect methods, may be considered as possible and significant interfering effects.

Radon isotopes, being gases, can permeate through barriers. Therefore, to minimize interfering effects associated with the loss of secular equilibrium between the radium parent and progeny radionuclides, it is important that the seal of the sample container used for gamma spectrometry is 'gas tight', and that the sample container itself is not permeable to radon. Gamma spectrometry intercomparison studies have shown that these requirements are important as inconsistencies in results occur due to failure to ensure equilibrium is reached and maintained during the measurement process [168].

There are a variety of container types that are suitable for solid samples, the specific types depending on the sample sizes and compositions. For small volume crystalline samples, such as co-precipitated radium (e.g. $Ba(Ra)SO_4$), radon emanation from the crystalline matrix is limited and therefore places less significance on the sample container specifications.

For larger-volume samples, such as soil or sediments containing radium isotopes, radon emanation, and sample container wall permeability, should be assessed and considered to avoid significant loss of radon [164–167]. This effect is more prominent for ^{222}Rn (for ^{226}Ra determinations) due to its longer half-life, and therefore higher probability in escaping the sample itself, and the sample container. As ^{220}Rn (for ^{224}Ra determinations) has a short half-life of around 56 seconds, emanation and permeation losses are negligible. For these larger volume samples, a moderately thick-walled plastic container with a tight-fitting cover, often taped around the seam or sealed with a non-permanent adhesive to minimize leakage, may be acceptable. Common sample containers (Marinelli beakers, jars, bottles and vials) are fabricated in a number of materials, such as polypropylene, high-density polyethylene, polystyrene and non-plastics including aluminium [169, 170]. Polypropylene/polyethylene containers are popular due to their availability and chemical resistance, but the literature suggests that these materials do not retain radon well compared to some others, and this should be considered in sample container material selection [171–176]. Rn diffusion of different plastics has been studied at some length [177–180] and the results provide a range of acceptable material types for sample containers. In addition to permeability issues, it is important to ensure that the amount of free-air volume above the sample in the closed container is minimized. This reduces the amount of radon that may effuse from the sample into the air space, thus changing the counting geometry and the associated counting efficiency that applies to the gamma-emitting radon progeny. Some authors have found that by mixing activated charcoal with the solid sample, the emanation of radon may be notably reduced [181–184].

Despite the above, few comprehensive, detailed studies of the radon retention characteristics of containers have been published. This topic is important for assurance of the reliability of the technique for ^{226}Ra determinations, and more research would be desirable.

Without sample concentration, the measurement of environmental samples generally relies on the use of large samples, primarily to increase sensitivity. Large sample volumes increase the path length that a photon has to travel before reaching the detector, and the chemical composition and density of the sample will effect attenuation, and therefore efficiency in measurement of the photon, this process being described as self-attenuation or self-absorption [185–189]. In order to obtain accurate quantitative data on the activity concentration of radioactive material in the sample it may be necessary to correct for self-attenuation. Self-attenuation effects are most significant for low energy photopeaks associated with the uranium and thorium primordial series (especially ^{210}Pb and ^{234}Th when considering ^{226}Ra series measurements). Various techniques have been developed to overcome the problem of sample self-attenuation caused by the density and / or chemical constituents of the material. These methods include semi-empirical methods, experimental determination of factors involving direct transmission and calibration methods [37, 190] and Monte Carlo based methods [191, 192].

4.1.3. Liquid scintillation spectrometry

The counting efficiency for radium isotopes is dependent of the sample type (type of scintillator, sample-scintillator ratio, etc.). Often alpha and high-energy beta events are considered to be counted with an efficiency close to 100% in LSS, but the efficiency must be evaluated for each particular batch of samples with use of suitable ^{226}Ra and ^{228}Ra standard sources and reference materials, using the same type of vial and same scintillation cocktail as used in the sample measurements. However, under differing measurement conditions the results could be affected by quenching and loss of energy resolution of alpha peaks. Particular attention needs to be given to the monitoring of quenching effects. Manjón et al. [193] reported that in their experiments EDTA was used to dissolve the Ba(Ra)SO_4 precipitate obtained from a spiked water sample with ^{226}Ra for efficiency calibration, and found that the total efficiency varied over the range of 55–69%. They considered that the low efficiency is due to the incomplete or non-dissolution of Ba(Ra)SO_4 with EDTA.

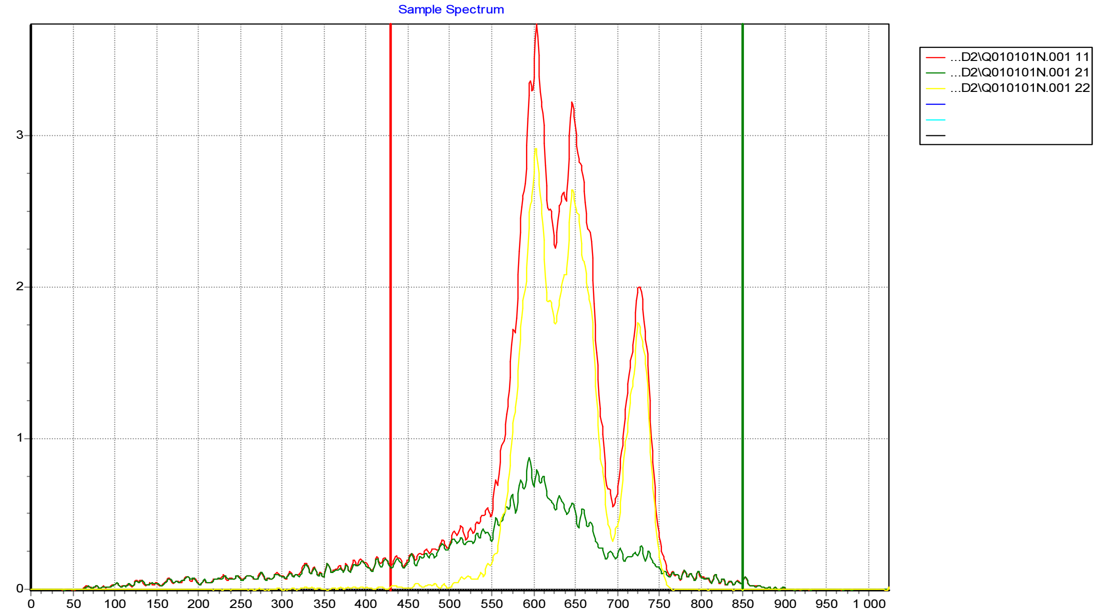

FIG. 9. Alpha/beta discrimination for the Ra-226 standard in Quantulus™– red spectrum (alpha+beta), yellow – alpha spectrum, green – beta spectrum.

The counting efficiency for ^{228}Ra is considerably lower with the efficiency being as low as 20–25%, especially for semi-homogeneous samples containing radium as a precipitate. Often samples for radium determination are prepared as a batch of several samples, together with a blank sample and radium standard samples, containing known activity of the respective radium isotopes. These samples may be used for the determination of the calibration factors (i.e. counting efficiency for the sample batch).

If the alpha/beta separation feature of the LS spectrometer is utilized for radium determination (Figure 9), misclassification (where misclassification relates to the effect where an alpha count may mistakenly identified as a beta event, and visa versa) must be considered in the method development and validation. A common procedure to calculate misclassification is to use measure pure alpha and beta emitters (^{241}Am for alphas, and ^{90}Sr or ^{40}K for betas) using incremental changes in separation parameters (e.g. pulse height, tail length, after burst etc.), after which a misclassification curve can be plotted and the instrumentation optimized for minimal crosstalk. Despite optimization of misclassification, a certain percentage of events (beta/alpha) are always misclassified. Additionally, the percentage of misclassified events can change due to changes of sample quenching. These issues typically affect more the determination of alpha emitters, i.e. ^{226}Ra, as ^{228}Ra, which is pure beta emitter. Under extreme situations it may be considered better to not use alpha/beta separation for samples with significant quenching effect.

Calculations of radium concentration in the sample are dependent on the method of measurement applied by the particular laboratory. For instance, Moreno et al [157] and Villa et al [159] applied two measurements for each sample: immediate measurement just after Ra separation, and delayed measurement 28 days after Ra separation (in secular equilibrium with decay products). In this case three different efficiencies, i.e. efficiency for alpha spectrum window ‘immediate’ (for first measurement), efficiency for alpha spectrum window ‘delayed’ (second measurement), and efficiency for the ^{214}Po window (second measurement), were used to calculate the ^{226}Ra activity concentration. Villa et al [159] concluded that in many cases the LSS method coupled with simple radiochemical procedure prevents the interference of contaminant alpha emitters in the measurement of ^{226}Ra. However, in some cases the presences of unknown alpha emitters that increase the counting rate in the total alpha window were observed. Being the case, it was proposed to use only the ^{214}Po window to determine ^{226}Ra.

Chau et al [54] and Hetman et al [194] reported an absolute method for determination of ^{226}Ra, ^{224}Ra and ^{228}Ra concentrations in water samples without using standards, which is based on the separation of alpha and beta intensities measured in the Ba(Ra)SO_4 precipitation by LSS in two time intervals (t_1=1 day and t_2=7 days). According to the authors, direct measurement of ^{228}Ra could not be achieved, and therefore the high-energy beta from ^{228}Ac, after attaining equilibrium with ^{228}Ra, was used for ^{228}Ra determination. It was assumed that the counting efficiency of the alphas is 100 %, and does not take into account misclassification corrections.

Methods for determination of ^{228}Ra (or ^{228}Ac) in environmental samples by LSS are less common as for ^{226}Ra. Improved background characteristic of modern LSS [195] allow determination of ^{228}Ra even in order of mBq. The method is very rapid and intended for surveillance of drinking water. Nevertheless, poor energy resolution of LSS results in extensive peak overlapping in the alpha and beta windows, thus making identification of interfering radionuclides (e.g. ^{224}Ra and ^{210}Pb) difficult (Figure 10).

Wallner and Steininger [196] report some data of ^{228}Ra concentration in drinking water measured by LSS. In their method Ra isotopes were co-precipitated with $BaSO_4$ or concentrated by filtration through an element specific filter, re-dissolve in EDTA solution, and measured by LSS after mixing with a cocktail. Although the declared LLD for ^{228}Ra was 4.5 mBq L^{-1}, “less than” values were given for 24 over 26 analyzed water samples. They explained that this was due to higher ^{210}Pb levels or rather long-lived chemo-luminescence raising the background in the ^{228}Ra region and so leading to higher LLD.

Several authors reported that although the LLD of LSS can meet the EPA regulation requirement of 37 mBq L^{-1} (1 pCi L^{-1}), it is not good enough to detect Ra isotopes with low concentration in many water samples, especially when interfering radionuclides are present in the water, such as ^{210}Pb, ^{210}Bi and ^{222}Rn etc [197, 198]. To some extent, the problems with resolution of traditional LSS have been improved with the PERALS™ spectrometer by incorporation of electronic pulse-shape discrimination, optimizing the detector design and associated electronics for alpha pulses, and use of an ultra-pure (and therefore minimizing quench effects) liquid-liquid extractive scintillator. Pulse shape discrimination reduces the backgrounds by rejecting beta and gamma pulses with a 99.95% efficiency, with energy resolution being substantially improved over typical LSS equipment. Users of PERALS (Photon-Electron Rejecting Alpha Liquid Scintillation) indicate that the resolution of 200–250 keV (FWHM) and background 0.01 cpm for PERALS can be achieved [64, 199, 200], however the system is limited to single sample presentation, and the need to use expensive reagents.

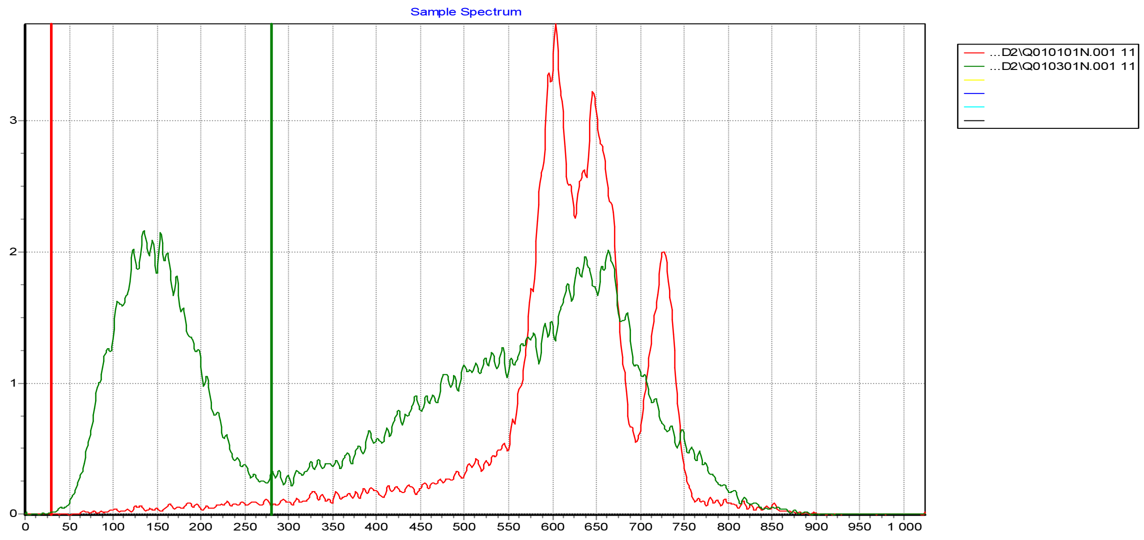

FIG. 10. Low energy window for measurement of ^{228}Ra beta emission (green spectrum), the influence of beta emission of ^{226}Ra decay products is clearly seen (red spectrum).

Reliable, simultaneous measurement of radium isotopes in water has been reported by Chalupnik and Lebecka [65], and Cook and Kleinschmidt [201] using chemical separation methods and low background, alpha/beta LS spectrometers.

Both methods require setting of two different energy windows and application of alpha/beta separation features of the spectrometer – low energy window for the direct measurement of beta emission of ^{228}Ra and high energy window for measurement of alpha and beta emission of ^{226}Ra [201] and its decay products as well as ^{228}Ac beta emission (partly as misclassified particles) [65].

Such methods enable simultaneous measurement of ^{226}Ra and ^{228}Ra in aqueous samples, but require significant validation and careful analysis of uncertainty propagation. For the Chalupnik and Lebecka [65] method, samples are placed in the LS spectrometer at least 28 days after chemical preparation (the whole batch, together with blank samples, standards of radium isotopes and reference sample). The counting time of a single sample must be at least 60 minutes. The obtained results are used for calculations of concentration of radium isotopes.

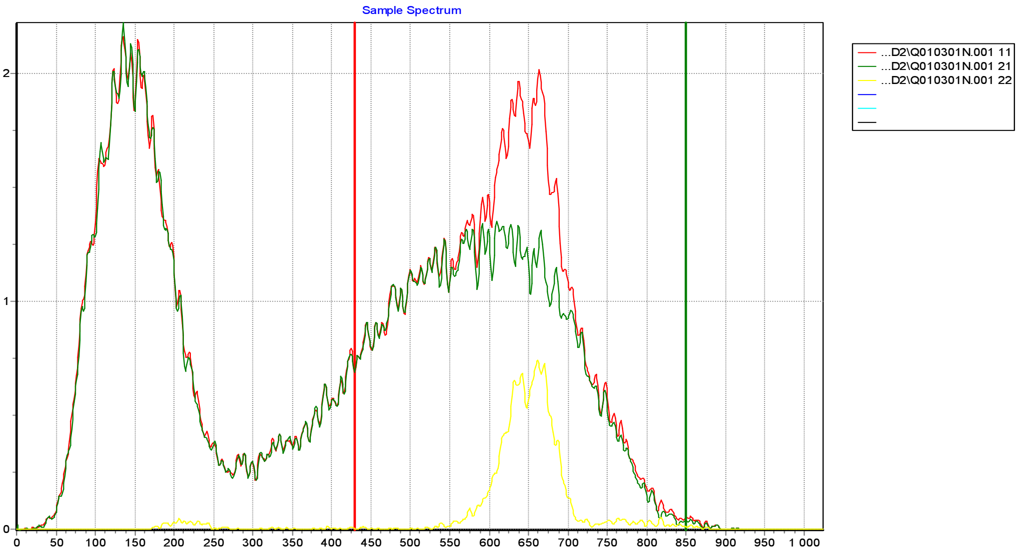

FIG. 11. Spectra of ^{228}Ra standard (total spectrum – red, beta – green, alpha – yellow), showing the misclassification of beta particles of ^{228}Ac and/or possible content of ^{228}Th, not removed completely during chemical preparation.

Chałupnik and Lebecka [65] published values of LLDs for radium nuclides – 4 mBq L^{-1} for ^{226}Ra and 30 mBq L^{-1} for ^{228}Ra, when the sample volume is 1 liter and the counting time is 60 minutes (Figure 11). In this method cross-calculations must be done to correct the influence of the beta spectrum of ^{226}Ra decay products in the low energy window of ^{228}Ra and to correct misclassified beta particles of ^{228}Ac in the upper energy window.

Another option for this method is to dissolve precipitate of barium sulphate in EDTA and mix the resulting solution with water miscible scintillator — for instance Perkin Elmer OptiPhase™ [201]. It is possible to measure samples very quickly after preparation, and optimum results are provided when measured within 5 days after preparation. In this approach both radium isotopes are determined directly, due to their emissions. The counting windows should be defined for ^{228}Ra in low energy region, similarly to the previous method, but for ^{226}Ra a very narrow window, corresponding to the 5.54 MeV alpha peak of ^{226}Ra should be applied (Figure 12). Due to the timing and setting of windows no cross calculations are necessary, although the efficiency in the upper window is much lower, affecting the detection limit for ^{226}Ra. In both methods quenching may affect the alpha/beta separation in the upper window, therefore resulting spectra must be inspected by experienced spectroscopists to avoid significant uncertainties of calculated values. Cook and Kleinschmidt [201] has indicated that LLD for radium nuclides of 10 mBq L^{-1} for ^{226}Ra, and 40 mBq L^{-1} for ^{228}Ra, when the sample volume is 0.5 liter and the counting time is 120 minutes, are achievable.

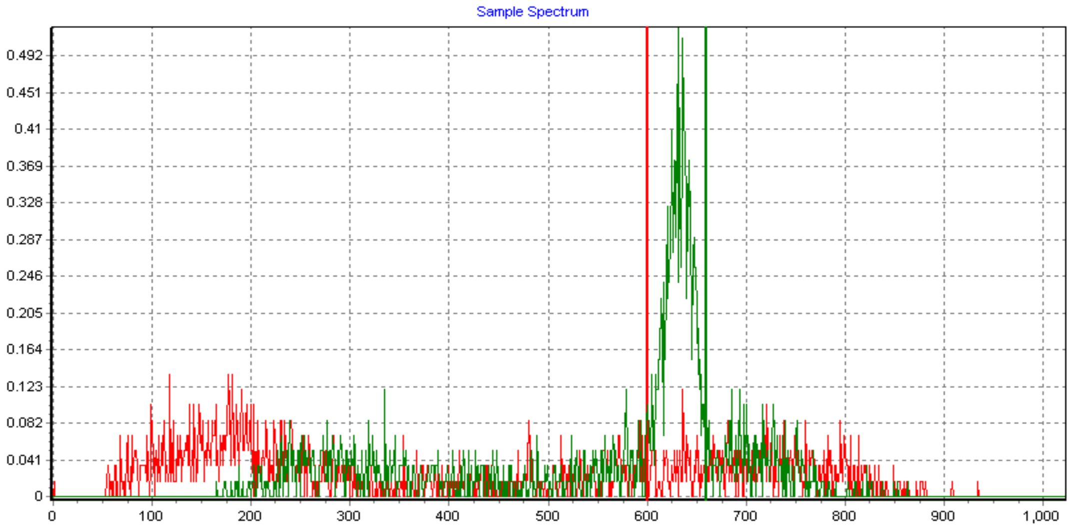

FIG. 12. Actual sample spectra of ^{226}Ra (alpha spectrum - green) and ^{228}Ra (beta spectrum - red) shortly after the chemical preparation using the method by Cook and Kleinschmidt 2009 [201].

4.1.4. Mass spectrometry

(a) Thermal ionization mass spectrometry (TIMS)

TIMS has been used for the determination of ^{226}Ra concentration and ^{228}Ra/^{226}Ra isotope ratio. In TIMS, a small volume of aqueous solution containing the analyte is deposited on a filament surface. The evaporated and ionized atoms are introduced mostly into a single magnetic sector field mass spectrometer that may be equipped with a multi-detector system. Using up-to-date TIMS facilities high internal precisions (0.001% or better on isotope ratios) can be achieved if isotope fractionation and isobaric interferences are taken into correction. TIMS is one of the most sensitive and most accurate mass spectrometric techniques. The major disadvantage is the necessity to perform complicated radiochemical separation procedure to concentrate the Ra in the small source volume, to separate the matrix components, to remove the possible interferences and to prepare the source on the filament.

TIMS is a sensitive method for the determination of ^{226}Ra, a detection limit of 40 µBq was reported by Cohen and O'Nions [99], this being better than the sensitivity of alpha spectrometry. The detection limit of 12 mBq for ^{228}Ra is comparable to that of beta counting. Cohen and O'Nions [99] proposed a procedure based on the co-precipitation of $Sr(Ra)SO_4$, followed by its conversion to the acid-soluble carbonate. Ra is separated from Mg, Ca and Sr by repeated cation exchange chromatography using 3 M HCl eluent and from Ba using 0.01M ammonium EDTA (pH 8.94) eluent. Ra recoveries were better than 98%. They obtained precise results for the ^{226}Ra content of seawater analyzing only 35 mL of sample. The drawback of this method is the interference from Ba (0.5% of the Ba was found in the Ra source), which tend to reduce the ionization of Ra and has to be completely separated.

An improved method for complete separation of Ra from seawater (200 mL) was developed more than ten years later by Ghaleb et al. [109]. Ra was co-precipitated with MnO_2 and purified either by cation exchange or Sr resin. Using the EC method Ba was well separated from Ra. The method was also applied for the determination of ^{226}Ra in coral samples of about 1 g. Chemical yields were high (> 80%) and the accuracy of the ^{226}Ra determination was also high (0.55%) meeting the requirements of ^{226}Ra dating of Holocene carbonates.

The precise and accurate determination of $^{228}Ra/^{226}Ra$ ratio in silicate rock samples (0.5 g) was performed by TIMS after radiochemical separation of Ra [202, 203] The Ra was pre-concentrated on one or two cation exchange resin columns while Mg, Ca and most of the lanthanides were removed. Impurities were removed by passing the through a tandem column containing Sr resin and TRU resin that retained Ba, the rest of alkaline earths and lanthanides. The final purification was performed with an additional Sr resin and a CG71C column removing the rest of Ba and organic materials, respectively. Ra was loaded on a tungsten filament and the total evaporation method was employed at a temperature above 1200°C to avoid Ra mass fractionation in the TIMS. The reproducibility of the method (≤ 0.6%) was better than that of conventional TIMS procedures.

(b) Inductively coupled plasma mass spectrometry (ICP-MS*)*

ICP-MS is the most frequently used mass spectrometric technique for the determination of ^{226}Ra concentration and $^{228}Ra/^{226}Ra$ isotope ratio.

In ICP-MS, the sample components are decomposed into their atomic constituents followed by their ionization in an argon plasma at a temperature of about 6000–8000 K. The positively charged ions are extracted from the inductively coupled plasma (at atmospheric pressure) into a high vacuum of the mass spectrometer where they are separated by mass filters of either quadrupole type time of flight or combination of magnetic and electrostatic sector, and finally measured by an ion detector. In low-resolution mode, the sensitivity and the precision of double-focusing sector field ICP-MS is generally higher than those of conventional quadrupole ICP-MS instruments. The detection limit of ICP-MS varies from 10^{-15} g to 10^{-8} g, and the precision varies between 0.1–0.5%. Better precision of isotope ratio measurements can be achieved by multi-ion collector devices in sector field ICP-MS [111, 204, 205].

Besides the high sensitivity, one of the major advantages of ICP-MS technique is the simple introduction of the liquid sample into the ion source at atmospheric pressure that allows shorter analysis time and higher through-put. The quantification procedure using aqueous standard solutions is relatively simple in ICP-MS compared to TIMS. Some of the polyatomic species may be resolved from the analyte using double-focusing sector field ICP-MS at a high mass resolution, but in this case the sensitivity is reduced. The application of a collision/reaction cell (CC) can significantly suppress some of the interfering isobaric ions.

In ICP-MS, all the possible interferences mentioned above can exist, they have to be suppressed both by radiochemical separations and appropriate instrumental techniques. Quadrupole ICP-MS equipped with an ultrasonic nebulizer containing a desolvation unit was used for the determination of ^{226}Ra in thermal water samples by Joannon and Pin [120] The conventional one-step cation exchange chromatography was compared with a two-step procedure using cation exchange columns, a two-step procedure using cation exchange and Sr resin columns and the one step Ra disk procedure. The best chemical purity was achieved when Sr resin was applied. Separation with the Ra disk also provided sufficiently good source for ICP-MS measurement. The instrumental detection limit was significantly reduced by decreasing the pressure in the expansion chamber (below 1 mbar). A detection limit of 2 fg g^{-1} for ^{226}Ra was reported.

^{226}Ra was also determined in environmental samples by quadrupole ICP-MS equipped with a collision cell [136, 206]. A combination of UTEVA and Sr cartridges was used to separate U, Sr, Pb, and Ba from Ra. Subsequently, the Ra fraction was purified with a Ln resin cartridge that removed Nd, La and Ce interferences. Use of the Aridus desolvator helped eliminate further polyatomic interferences. An absolute detection limit of 0.02 fg (0.75 mBq) ^{226}Ra was reported when 25 mL of water or 100 mg solid sample was treated.

Two sample introduction systems, i.e. an Apex-Q high sensitivity system and a concentric nebulizer were compared by Lariviere et al. [136] using a sector-field ICP-MS. A 12-fold improvement in instrumental sensitivity was reported when the Apex-Q system was used (detection limit was 1.5 pg L^{-1} or 55 mBq L^{-1}). Two separation procedures, the conventional cation exchange chromatography and the combination of that with extraction chromatography using Sr resin were compared. The method detection limit in the latter case was 0.19 pg L^{-1} (7 mBq L^{-1}) and about 20 samples could be processed in 8 hours.

Multicollector ICP-MS techniques were used by Foster et al. [111] and Pietruszka et al. [117] for the determination of ^{226}Ra in sea water and volcanic rocks, respectively. The use of multiple ion counting provides a fast and precise measurement for ^{226}Ra and ^{228}Ra suppressing mass discrimination of the instrument. The radiochemical separation procedure of Foster et al. [111] consists of the preconcentration of Ra by coprecipitation with $CaCO_3$, removal of U and Th by anion exchange, removal of Ca and Sr by cation exchange chromatography followed by separation of Ra from Ba using Sr resin. By this method femtogram quantities of ^{226}Ra were measured using 100 mL of sea water samples. In the procedure of Pietruszka et al. [117], TRU resin, cation exchange resin, Sr resin, Eichrom pre-filter material were used to separate Th and U; Ca, Sr and lanthanides; Ba; and organic residue, respectively. The method was successfully used for the simultaneous determination of ^{226}Ra-^{230}Th-^{238}U disequilibria in volcanic rocks analyzing about 0.5 g sample.

^{226}Ra was determined in groundwater and soil samples by high resolution ICP-MS by Kim et al. [104] Ra was concentrated from water samples by a batch technique using cation exchange resin, followed by cation exchange chromatography. In case of soil samples Ra was co-precipitated with $PbSO_4$ and interfering elements were separated by cation exchange chromatography. The detection limits for ^{226}Ra in groundwater and soil were 0.19 mBq L^{-1} and 0.75 mBq kg^{-1} using 1.4 L water and 1 g of soil for the analysis.

ICP-MS was also used for ^{226}Ra determination in ground water and sea water samples by Zoriy et al. [75] and Varga [207].

(c) Accelerator mass spectrometry (AMS)

In AMS facilities two mass spectrometers (called 'injector' and 'analyzer') are linked with a tandem accelerator. The analyte in the form of a solid target is injected to the system as a negative ion by ion sputtering (e.g. using a Cs^+ primary ion source). The negative ions are accelerated and mass analyzed by a magnet. Then, the negative ions are accelerated to the positive high-voltage terminal of a tandem accelerator and are converted to multiply charged positive ions that pass through a magnetic analyzer, where the ions of interest are directed to a detector.

In AMS many of the interferences are suppressed or eliminated during the combined ionization, acceleration and mass analysis steps. By AMS isotopic ratios below 10^{-10} can be measured. AMS is one of the most sensitive measurement methods for those elements that form negative ions, but it is a very expensive technique, hence there are only less than 100 AMS facilities worldwide.

In AMS, the separated Ra is adsorbed in a carbon powder matrix, and RaC_2^- is the injected negative ion. The mass separated Ra ions are measured by multi-anode gas ionization detector. A detection limit of 10^7 atoms or 0.1 mBq for ^{226}Ra and 40 mBq for ^{228}Ra has been reported by Tims et al. [208] using test solutions. This sensitivity is comparable to the alpha spectrometric method for ^{226}Ra, and LSS and beta counting methods for ^{228}Ra. The major advantage of AMS for radium measurements is the ability to measure both isotopes within a short time.

Comparing mass spectrometric and radiometric methods for the determination of ^{226}Ra and ^{228}Ra the following conclusions can be drawn:

- Mass spectrometric methods are sensitive for ^{226}Ra analysis, their sensitivity is comparable to those of LSS and alpha spectrometry.
- Radiochemical pre-concentration and separation procedures are unavoidable, requirements for purity are higher than in case of radiometric methods.
- Process times are typically shorter due to the small sample sizes and much shorter analytical times.
- Sample throughput is higher.
- Mass spectrometric methods are more expensive.
- Radiometric methods are the most sensitive methods for the determination of ^{228}Ra.

4.2. Detection limits

The limit of detection (L_d) must be determined to evaluate the performance of the whole method for analysing a given radionuclide, taking into account following parameters - the detector background and efficiency, the counting time (of standards, blanks and sample), the chemical yield or recovery, the analyzed aliquot of the sample (mass or volume). In the past the most common approach was due to Currie publication [209], which defined two values: the critical level or decision threshold, L_c, as the level of the net signal below which the gross signal has no difference from the blank sample (no nuclide in the sample). The limit of detection, L_d, can be defined as the level of the net signal, showing that a particular nuclide is definitely present in the sample, additionally, the limit of quantification, Lq was also derived). The same values are defined in the ISO standard 11929-7, but the mathematical assessment regarding ionizing radiation measurements utilizes the Bayesian statistics, which comprises the calculation with conditional probabilities [210].

From the ISO [210] the decision threshold should be calculated with application of following formula (see Eq. (1)):

$$L_c = \frac{1}{w} \cdot k \cdot \sqrt{\frac{R_0}{t_{M,S}} + \frac{R_0}{t_{M,0}}} \quad (\text{Bq L}^{-1} \text{ or Bq kg}^{-1}) \tag{1}$$

While the detection limit can be estimated as (Eq. (2)):

$$L_d = \frac{2 \cdot L_c + \frac{1}{t_{M,S}} k^2 \cdot w}{1 - k^2 \cdot s^2(w)} \quad (\text{Bq L}^{-1} \text{ or Bq kg}^{-1}) \tag{2}$$

where,

R_0 is the background count rate (s^{-1}), k is the coverage factor, $t_{M,S}$ is the counting time of the sample (s), and $t_{M,0}$ is the counting time of the background (s). w is determined using the fomulae (Eq. (3))

$$w = \frac{1}{q_S \cdot \varepsilon \cdot \eta} \tag{3}$$

where, q_S is the sample quantity (mass m_S (kg) or volume V_S (l)), ε is the counting efficiency, η is the chemical yield or recovery of the radionuclide to be analyzed, and $s(w)$is the uncertainty of the factor w.

4.3. Quantification of uncertainty

Quantification of uncertainty is a complex topic which cannot be comprehensively covered in this publication. In the following, some major publications relevant for radium determinations are briefly discussed.

In 1993 the International Standards Organization (ISO) pulished a concept of measurement uncertainty in collaboration with BIPM, IEC, IFCC, IUPAC and OIML, which formally established general rules for evaluating and expressing uncertainty in measurement across a broad spectrum of measurement [211]. The EURACHEM guide [212] has been prepared in the light of practical experience of uncertainty estimation in chemistry laboratories and the even greater awareness of the need to introduce formal quality assurance procedures by laboratories. The IAEA [213] published a technical report where the methods of quantifying uncertainties in several nuclear analytical measurements are introduced. Kanisch [214] introduced the way of quantifying of uncertainty in analysis of environmental samples by alpha-spectrometry. Holmes [215] reported a spreadsheet approach for alpha-spectrometric analysis of environmental samples. Spasova et al. [216] reported uncertainty components in the measurement of ^{226}Ra in water by alpha-spectrometry. Chalupnik and Mielnikow [53] reported uncertainty budget in radium measurements by LSS. VIAN [217] introduced the approach to quantification of uncertainty in the measurement of uranium concentration and its isotopic ratio by mass spectrometry.

4.4. Quality assurance

Quality assurance is one of the most important requirements for laboratories undertaking radioanalytical techniques. It is especially important for research laboratories, dealing with environmental and occupational monitoring, because there is an increasing demand for assessment of data quality in these applications. The data from these measurements are used not only for assessment of effective doses (health effects) but also for supervising and control of radiation hazards. The precision and accuracy of the data must be assured to ensure that decisions concerning environmental or occupational impact are based on data of known reliability. Each laboratory providing environmental radiation measurements should have an internal quality assurance system in operation to ensure that instrumentation is calibrated properly and applied analytical procedures are being carried out consistently. Such a program also includes the validation of applied methods, continuous monitoring of instrumentation, frequent analysis of replicate samples to check precision and regular measurements of samples with known activity, and participation in intercomparison and proficiency exercises.

Validation of the method can be defined as a way to prove, that the particular technique can be applied as the analytical method for a certain type of samples, giving reliable and accurate results of analysis. The main goal of any validation of an analytical method is to prove that the method is adequate for measurements of radium content in defined sample types, to calculate detection limit(s) and to compare them with requirements of the legal regulations, and to prepare the uncertainty budget for the method and apply it for the calculations of uncertainties of obtained results. ISO 11929-7 [210] provides a summary of the necessary components of the validation process.

5. CONCLUSIONS

A review of analytical methodologies for the determination of radium isotopes in environmental samples has been conducted. Alpha and gamma spectrometry, liquid scintillation spectrometry and mass spectrometry techniques have been included in the review to accommodate the need to provide a range of options to the reader in selecting a suitable technique to meet their analysis needs. The methods selected for the review, and associated sample preparation, measurement and interpretation, cover a range of applications and sample media that could be expected when undertaking environmental analysis.

While it is acknowledged that the range of matrices and potential activity concentration ranges can be exhaustive, the selected methods were chosen on the basis that they can be directly applied, or adapted to suit specific or non-routine applications. An emphasis was placed on reviewing techniques that allow for the rapid and simultaneous measurement of several important radium isotopes (gamma spectrometry, liquid scintillation spectrometry and mass spectrometry), but still describing those more suitable for single isotope analysis at very low detection limits (alpha spectrometry).

Table 1 provides a comparison of the techniques under described measurement conditions as adapted from Hou [74].

TABLE 1. COMPARISON OF THE RADIOMETRIC AND MASS SPECTROMETRIC METHODS FOR THE DETERMINATION OF ^{226}Ra AND ^{228}Ra BASED ON METHOD SENSITIVITY AND ANALYSIS TIME (ADAPTED FROM HOU 2007 [74], AND COOK AND KLEINSCHMIDT 2009 [201])

Sample type	Detection method	Detection limit (mBq)	Sample preparation time	Delay time	Counting time (h)
^{226}Ra					
Environmental samples[74]	γ-spectrometry	0.1-1	no	no	5
Water[74]	γ-spectrometry	80	no	no	40
Environmental samples [74]	LSC	0.3-1.4	2 h	30 days	6
Water (simultaneous) [201]	LSS	10	2 h	no	2
Environmental samples [74]	Alpha spectrometry	0.2 -0.5	2-4 days	no	48
Environmental samples [74]	TIMS	0.037	4-5 h	no	0.5
Water [74]	ICP-MS	0.1-0.5	2-4 h	no	0.2
Water [74]	ICP-MS flow injection separation	0.34	0.5 h	no	0.4
Water [74]	AMS	0.1	3-5 h	no	0.5
^{228}Ra					
Environmental samples [74]	α-spectrometry	0.2	2-4 days	6-12 months	48-72
Water [74]	LSC	25	1-2 days	no	1
Water (simultaneous) [201]	LSS	40	2 h	no	2
Water [74]	GM counter	15	4-8 h	no	2
Water [74]	Gamma spectrometry	100	no	no	40
Environmental samples [74]	TIMS	12	4-5 h	no	0.5
Water [74]	AMS	40	3-5 h	no	0.5

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ABBREVIATIONS

AMS:	accelerator mass spectrometry
BIPM:	bureau international des poids et measures
CyDTA:	1,2-cyclohexylenedinitrilotetraacetic acid
DGA:	N,N,N',N'-tetra-n-octyldiglycolamide
DHC:	diammonium hydrogen citrate
DTPA:	diethylenetriaminepentaacetic acid
EC:	extraction chromatography
EDTA:	ethylenediaminetetraacetic acid
EU:	european union
FWHM:	full width half maximum
HEDPA:	hydroxyethane-1, 1-diphosphonic acid
HPGe:	high purity Germanium
ICP-MS:	inductively coupled plasma mass spectrometry
IEC:	international electrotechnical commission
IFCC:	international federation of clinical chemistry and laboratory medicine
ISO:	international standards organization
IUPAC:	the international union of pure and applied chemistry
LLD:	limit of detection
LNHB:	laboratoire national henri becquerel
LSC:	liquid scintillation counter
LSS:	liquid scintillation spectrometry
MCA:	multichannel analyzer
NORM:	naturally occurring radioactive material
OIML:	international organization of legal metrology
PERALS:	photon-electron rejecting alpha liquid scintillation
PTFE:	polytetrafluoroethylene
ROI:	region of interest
TIMS:	thermal inonization mass spectrometry
TOPO:	trioctyl phosphineoxide

CONTRIBUTORS TO DRAFTING AND REVIEW

Chalupnik, S.	Central Mining Institute, Katowice, Poland
Hampe, D.	Verein für Kernverfahrenstechnik und Analytik Rossendorf e.V., Dresden, Germany
Kim, C. K.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Kleinschmidt, R.	Queensland Health, Brisbane, Australia.
Martin, P.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Sansone, U.	IAEA Terrestrial Environment Laboratory, Seibersdorf, Austria
Vajda, N.	RadAnal Ltd., Budapest, Hungary

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