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Liquid Scintillation Counting for Determination of Radionuclides in Environmental and Nuclear Application

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Abstract

Liquid scintillation counting (LSC) is a major technique not only for measurement of pure beta emitting radionuclides, but also radionuclides decay by electron capture and alpha emission. Although it is a conventional radiometric technique, but still a competitive techniques for the measurement of many radionuclides. This paper summaries the major development of this measurement technique in instrumentation, methodology and applications in the past decades. The progresses in the instrumentation and methodology mainly focus on the commercialization of triple-to-double coincidence ratio based LSC techniques and its application in the determination of different types of radionuclides. An overall review and discussion on the LSC based analytical methods for the determination of major radionuclides in environmental researches, decommissioning of nuclear faculties and nuclear application are presented, in both measurement techniques and sample preparation using radiochemical separation. Meanwhile the problems and challenges in the development and application of the LSC are also discussed.

Keywords

Liquid scintillation counting, triple-to-double coincidence ratio, Cerenkov counting, alpha-beta discrimination, characterization of decommissioning samples, measurement of radionuclides

Introduction

Liquid scintillation counting (LSC) is a conventional radiometric method for measurement of beta emitting radionuclides including those decay by electron capture. With the application of alpha-beta discrimination using pulse shape analyzer (PSA), alpha emitting radionuclides can be also measured by LSC in the presence of beta emitting radionuclides. The major advantages of LSC are high counting efficiency (up to 100%), relative simple procedure for target preparation, and the feature to obtain beta spectrum of the samples. This measurement technique is still a major radiometric method in the determination of beta emitting radionuclides, especially those emitting low energy beta particles and decaying by electron capture, and still a competitive method compared to mass spectrometry for the short-lived radionuclides ($t½ < 100$ years).

Although the LSC techniques has been developed and applied for more than 60 years since its first application in the 1950’s and was considered as a mature measurement methods, further development in the methodology and new applications continue in the past decades. A series of international conferences dedicated to this technique have been organized for 23 editions since 1957, and the last conference (LSC 2017) was organized in 2017 in Copenhagen (http://lsc2017.nutech.dtu.dk). In the instrumentation and methodology aspects, the major progresses in the past decades are the commercialization of triple-to-double coincidence ratio (TDCR) based instrument, which can implement so-called absolute measurement without the quench curve or standard addition for efficiency calibration [1-4]. The determination of radionuclides using plastic scintillation resin and conventional LSC instrument has being proposed and shown a promising application, especially for the rapid analysis, which can avoid the utilization of the organic scintillator, therefore reduce the organic radioactive waste [5-8]. In the past years, an increased application of LSC occurred in the measurement of radionuclides for decommissioning of nuclear facilities, such as ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{93}Zr, ^{99}Tc and ^{129}I [9-16]. The LSC has also shown a competitive application in the rapid analysis of radionuclides for emergency preparedness and homeland security purposes due to its relative short measurement time and simple target preparation [17-20]. In the studies of environmental process using radionuclides, which are naturally occurred and released from human nuclear activities, LSC is also a major technique, especially in the measurement of ^{14}C, ^{3}H, ^{234}Th and ^{210}Pb/^{210}Bi/^{210}Po [21-26]. LSC is still a common used measurement method in the routine monitoring work in the nuclear facilities and medical researches. Besides the anthropogenic radionuclides, the LSC is a key measurement technique for the measurement of natural occurred radionuclides, such as ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{222}Rn [27-28] due to its high availability in radioanalytical laboratory and simple sample preparation. The LSC is also widely used for the measurement of gross alpha and gross beta in water samples for screen purpose due to its simple sample preparation.

This paper aims present the major progresses in the LSC methodology and new applications of LSC in the determination of radionuclides in different fields, the basic principles and main features of the LSC can be find in many books and papers [29-32].

Progress on the instrumentation and methodology of LSC

The major progress on the instrumentation of LSC in the past decades is the commercialization of triple-to-double coincidence ratio (TDCR) LSC technique, which makes this technique become a routine method for measurement of beta emitting radionuclides.

TDCR liquid scintillation counting

The TDCR method is considered as an absolute measurement technique of LSC for the measurement of the activity of pure β-emitting and pure electron capture (EC) nuclides. In the liquid scintillation analyzer (LSA) based on TDCR technique, three photomultiplier tubes (PMTs) and two different coincident outputs are equipped (Fig. 1). The integration of theoretical calculation of counting efficiency (TDCR value) is based on a physical and statistical model of the distribution of scintillation photons and their detection probability by the LSA. When a relationship between TDCR values and the real counting efficiency obtained by measurement of a standard solution with different quench level is established, the radioactivity of the target radionuclides can be obtained without the quench curve or standard addition. The detailed principle of the TDCR method, the configuration of the TDCR detector system, and the TDCR efficiency calculation technique have been reported in many literatures [30-32.

In TDCR based LSC, both triple and double coincidences are measured to obtain the TDCR value for efficiency calculation. Triple coincidences are more sensitive to quench compared to double coincidences, a correlation between the quench level (or counting efficiency) and the measured TDCR value can be established for quench correction. Unlike external standard methods, TDCR is a universal method applicable for both chemical and color quenching, for aqueous and organic samples and for different cocktails and range of isotopes. In TDCR based LSA, an external standard for monitoring quench level is not needed. The TDCR efficiency calculation technique enables the determination of pure beta-emitting and pure electron capture nuclides in samples of various states of quench. Alternatively, quench correction can also be made with a curve fit option. Using a set of quench standard samples for the analyte nuclide, a standard quench curve of counting efficiency vs. the TDCR value is first established, and the counting efficiency of an unknown sample can then be determined from the measured TDCR value of the sample. Once established, the TDCR quench curves are quite generic and do not need to be redone. For pure beta emitting radionuclides, the TDCR values usually approximate the overall counting efficiencies. In the Hidex 300SL LSA, a standard quench curve can be stored with the curve fit option, which can be automatically employed to determine the real counting efficiency based on the TDCR value of the sample. The TDCR efficiency calculation technique has been approved to be suitable for routine analysis of beta-emitting nuclides in samples with different quench levels [30-32].

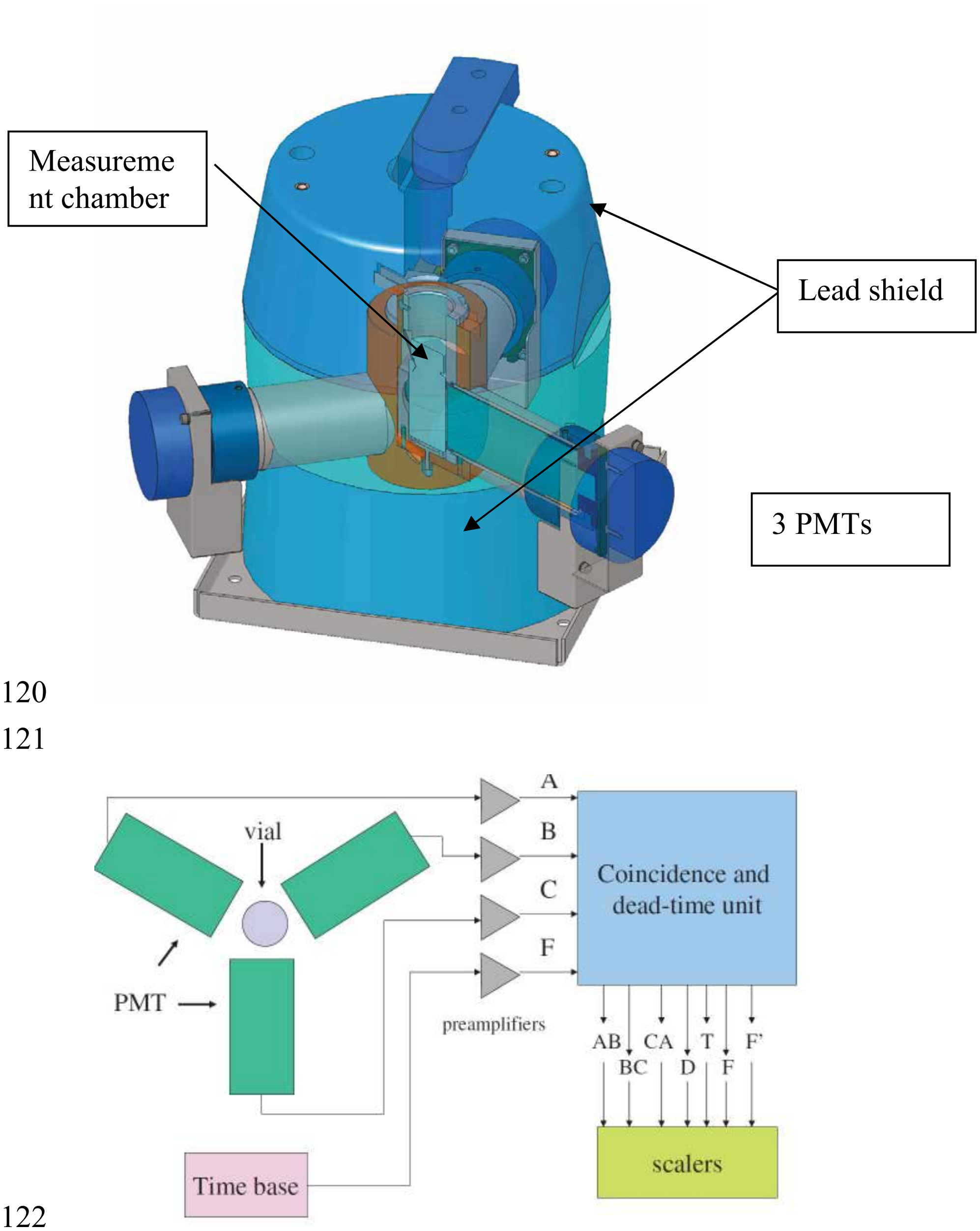

Fig. 1 Diagram of principle of TDCR system in LSC instrument and the Hidex 300SL detector structure

The TDCR based LSC method has been reported in the 1980's [33], since then many laboratories have built their own TDCR system for LSC measurement. However, these early applications of the TDCR method was exclusively employed in metrological laboratories for radionuclide standardization [31, 32, 34-37]. The first commercial TDCR

LSA (Hidex 300 SL) was introduced by Hidex Oy in 2008. Recently, two more types of TDCR LSAs, the Hidex 300SL Super Low level and Hidex 600SL were introduced to the market by Hidex Oy. By equipped with additional lead shielding, low level PMT detectors and an active guard detector in the Hidex 300SL super Low Level instrument for further background reduction, the detection limit is significantly improved to be used for environmental monitoring, radiocarbon dating and biofuel verification applications. By extending sample load capacity and queuing, Hidex 600SL TDCR LSA can hold over 500 small vials or 210 large vials, and can automatic determination large number of samples. Pulse shape analyzer is also equipped in the Hidex TDCR LSAs, so the alpha emitting radionuclides can be also measured in the presence of beta emitters using alpha-beta discrimination setup. In the past 5 years, many Hidex TDCR LSAs have been installed and applied in many laboratories, which makes the TDCR LSC method has becoming a widely used LSC method for measurement of radionuclide for many applications such as environmental monitoring, radiological protection, and biomedical studies.

By compared with conventional LSC method using TriCarb 2200/2500, it was demonstrated that Hidex 300SL performed a good measurement for ^{90}Sr and ^{241}Pu in soil and radioactive slurry samples [38]. A comparison of the Hidex 300SL with Quantulus 1414 and TriCarb 2800 in different labs by measurement of ^{89}Sr standard solution has also demonstrated a good performance of this method [1]. Hidex TDCR LSA has also been successfully applied for the measurement of ^{3}H, ^{63}Ni, ^{68}Ga, ^{99}Tc and ^{228}Ra and ^{210}Pb in environmental and waste samples [3, 17, 39-41], it was also used for the determination ^{68}Ga ^{51}Cr, ^{90}Sr and ^{32}P in various biological samples [20, 42-43].

The TDCR LSC has also been investigated for measurement of ^{14}C samples using Hidex 300SL instrument, it was found that the TDCR quench correction worked well for measuring the activity of ^{14}C in quench standards with high activity levels, it may not be preferred for the correction of benzene impurities in very low activity samples for radiocarbon dating. Thus, based on the observed position of the right slope of the ^{14}C or muons spectrum, a quench correction method was proposed and seemed to be more optimal for ^{14}C dating. However, a relative high background level of 13.7 CPM was observed in triple coincidence model, it prevents from the precise measurement of ultra-low-level samples for ^{14}C dating purpose [44]. The introduction of the Hidex 300SL Super Low Level instrument in the recent years can significantly suppress the background level, which will makes it comparable to the conventional Quantulus 1220 instrument and enable to be applied for ^{14}C dating.

With the feature of PSA, alpha-beta discrimination can be applied and alpha emitting radionuclides have been measured by Hidex TDCR LSA, e.g. ^{226}Ra a solution containing ^{210}Pb, ^{210}Bi, and ^{228}Ra [3]. Meanwhile Hedix TDCR LSA was also used for measurement of gross alpha/gross beta in water samples [45].

For electron capture nuclides, such as ^{55}Fe, ^{41}Ca and ^{139}Ce, there can be more than one counting efficiencies corresponding to a given TDCR value, as the decay spectra are not continuous due to the contribution of two or more separated group of scintillation energy from conversion electrons and gammas. Thus, the introduction of a new parameter into the algorithm of counting efficiency determination would be required to yield a single-valued efficiency vs. TDCR curve [46]. Hidex TDCR LSA has been used for the measurement of ^{55}Fe in radioactive waste, irradiated steel and urine samples [4, 47-48]. An obvious discrepancy was observed between the measured TDCR value and the counting efficiency of ^{55}Fe. Therefore, a quench correction needs to be conducted by fitting with a quench calibration curve, especially for the solution with high color quench due to the ferric ion in HCl or water solution. By obtaining a simple power function of counting efficiency vs. the TDCR value with a set of quench standards, satisfactory results of quench correction for ^{55}Fe has been achieved [47]. To reduce the color quench in the measurement of ^{55}Fe, H_3PO_4 can be used to dissolve the separated iron in precipitate, a colorless solution can be obtained by formation of an iron complex with H_3PO_4 [12].

Cerenkov counting using TDCR LSA

Besides the typical beta-emitting radionuclides by counting the electrons produced in their radioactive decay, the TDCR LSA can be also used for the measurement of high-energy beta emitting nuclides (e.g., ^{89}Sr, ^{90}Y, ^{32}P, ^{106}Rh, ^{204}Tl) by Cerenkov counting [2].

In the Cerenkov counting, the samples are measured by directly counting Cerenkov photon/s without addition of the scintillation cocktail. Since Cerenkov photons are produced directly in sample solutions, no inhibition of the photon emission process due to fluorescence is involved; thus, Cerenkov counting is free of chemical quenching. However, Cerenkov counting efficiency could be affected strongly by color quenching. Even very light color can produce a significant quench effect with a noticeable reduction in counting efficiency.

The color quench for Cerenkov counting is usually corrected by internal standard method or quench curve method using an external gamma source in the ordination LSC method. In the TDCR LSC, constructing of quench correction curves is not needed, the effects of color quenching on Cerenkov efficiency can be automatically corrected based on the measured TDCR values. A free parameter model has been proposed for standardization with the TDCR LSC [2, 49]. A stochastic TDCR model based on the Monte Carlo code Geant4, has also constructed to determine the Cerenkov efficiency using the experimental TDCR value [50]. These TDCR Cerenkov models have been successfully tested for the activity standardizations of ^{90}Y, ^{89}Sr and ^{68}Ge in nuclear medicine applications [4, 51]. The TDCR Cerenkov method would allow for calculating the counting efficiency without an external or internal standard source.

Using a TDCR LSA (Hidex 300SL), the TDCR Cerenkov method has been successfully used for quantitative determination of high-energy beta emitters in environmental samples. An empirical correlation between the Cerenkov counting efficiency for ^{90}Y and the measured TDCR value was established for the correction of color quench effect on the determination of ^{90}Sr/^{90}Y in aqueous samples [18-19]. The direct TDCR Cerenkov counting can serve as a rapid screening method for high-energy beta-emitting radionuclides in environmental water samples without any radiochemical separation procedure. TDCR Cerenkov counting without chemical separation has been compared with ordinary LSC following radiochemical separation for the measurements of ^{90}Sr-^{90}Y in groundwater samples collected in a contaminated riverbed, and found a good agreement between two methods [52]. Using three commercial liquid scintillation analyzers (Triathler, Tri-Carb 3180 and Hidex 300 SL) with one-, two- and three PMTs, the effects of measurement conditions for Cerenkov counting efficiency has been investigated, it was found that the TDCR Cerenkov counting would be well suited for routine quantitative determination of high energetic beta-emitting radionuclides in low level environmental samples [53]. However, to date, the TDCR Cerenkov counting is still not yet widely applied for measurement of high-energy beta-emitting radionuclides with only few publications focusing on the determination of ^{90}Sr-^{90}Y in environmental samples [18, 52, 54-55].

Determination of anthropogenic radionuclides

LSC is the major technique for measurement of pure beta-emitting radionuclides, including the radionuclides decay by electron capture. The most important anthropogenic radionuclides in view of environmental radioactivity, tracer application in various disciplines and nuclear waste management are ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{89}Sr, ^{90}Sr, ^{129}I and ^{241}Pu. Large efforts have been given in the past decades in the establishment and improvement of the analytical method for these radionuclides, especially with the rapidly increased requirement in the characterisation analysis of decommissioning waste in the past years. The progress on the analytical methods for these radionuclides using LSC are presented below.

Tritium (^{3}H)

Tritium is a low-energy ($E_{\max}$ = 18.6 KeV) pure beta emitter with a half-life of 12.32 years，the LSC is the most often used method for its measurement. Ionization chamber and proportional counter methods can be also used for the measurement of tritium, but often used for measure relative high-level tritium because of high detection limit. In these methods, gas tritium (HT, T_2) and ^{14}C ($^{14}CO_2$, CH_4) are direct introduced to detector chamber and measured for on-line monitoring for tritium level [56].

Besides the production in the upper atmosphere through cosmic ray reactions of nitrogen and oxygen, tritium in the present environment is mainly from atmospheric nuclear weapons testing and on-going nuclear fuel cycle operations. Since the partial atmospheric nuclear test ban treaty in 1963, the worldwide levels of tritium in the environment have been decreasing at a rate approximately equal to its half-life. Generally, nuclear fuel cycle operations are of concern to the immediate locale only, with relatively minor contributions to more general environmental tritium levels. Regulated monitoring of specific sites and hydrological studies are the principal applications of environmental tritium analysis.

Tritium in water form is normally prepared as purified water for measurement using LSC. To improve the counting efficiency, water is filtered, neutralized and distilled to remove the particles and chemicals (including salts) to reduce the quench effect. To overcome the color quench (e.g. urine sample), charcoal adsorption is often utilized to remove the colorful organics before further neutralization and distillation. A commercial available tritium column (Tritium resin, Triskem International) is dedicated to purify water sample for tritium (tritated water) determination using LSC, this column is filled with cation and anion exchange resins for removal of ions and a prefilter for removal of organics. A scintillation cocktail is mixed with the purified water for LSC measurement, a better compatible cocktail is normally selected to use bigger volume of water and to obtain a better counting efficiency, and finally a good detection limit. For determination of tritium in environment, 10 ml water sample is often used and mixed with 10 ml scintillation cocktail for LSC measurement. In this case, a detection limit of 1-2 Bq/L can be obtained using ultra-low level LSA (e.g. Quantulus 1220, PerkinElmer, USA). For improvement of detection limit, a high capacity LSA (e.g. AccuFLEX LSC-LB7, HITACHI ALOKA, Japan) with 145 ml vial can be used. In this case, up to 70 ml water sample can be used, and a detection limit down to 0.3 Bq/L can be reached.

Since tritium in the present environmental water samples is already declined to < 2 Bq/L, the direct measurement using LSC is not sufficient sensitive for its reliable determination. Electrolysis method is therefore often applied for the enrichment of tritium in water. This method is based on the slightly higher binding energies of tritium with oxygen in tritated water compared to hydrogen, and molecules of THO are not decomposed to form HT and O_2 as readily as H_2O or DHO (T = tritium, D = deuterium). With this method, tritium can be enriched by a factor of 15-40, depending on the volume of the electrolysis cell and final volume of the enriched tritiated water. It should be mentioned that the electrolysis process is quite slow; 5-10 days are normally needed for treatment of 100-500 ml water in each cell. Combined the electrolysis enrichment, the detection limit of LSC for tritium can be improved to be lower than 0.1 Bq/L. Noble gas mass spectrometry is the most sensitive technique for measurement of tritium in very low-levels (< 1 mBq), which is based on the measurement of ^{3}He, the decay daughter of tritium. Helium in the sample is first removed by vacuum, and the sample in a tight container is kept for a few months for ingrowth of helium from tritium decay, the produced ^{3}He is separated and measured using noble gas mass spectrometry [57]. The major drawback of this method is its long analytical time of a few month to years due to the ingrowth of ^{3}He, and LSC is still the dominant method for measurement of tritium.

Tritium in solid sample such as biological and soil samples needs to be separated first from the solid matrices. Tritium exist in biological samples as part of the water component (FWT, free water tritium) or as part of the organic structure (BT, bound tritium). The free water tritium is often separated from the sample by freeze drying and collecting the evaporated water. To analyze the bound tritium, the sample is dried first (freeze drying or low-temperature oven drying at ~60–80°C) and then combusted to separate the bound tritium. The water of combustion is collected, purified as required and measured using LSC.

Azeotropic distillation is also used for extraction of free water tritium, and cyclohexane is the most often used azeotrope for extracting water from various biological samples, such as honey, milk, vegetation, soil, and fish for tritium measurement using LSC. The organic bound tritium in biological samples and firming binding tritium inside of the crystal of grains of soil and sediment are often separated using combustion with oxygen flow at high temperature. In this case, tritium in organic substance is converted to water vapor and collected by condensing [58-59], and the firmly binding tritium in the crystal of soil and sediment grains and metals can be also separated by converting it into water vapor by combustion with oxygen flow [60-62]. The converted tritium in water vapor form is condensed and collected as liquid water and finally measured using LSC.

In the past decades, the major progress on the determination of tritium focus on the analysis of various decommissioning samples because of the increased requirement in the characterization of decommissioning waste, and highly present of tritium in all types of samples in the nuclear facilities and the high mobility of tritium [10, 61-65]. Hou [10, 61] has reported a combustion method for separation of tritium from decommissioning samples, such as concrete, graphite, steel, aluminum for its determination using LSC. A Sample Oxidizer (PerkinElmer) was used for the separation of tritium in all species. The solid sample was ground/cut to fine powder/small pieces and mixed with combustible materials (e.g. cellulous powder), all tritium in the samples is converted to THO by combustion with an oxygen flow and at temperature of more than 1000 °C. The formed water vapor is converted to liquid water in an air condenser and is directly collected in a LSC vial; scintillation cocktail is flow into the vial through the tube for rinsing. After mixing, tritium is then measured using LSC. The entire process only takes less than two minutes, and therefore very suitable for the rapid analysis of large number of decommissioning sample. An attention should be given in the sampling and sample preparation steps to avoid the loss and contamination of tritium because of high volatility and mobile property of tritium. Warwick et al. [61] investigated the release feature of different species of tritium from solid samples using a programmable combustion system (Fig. 2), and demonstrated that combustion method can be used not only for separation of total tritium, but also for speciation analysis of tritium [61,63].

Carbon-14

Carbon-14 has a half-life of 5730 years and decays by pure beta emission ($E_{\max} = 156$ keV). In the environment, ^{14}C is produced by the interaction of cosmically produced neutrons with atmospheric nitrogen in the upper atmosphere, which provides a continuous and constant source of ^{14}C in the atmosphere. The uniform uptake as $^{14}CO_2$ into living plant material, conversion to plant carbohydrates, and subsequent transfer through the food chain are the basis of the radiocarbon dating technique. ^{14}C dating is used in a wide range of scientific disciplines including archaeology, geology, soil science, climate reconstruction, and oceanography, and LSC has been the widely used measurement technique for ^{14}C dating. Human nuclear activity such as atmospheric nuclear weapons tests (principally during the 1950s and 1960s) has injected huge amount of ^{14}C (1.2×10^8 GBq) to the atmosphere, which increased ^{14}C level in the atmosphere by a factor of two. With the exchange of ^{14}C in the ecosystem, the ^{14}C level in the environment decreased gradually, but still higher than the pre-nuclear level at present environment. Discharges from facilities associated with the nuclear fuel cycle (principally nuclear power plants and fuel reprocessing plants) have also releases ^{14}C to the environment. Although ^{14}C is not the most abundant anthropogenic radionuclides released to the environment, its long half-life, high environmental mobility, and ability to enter the food chain mean that it delivers one of the highest collective effective dose equivalents to the global population, hence the level of ^{14}C in the environment is critical for environmental monitoring of the nuclear facilities [66]. Petroleum derivatives are occasionally used to adulterate natural food and drink products (e.g. wines, spirits, or cider vinegars) without the buyer's knowledge. Because petroleum-based products are sufficiently old that they contain no ^{14}C, depletions in ^{14}C content are normally indicative of adulteration. Carbon dioxide is the main greenhouse gas released to the atmosphere as a result of human activities. A 30 % rise in CO_2 concentration has been observed since the start of the industrial revolution, this is mainly attributed to the increased use of fossil based fuel for energy production and transportation. Since the ^{14}C in the fossil fuel is absent, measurement of atmospheric ^{14}C level and its distribution can be used for directly estimating the amount of fossil CO_2 releases, and has been widely applied in the past years [22-23].

Carbon-14 is often measured by LSC after separation from the sample matrices and other radionuclides. Combustion is the most effective method for separation of ^{14}C from solid samples, Acid digestion is also used for water and solid sample by converting carbon species to CO_2. The released CO_2 can be absorbed using NaOH or quaternary amines for the LSC measurement of ^{14}C. Carbo-Sorb E (PerkinElmer, Inc.) and Solusol (National Diagnostics) are examples of high-capacity carbon dioxide absorbers that are compatible with LSC cocktails. Due to strong quenching, less trapping capacities and severe chemiluminescence, $^{14}CO_2$ absorbed in NaOH solution is not often directly used for LSC, but for further purification.

The combustion and direct absorption of CO_2 in quaternary amine is simple and effective method for the separation and measurement of ^{14}C. The major disadvantage of the CO_2 absorption technique is the relative small amount of carbon that can be absorbed, therefore often applied for analysis of samples from nuclear facilities or surrounding environment, which have a relative high ^{14}C concentration. Hou [10, 61] have reported a method for the determination of ^{14}C in samples from nuclear decommissioning, such as graphite, concrete and metals. ^{14}C was released from the sample matrix as CO_2 by oxidation combustion with O_2 flow at a temperature higher than 1000°C with Pt as catalyzer to convert all CO to CO_2. It was also confirmed that both organic and inorganic carbon in the samples can be completely converted to CO_2 in this condition. The released $^{14}CO_2$ is trapped using 8-12 ml of Carb-Sorb E solution filled into a trapping column to ensure a high absorption efficiency. The trap solution was then mixed with Permafluor E+ scintillation cocktail for LSC measurement. The entire separation was implemented with a Sample Oxidizer (PerkinElmer Inc.), which makes the separation to be completed within 2 minutes. The major disadvantage of this method is that the sample amount can be treated is relative small (0.2-1.0 g), which limits the analysis of big sample and the detection limit of the method. A tube furnace was also reported for separation of ^{14}C from solid sample using combustion. In this case, the sample amount can be increased to 20 g, therefore improve the detection limit [67]. **Fig. 2** shows diagrams of these two systems for ^{14}C analysis. This method was also confirmed to be applicable for other solid samples, such as soil, sediment, vegetation, tissues, exchange resin, filter, and plastic materials [62, 67].

A method for the determination of ^{14}C in water samples was reported using evaporation and combustion for carbon separation and LSC for ^{14}C measurement [10]. In environmental water samples, ^{14}C presents as both inorganic (carbonate) and organic associated form, evaporation with addition of stable carbonate as carrier is first used to concentrate ^{14}C and convert to solid. The residue with concentrated ^{14}C was used for the analysis using the same procedure as other solid sample described above.

Wet oxidation using strong oxidative reagents ($K_2S_2O_8$ with $AgNO_3$ in acidic media or CrO_3 and H_2SO_4) and acid digestion (H_2SO_4) has also been applied for separation ^{14}C in water and ion exchange resin samples. Acid digestion is used to separate ^{14}C in carbonate/bicarbonate form, while wet oxidation in acidic media for decomposing organic compounds is used for separation of ^{14}C in both organic and carbonate forms. The released ^{14}C is adsorbed in alkaline solution for LSC measurement of ^{14}C [68]. In the combustion and wet digestion process, other volatile radionuclides such as tritium, ^{36}Cl and ^{99}Tc might be also released from sample with ^{14}C and interfering the measurement of

^{14}C. A pre-condensing or pre-absorption with diluted acid (H_2SO_4) is often applied for removal of these interferences. In this case, CO_2 can pass through the condenser or the acidic solution and absorbed in the alkaline solution, but all other radionuclides deposited on the condenser or absorbed in the acidic solution and removed from ^{14}C.

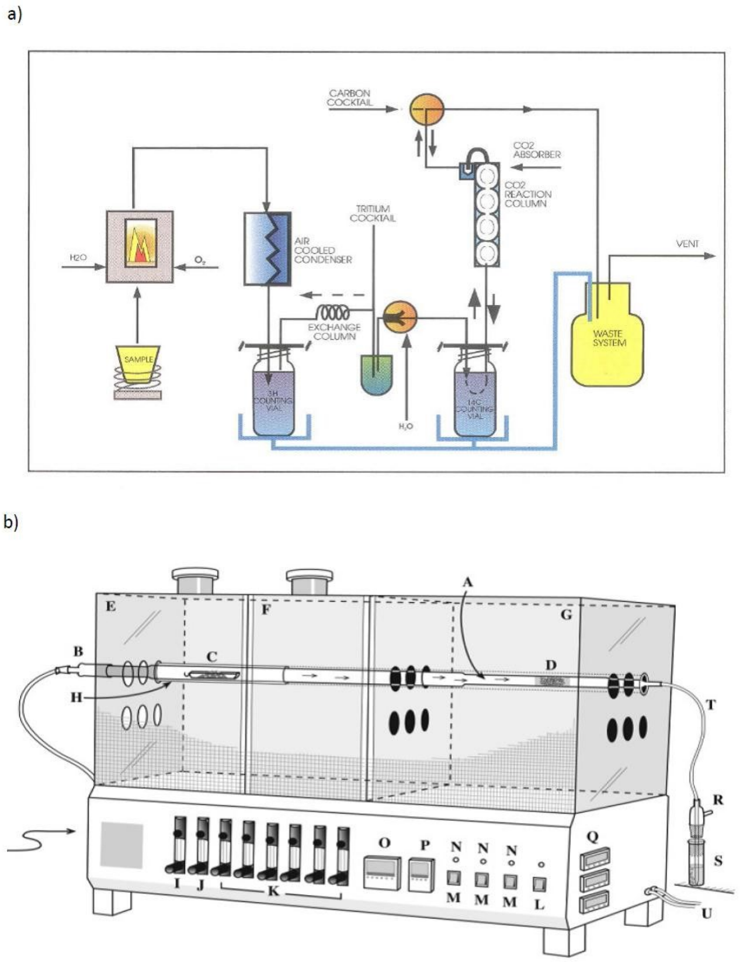

Fig. 2 Diagram of two combustion system for separation ^{14}C and tritium from solid samples.

The absorption capacity of alkaline solution for $^{14}CO_2$ is relative low, 10 mL of Carbo-Sorb can only absorb 58 mmol of CO_2, which is equivalent to 0.7 g of carbon. Therefore, the combustion and direct absorption of $^{14}CO_2$ in alkaline solution for ^{14}C measurement using LSC is not sufficient good for determination of low-level ^{14}C in environmental samples, especially for the ^{14}C dating and application in the estimation of fossil CO_2 emission. The conventional benzene synthesis method is still used, which enable to use 19 g of carbon in maximum for ^{14}C measurement [69]. In this method, all species carbon is first converted to CO_2 by combustion or acid hydrolysis. The collected CO_2 is subsequently converted to lithium carbide by reaction with molten lithium, and on cooling, the addition of water to C_2H_4 causes the production of acetylene (C_2H_4). The acetylene is then cyclotrimerized to benzene using a chromium- or vanadium-based catalyst. Duo to high carbon content (92.3%), a clear aromatic solvent capable of dissolving sufficient Fluor, excellent energy transmission properties, benzene is an ideal counting medium for ^{14}C. In most instances, solid flours would be added directly, rather than a scintillation cocktail. This minimizes volume additions and therefore any increase in quenchable background, meanwhile highest volume of sample for measurement. However, compared to the direct alkaline absorption and LSC measurement, this method is tedious and more expensive, therefore mainly applied for the ^{14}C dating or precise measurement of ^{14}C in low level or background level environmental samples. With the rapid development of accelerator mass spectrometry (AMS) and its wide application, ^{14}C measurement for dating purpose is now mainly carried out by AMS technique.

Chloride-36

^{36}Cl is a long-lived ($t_{1/2}$ =301 ky) pure beta-emitter (E_{max} = 709 keV), formed by neutron activation reaction of stable chlorine $^{35}Cl(n,\gamma)^{36}Cl$ in nuclear reactor. Less important sources are nuclear reactions induced by cosmic radiation in atmosphere, water and bedrock. Because of its low specific activity, ^{36}Cl is not considered substantial danger to humans at present environmental level. However, since the high mobility of chlorine and long half-live, ^{36}Cl is a useful tracer in interpreting environmental processes [70-72] and important for waste depository.

Many methods have been reported for the determination of ^{36}Cl in environmental and waste samples [11, 73-76]. For soil, concrete and other solid materials, chlorine is separated from the sample in one of two ways: vaporizing chlorine to Cl_2 gas by subjecting the sample to high temperature or by boiling the sample in strong oxidizing acids. The released chlorine gas from the samples is captured in a NaOH solution. The sample can also be dissolved so that the chlorine remains in solution as chloride ions. It should be mentioned that no (or very small amount of) HCl or HClO4 should be added for sample decomposition, otherwise a huge amount of Cl from the acid will be transfer to the final sample, make it impossible to be measured. In all three cases, a known amount of chlorine carrier, in the form of NaCl or $NaClO_3$ is added to the sample. Chlorine gas trapped in the NaOH solution is reduced to chloride with $NaNO_2$, and the chloride is precipitated as silver chloride (AgCl) by adding $AgNO_3$ after acidifying the solution to a weakly acidic medium using HNO_3. Iodine can be removed by dissolving the precipitate with NH_4OH, in which AgCl is dissolved but AgI does not. The AgI precipitate is discarded and the chloride in the NH_4OH solution is again precipitated by acidification to pH<2. The chemical yield of the separation is determined by measuring the amount of chlorine using ICP-MS or ion chromatography. Finally, ^{36}Cl in the purified AgCl precipitate is counted by LSC after dissolving the precipitate with ammonium and adding scintillation cocktail. Because of the relative high beta energy of ^{36}Cl, the counting efficiency of ^{36}Cl is normally higher than 85% depending on the quench level, and need to be corrected using quench curve or standard addition method. Because AgCl dissolved in ammonia solution is not stable, Ag^+ can be gradually oxidized to Ag_2O, worsen the quench level of the sample, making the analytical results not precise.

Hou et al. [11] reported a method for the determination of ^{36}Cl in decommissioning samples, including graphite, concrete and metals. **Fig. 3** shows an analytical procedure for the determination of ^{36}Cl in waste samples. In this method, the sample is first decomposed. Graphite sample is decomposed by acid dissolution with a mixed acids (H_2SO_4:HNO_3:$HClO_4$=15:4:1); the metals such as lead, aluminum and stainless steel are dissolved with 5M HNO_3, 5M H_2SO_4, and H_2SO_4-H_3PO_4, respectively. During the decomposition by heating, the solution is bubbled with nitrogen gas, and the released gas (including Cl_2) is trapped in 3 sequential trapping solutions: one H_2O, two 0.4M NaOH. The concrete sample is decomposed by alkaline fusion by mixing sample with NaOH-Na_2CO_3 and fused at 500 °C for 3-4 h, the fused cake is dissolved with H_2O, and the leachate is used for the determination of ^{36}Cl. Before sample decomposition, stable chloride as carrier and other stable elements as hold back carriers are added. The decomposed sample solution is then transferred to a separation funnel. $NaHSO_3$ solution is added to convert all iodine to iodide, HNO_3 is then added to adjust pH <2. After addition of CCl_4, $NaNO_2$ solution is added to oxidize iodine to I_2, and chlorine is reduced to Cl^-, I_2 is then extracted to CCl_4 phase by shaking. $AgNO_3$ solution is then added to the aqueous phase after extraction of iodine, stirring the solution to aggregate the AgCl precipitate. The AgCl precipitate is separated by centrifuge, and washed with 1 M HNO_3 to remove the interfering metal radionuclides. The precipitate is dissolved with 25% NH_3, HNO_3 is then added to the solution to pH<2 to re-precipitate AgCl. The AgCl precipitate separated by centrifuge is dissolved in 25% NH_3 solution. The solution is loaded to an anion exchange column, which is converted to OH^- form and conditioned with 25% NH_4OH. The column is washed with 25% NH_3 until no Ag^+ in the rinsed solution. Chloride on the column is then eluted with 0.2 mol/L NH_4NO_3-0.6 mol/L NH_4OH. The eluate is evaporated to dryness on a hotplate; the residue is dissolved with 2 ml water and transferred to a LSC vial. 0.1 ml of the solution is taken to measure stable chlorine by ICP-MS for chemical yield monitor. 15 ml of cocktail is added to the remaining solution, ^{36}Cl in the solution is measured by LSC. The decontamination factors for all interfering radionuclides are higher than 10^6, and recovery of Cl is higher than 90%. Since the final solution of ^{36}Cl is prepared in 2 ml of water, the quench level is very low and the counting efficiency is higher than >98%.

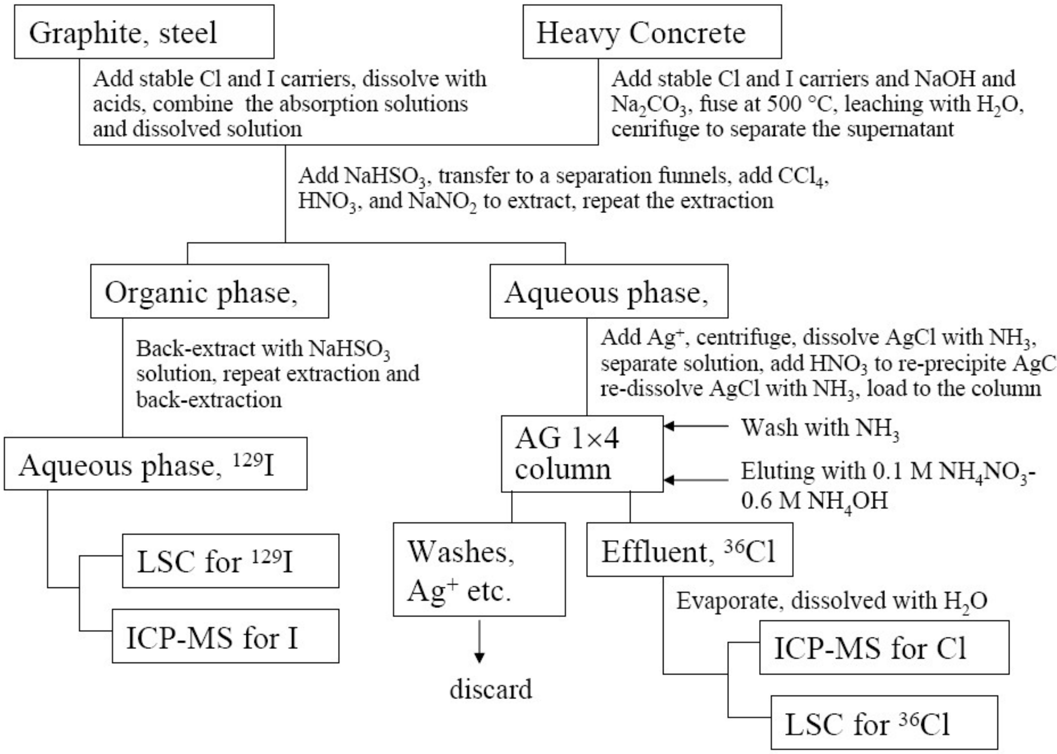

Fig. 3 Analytical procedure for the determination of ^{36}Cl in nuclear waste samples [11]

For the nuclear waste samples, ^{36}Cl level is normally relative high to be measured by LSC. While, for most of environmental samples, especially the sample with natural originated ^{36}Cl ($^{36}Cl/Cl < 10^{-11}$), LSC is not sensitive enough to measure such a low level ^{36}Cl (< 1 mBq or $^{36}Cl/Cl < 10^{-10}$ for 10 mg Cl in the sample). The most sensitive accelerator mass spectrometry (AMS) is needed, which can measure ^{36}Cl in the sample target with $^{36}Cl/^{35}Cl$ atomic ratio of 10^{-15}.

Calcium-41

^{41}Ca ($t½=1.03\times10^{5}$ years) is mainly produced by neutron activation reaction of $^{40}Ca(n, \gamma)^{41}Ca$. It is also a naturally occurring radionuclide produced by the reaction of stable calcium (^{40}Ca) of the earth with neutrons from the cosmic rays and fission of uranium. Human nuclear activities including atmospheric nuclear weapons testing and operation of nuclear facilities have also released some ^{41}Ca to the environment. In the nuclear reactor, ^{41}Ca is mainly produced in the concrete shielding because of its high calcium content and its exposure to the neutrons from the reactor. ^{41}Ca is an important radionuclide in the disposal of radioactive waste, because of its long half-life and high mobility in the environment and high bioavailability.

^{41}Ca decays to the ground state of ^{41}K by pure electron capture, emitting X-rays and Auger electrons of very low energy (0.3-3.6 keV). It can thus be measured by X-ray spectrometry and LSC, but the LSC is much more sensitive [9, 77-80] compared with X-ray spectrometry because of its low counting efficiency (<0.08%) and low abundance of X-ray of ^{41}Ca (11.4% for 3.31 keV X-ray).

Due to the pure electron capture decay of ^{41}Ca, chemical separation from the sample matrices and purification from all other radionuclides are necessary before measurement of ^{41}Ca using LSC or other techniques. Suárez et al. [77] reported a radiochemical separation procedure for separation of calcium from other radionuclides, which is based on the hydroxides precipitation of transition metals and chromate precipitation of Ba, Sr and Ra with a chemical recovery of 40%. In this procedure, the separation of Ba, Sr and Ra by chromate precipitation is very critical because of very restrict control of pH value. Ion exchange and extraction chromatography have also been used for separation of calcium [78, 80]. Anion exchange chromatography was used to remove all radionuclides presenting as anion in high concentration HCl media, and extraction chromatography using TRU resin was applied to remove actinides and lanthanides. However, this procedure is not well suitable for removal of earth alkaline radionuclides such as radiostrontium, radium and barium. An tertbutylmethylether/ethanol extraction step was proposed to extract calcium and to remove Sr, Ba and Ra [80]. With all these steps, a recovery of more than 65% and decontamination factor of $<10^3$ for most of interfering radionuclides were obtained. Hou [9] reported a simple and effective method for determination of ^{41}Ca in ordinary and heavy concrete (containing more than 75% of $BaSO_4$) based on the relative low solubility production of $Ca(OH)_2$ compared to the hydroxides of Sr, Ba and Ra in NaOH solution. Calcium (mainly as calcium carbonate) is first leached using *aqua regia*, and the experiment shows that more than 95% of Ca can be leached out from the concrete sample in this step. There are 3 main steps for the separation of Ca from the interfering radionuclides. Ca is first separated from the transition metals, such as Co, Eu, Fe, Ni and transuranic by precipitation at pH 9 using NaOH. In this step, the interfering radioisotopes of these elements are precipitated, while

Ca remains in the solution with Sr, as well as Ba, Ra, Cs, etc. Ca and Sr in the supernatant are then precipitated as carbonates with Ba and Ra by adding Na_2CO_3 and separated from alkali metals and non-metal elements. Ca is then separated from Sr, Ba and Ra by precipitation of Ca as $Ca(OH)_2$ in 0.5 mol/L NaOH solution after dissolution of the carbonate precipitates. This is based on the low solubility of $Ca(OH)_2$ in high concentration of NaOH (higher than 0.5 mol/L) compared with Sr, Ba, and Ra. This step is repeated and the separated $Ca(OH)_2$ is dissolved with HCl for measurement using LSC after neutralizing to pH 6-8. The chemical yield of 80-90% for ^{41}Ca was obtained by measurement of Ca before and after chemical separation using ICP-OES. The decontamination factor for the interfering radionuclides such as ^{60}Co, ^{152}Eu, ^{133}Ba, ^{85}Sr, ^{137}Cs, ^{55}Fe, and ^{63}Ni are higher than 10^5. The detection limit of 20 mBq for ^{41}Ca was achieved by using low background LSC instrument (Quantulus 1220) [9].

However, this method could not separate ^{45}Ca from ^{41}Ca. If both isotopes exist in the sample, interference of ^{45}Ca to the measurement of ^{41}Ca has to be corrected, which can be carried out by measurement of the contribution of ^{45}Ca to the window of ^{41}Ca at lower channel. Due to the low energy of Auger electrons (0.3-3.6 keV) used for measurement of ^{41}Ca by LSC, the counting efficiency is relatively low (<25%), and highly influenced by quench. The separated calcium sample is normally prepared in a neutral solution of $CaCl_2$ and all other element (especially iron) has to be completely removed. The major quench effect is the amount of calcium in the samples. In addition, luminesce is also an interference for the measurement of ^{41}Ca, which has to be considered in the measurement of ^{41}Ca using LSC.

For measurement of ^{41}Ca in natural environmental level (< 1 mBq), more sensitive mass spectrometry techniques such as AMS [81] and resonance ionization mass spectrometry (RIMS) [82] are needed, a $^{41}Ca/^{40}Ca$ atomic ratio as low as 10^{-15} can be measured by AMS.

Iron-55

^{55}Fe ($t_{1/2}$=2.7 years) decays via electron capture with the emission of Auger electrons and low energy X-rays (5.89 keV, 16.9%). ^{55}Fe is mainly measured by LSC although X-ray spectrometry and gas flow proportional counter can be also used, but very low counting efficiencies (<1%). ^{55}Fe is produced by neutron activation reactions of two major stable iron isotopes: ^{54}Fe(n,γ)^{55}Fe and ^{56}Fe(n,2n)^{55}Fe. Since iron is the main component of construction materials in nuclear reactors, huge amounts of ^{55}Fe were produced in nuclear reactors and other nuclear facilities/devices with neutron production. ^{55}Fe enters into the environment mainly through the release of radioactive effluents of nuclear reactors, as well as atmospheric nuclear weapons tests in 1945-1980. Determination of ^{55}Fe is often required for monitoring the radioactivity in the nuclear facilities and their discharges, as well as characterisation and depository of nuclear wastes. Iron has to be separated from the sample matrices and then completely purified from other radionuclides prior to the measurement of ^{55}Fe.

Most of work on the determination of ^{55}Fe is addressed to the analysis of decommissioning waste, and the key issue on the analytical method is the separation of iron from other radionuclides and its high efficient measurement.

The separation of iron from the sample matrices (solution) is often carried out by hydroxide precipitation based on the formation of $Fe(OH)_3$ and $Fe(OH)_2$. However, for some special samples, the matrix component need to be first removed. For instance, in acid-dissolved lead sample, lead has to be removed by $PbSO_4$ precipitation to avoid the formation of a large amount of $Pb(OH)_2$ during the $Fe(OH)_3$ precipitation step. For aluminium sample, the bulk $Al(OH)_3$ in the $Fe(OH)_3$ precipitation step can be removed by adding more NaOH to a concentration 0.2 M for converting $Al(OH)_3$ precipitate to soluble $NaAlO_2$ [12].

All transition metals can be co-precipitated with $Fe(OH)_3$ in alkali solution, among them the most important radionuclides are ^{60}Co, ^{63}Ni, ^{54}Mn, ^{152}Eu and ^{154}Eu in decommissioning waste and further chemical separation is necessary to isolate iron from these interfering radionuclides. Chelating and anion exchange chromatography combined with solvent extraction have been used to separate iron from other nuclides [83, 84]. The commonly used extraction reagents include ethyl acetate, isobutyl ketone and isopropyl ether, particularly iron has a high partition coefficient in ethyl acetate [85]. However, as solvent extraction is not very specific for iron, the decontamination of interfering radionuclides is not sufficient with one extraction. To improve the separation efficiency of iron from other radionuclides, an extraction chromatography based on di-isobutyl-ketone has been proposed [85]. A commercial solid phase extraction chromatographic resin, TRU resin, has also been applied to separate iron for the determination of ^{55}Fe [86, 87]. One limitation of this resin is the low capacity for a small extraction chromatographic column (2 ml), which can only allow for upload of sample solution with less than 2 mg iron. For sample with high iron content, such as soil, sediment and steel, anion exchange chromatography using strong basic anion resin (e.g., AG1×-4) has been confirmed to be an effective method for separation iron from other interfering radionuclides with a high recovery (>95%) and a high decontamination factor (>10^4) for most of interfering radionuclides (e.g. ^{60}Co, ^{58}Co, ^{152}Eu, ^{154}Eu, ^{63}Ni, ^{137}Cs, ^{90}Sr). This is mainly due to the high distribution coefficient of $FeCl_4^-$ on the anion resin in high concentration of HCl solution. **Fig. 4** shows a separation procedure of iron from the most important interfering radionuclides using a strong basic anion exchange chromatography. By this way, ^{55}Fe can be completely separated from ^{58,60}Co, ^{63}Ni, ^{152,154}Eu and ^{65}Zn. Other radionuclides, including all alkali and alkaline earth metals, could not form anion complex with chloride and would be removed. In combination with hydroxides precipitation, a chemical separation procedure has been successfully applied for separation of iron from different waste samples for ^{55}Fe determination. This method has also been used to investigate the distribution of ^{55}Fe in the environment surrounding nuclear power plant [88]. For samples with high iron content (> 50 mg) and high ^{60}Co radioactivity, a repeated anion exchange chromatographic separation can effectively remove ^{60}Co with a high recovery of iron (**Fig. 5**).

A modified procedure using hydroxide precipitation followed by anion exchange chromatographic separation and LSC measurement has also been applied to determination of ^{55}Fe in urine samples [47]. Due to complicated matrix component in urine, the concentration of NaOH in the sample solution needs to be increased to 2 M to get a high recovery of iron in the hydroxide precipitation step.

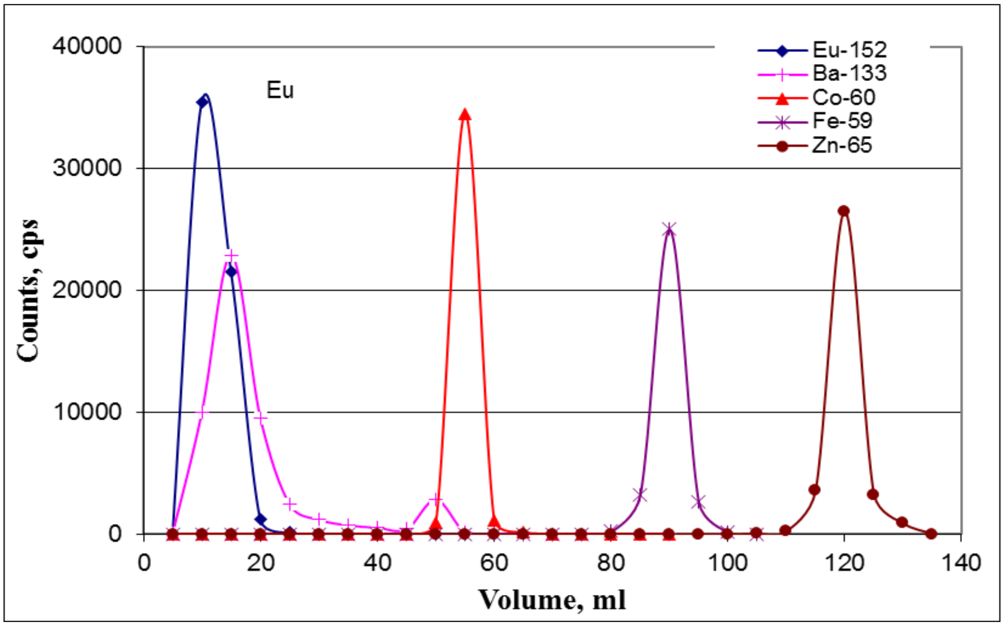

Fig. 4 Separation of Eu, Ba, Co, Cu, Fe and Zn by anion exchange chromatography (Bio-Rad AG1x-4, ϕ1 x 20 cm), 0-40ml: 9 mol/l HCl, 40-70ml:5 mol/l HCl, 70-105 ml: 0.5mol/l HCl and 105-135: 0.05 mol/l HCl

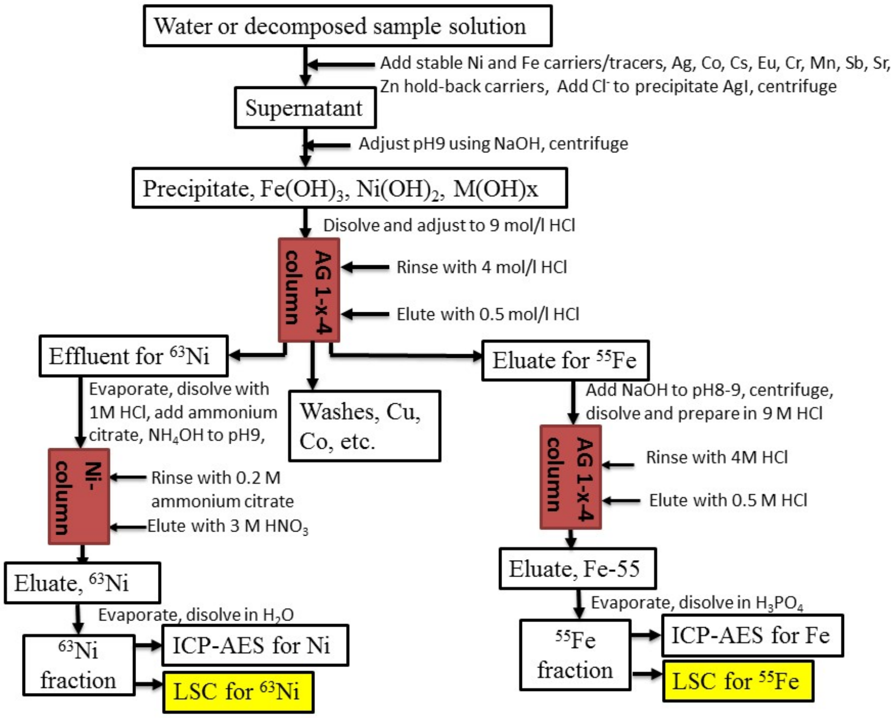

Fig. 5 Analytical procedure for ^{55}Fe and ^{63}Ni in environmental and waste samples.

The distinct yellow color of Fe^{3+} can cause a very strong color quench, which significantly reduces the counting efficiency of ^{55}Fe by LSC. Because the very low energy of Auger electrons emitted by ^{55}Fe (5-6 keV) is measured by LSC, the high color quench could reduce the counting efficiency to <10%, causing a worse detection limit. A number of approaches have been adopted to reduce the color quenching of Fe, such as solvent extraction to transfer iron to organic phase and reduction of Fe^{3+} to Fe^{2+} by ascorbic acid. These approaches could not completely overcome the color quench of Fe. In addition, the Fe^{2+} is not very stable and can be re-oxidized to Fe^{3+} slowly in air, causing a gradually increased quench level and decreased counting efficiency. An effective method for removing the yellow color of Fe^{3+} using H_3PO_4 has been proposed [12, 84]. By this method, a colorless Fe^{3+} solution is obtained and the counting efficiency is significantly improved to more than 40%. Since H_3PO_4 has less quench effect and high compatibility with scintillation cocktail compared to other acids, and the amount of Fe mixed with cocktail can thus be significantly increased. It has been confirmed that for less than 10 mg Fe carrier, 40% counting efficiency is obtained; and for 200 mg Fe, the counting efficiency is 15% [12].

Nickel-63

^{63}Ni ($t_{1/2}$ =101.2 y) is a neutron activation product formed by neutron capture of stable nickel (^{62}Ni). ^{63}Ni in the environment was released through corrosion of steel components, associated with the primary coolant system of nuclear power reactors. ^{63}Ni is pure beta emitter with relative low energy ($E_{\max}$ = 67 keV), LSC is the most often used method for its measurement. Another nickel isotope, ^{59}Ni ($t_{1/2} = 7.5\times 10^4$ y), is similarly formed from stable ^{58}Ni. The initial activity ratio of ^{63}Ni/^{59}Ni is around 100 or more, and ^{59}Ni decays by electron capture with emission of X-rays. Given the low sensitivity of LSC to X-rays, ^{59}Ni has very minor effect on the low-energy part of the beta spectrum of ^{63}Ni [89. ^{63}Ni in the environment originates from radioactive effluents from nuclear facilities and from nuclear weapons tests and accidents. The principal requirement for the determination of ^{63}Ni is to characterize nuclear waste for decommissioning and radioactive waste disposal. The determination of ^{63}Ni in the environmental samples was also applied to evaluate the impact of the nuclear facilities.

Due to its low beta energy, the determination of ^{63}Ni requires chemical separation and purification of nickel from coexisting elements and radionuclides. Methods for determining ^{63}Ni have been reported for many sample matrices including liquid effluent, sludge, ion exchange resin, graphite, heavy concrete, steel, copper, lead and aluminium from nuclear power plants and environmental samples like soil, sediment, sea water, fish, vegetation and urine [12, 84, 87, 88, 90-92].

The pre-treatment of samples containing organic matter is started by wet or dry ashing and then continued by leaching the residue with concentrated HCl or HNO_3 to dissolve nickel and other elements. For concrete, graphite and metals, acid digestion or dissolution is often used and confirm to be reliable. Graphite, concrete, soil and sediment do not have to be completely dissolved using mixed acids and/or alkaline fusion following by acid digestion. Stable nickel as carrier and other elements as holdback carriers are added before chemical separation to determine chemical yield and to effectively removal interfering radionuclides. Some methods are often applied for pre-concentration and separation of Ni from interfering radionuclides, e.g. precipitation of $Fe(OH)_3$ with ammonia to remove many metals, while nickel remains in the supernatant; precipitation of nickel using insoluble Ni-DMG complex; solvent extraction of Ni using DMG or tri-n-octylphosphine (TOPO) as extractant; anion exchange chromatography, and extraction chromatography using Ni resin. It was observed that large fraction of Ni can be also co-precipitated with $Fe(OH)_3$ when using ammonia, these might be attributed to the wrap of Ni in the $Fe(OH)_3$ when high amount of iron presents in the solution. Hou e*t al*. [12] (2005) developed a chemical separation procedure for determination of ^{63}Ni in decommissioning waste and environmental samples. Ni in the sample solution is first separated using hydroxide precipitation by addition of NaOH, most of anions, alkaline elements (e.g. ^{3}H, ^{137}Cs, ^{36}Cl, ^{90}Sr, ^{133}Ba etc.) are removed. The precipitate is then dissolved in HCl and prepared in high concentration of HCl (9 M), which is loaded to a strong basic anion exchange resin column. Ni^{2+} passed through the column, but most of transition metals (e.g. ^{60}Co, ^{55}Fe, ^{65}Zn) are retained on the column. Thereafter Ni is further purified using the Ni Resin extraction chromatography, to remove the remaining interfering radionuclides (e.g. ^{152,154}Eu, ^{60}Co, ^{54}Mn, etc.). They used this method for determining ^{63}Ni in nuclear waste samples including heavy concrete, aluminium, lead and graphite, and achieved high decontamination factors (> 10^5) for all interfering radionuclides. Chemical yields were over 90 % and the detection limit of 0.014 Bq for ^{63}Ni using a low-background LSA. This method has also been applied for environmental samples [88] Warwick and Croudace [84] developed a method that was based on the same separation steps as those of Hou *et al*. [12]; but the extraction chromatography separation using Ni resin was performed prior to the anion exchange. It has also been observed that ^{60}Co and ^{58}Co could not be sufficiently removed by using only Ni resin extraction chromatography, making the method unreliable and a correction have to be implemented to subtract the interference from ^{58}Co and ^{60}Co. Two sequentially connected Ni resin extraction chromatography separation steps can reduce the contribution of radioactive cobalt. Therefore, a separation step using anion exchange chromatography is necessary for the samples with high radioactive cobalt isotopes (^{58}Co, ^{60}Co) [87]. **Fig. 5** shows a combined procedure for separation of nickel and iron for the determination of ^{63}Ni and ^{55}Fe.

The sample preparation for measuring the ^{63}Ni activity by the LSC counter is quite simple. The eluate containing the sample fraction is collected from the chromatographic column at the end of separation procedure. The eluate is evaporated to near dryness and the residue is dissolved in a few milliliters of dilute HCl or HNO_3, which is placed in a LSC vial for counting. Attention has to be given when evaporating the Ni eluate to dryness, because nickel in the HNO_3 (3-12 M) eluate presents as $Ni(NO_3)_2$, which has a low boiling point (136.7 °C) and can be easily lost during evaporation at high temperature (>137 °C). Therefore, the eluate of Ni is often evaporated to near dryness (<0.5 ml) on a hotplate with low temperature (< 120 °C) in the end of the evaporation (< 3 ml).

The counting efficiencies of the prepared ^{63}Ni sample vary from ~50% to ~80% depending on the sample composition. Quench corrections are applied in most cases. Detection limits of 0.005− 0.014 Bq/sample for ^{63}Ni has been reported by using a combined chemical separation procedure and ultra-low background LSC instrument [12, 84].

Besides the radiometric techniques, ^{63}Ni can be also determined using AMS [93]. The comparison by Hou and Roos [89] showed that the detection limits of 0.12−45 mBq achieved by the AMS methods. For both methods, chemical separation is necessary.

Nevertheless, the ^{63}Ni assays are mostly performed using LSC, because of the accessibility of the LSC counters in radiochemical laboratories.

Strontium-89 and Strontium-90/Yttrium-90

^{90}Sr (E_{max} = 546 keV, $t_{1/2}$ = 28.8 y) and ^{89}Sr (E_{max} = 1495 keV, $t_{1/2}$ = 50.57 d) are fission products, ^{89}Sr can be also produced by neutron activation of stable ^{88}Sr. The main sources of ^{90}Sr and ^{89}Sr in the environment are atmospheric nuclear weapons tests, nuclear accidents and discharges from nuclear facilities. Fallout from nuclear weapons testing is primarily responsible for the ^{90}Sr/^{90}Y concentrations found globally in the environment. ^{90}Sr is important for environmental monitoring because of its relatively high fission yield (5.7% for ^{235}U), its long physical and biological half-lives, and its transfer to food chains. It is highly toxic because it accumulates in bone tissue which is exposed by high energy betas of ^{90}Sr/ ^{90}Y. ^{89}Sr shares the same biological significance but is less hazardous. It has a much shorter physical half-life and thus will not have a long-term environmental impact.

Both ^{90}Sr and ^{89}Sr are pure beta emitter, and ^{90}Sr decays to short-lived pure beta emitter ^{90}Y ($t_{1/2}$ = 64.05h), LSC is the major method for their measurement. For quantitative analysis of radiostrontium, strontium has to be separated from sample matrix and all other radionuclides before measurement [94]. Strontium is one of alkaline earth elements; it mimics calcium in its behaviour but much less abundance. The emphasis on the assay of radiostrontium has been focused on the separation chemistry, especially its separation from other alkaline earth elements and similar property radionuclides (^{226,228}Ra, ^{133}Ba, ^{210}Pb, etc.). These methods are mainly based on precipitation/co-precipitation, solvent extraction, ion chromatography or ion exchange, extraction chromatography or combination of these techniques [94].

The oldest method for radiostrontium determination is based on precipitation of $Sr(NO_3)_2$ in high concentration of HNO_3 (72%) solution by using fumic nitric acid for separation of strontium from most of elements including calcium, from yttrium and fission products by the hydroxide precipitation, and from barium, radium and lead by chromate precipitation. For pre-concentration of strontium, carbonate precipitation ($SrCO_3$) is often used. In this step, calcium and many other elements including metals are also precipitated. The method is efficient but not selective for strontium although it is still used in some labs. The main disadvantage of this procedure is its involvement of large amount of fumic nitric acid and chromate, which are more dangerous and harmful for the operators.

In the past decades, the extraction chromatography using the Sr•Spec resin has been widely used for the determination of radiostrontium. In this resin, a crown ether [bis-4,4'(5')-*tert*-butylcyclohexano-18-crown-6] in 1-octanol is grafted on an inert polymeric resin (Amberlite XAD-7 or Amberchrom CG-71ms) and packed it into a chromatographic column. The Sr Spec resin shows a high selectivity for strontium ions over calcium, magnesium and most other metals and fission products. In this method, the sample is first ashed or acid digested to transfer Sr to a solution, and then pre-concentrated using $SrCO_3$ or $Sr_3(PO_4)_2$ precipitation After dissolved and prepared in 2-8 M HNO_3 medium, the sample solution is loaded to the Sr Spec column. If phosphate precipitation was applied, $Al(NO_3)_3$ should be added to the solution to remove the effect of phosphate. The column is then rinsed using 8M HNO_3, and strontium adsorbed on the column is finally eluted with 0.05M HNO_3 solution. Strontium is strongly adsorbed on the Sr column, whereas most interfering elements, including yttrium, were removed with the feed and rinse solutions. Barium, lead and tetravalent neptunium and plutonium are also retained by the column, and an attention should be given to avoid these element enter to the eluate of Sr.

TRU column stacked with Sr resin column has been proposed to get a better decontamination for Ba, Pb, Pu, Th and U [20]. Sr resin method has been widely used for determination of radiostronium in various matrices such as water, soil, sediment and diet [95-98]. For rapid determination of radiostrontium in milk samples, HCl and trichloroacetic acid were first added to the sample to flocculate the suspended fat and proteins in milk after addition of stable strontium carrier. The strontium in the supernatant was then precipitated as carbonate and used for further separation using Sr Spec column [17]. For determination of radiostronium in steel and iron samples, a procedure was reported by using SrF_2/CaF_2 precipitation for separation of Sr from large amount of iron, following by Sr Spec column to purify strontium [96]. In general, the separations using Sr resin is considered simple, rapid, economic and safe.

Besides the Sr Spec resin provided by Triskem and Eichrom, other similar resins for separation of strontium have also been developed. AnaLig®Sr01 (or SuperLig® 620) resin is prepared by covalently bonding of ligand, most likely a variation of an 18-crown-6 (18C6) structure on silica gel [98]. Another one was prepared by grafting two extractants, 4,40(50)-bis-t-butylcyclohexano-18-crown-6 and di(2-ethyl-hexyl) phosphoric acid onto Amber chrom CG-71 [99]. These resins showed similar features in the separation of radiostrontium for the determination of ^{89}Sr and ^{90}Sr using LSC. However, they are not well commercialized and not easy to obtain. The most popular Sr resin is still the Sr Spec resin from Triskem and Eichrom.

The main limitation on the application of Sr Spec and similar resin in the determination of radiostronium is its low capacity for Sr and the interferences of high calcium and salt content in sample on the strontium separation. For a 1.5 g Sr Spec resin column, loading of no more than 5 mg Sr should be followed. For analysis of high Sr and Ca containing sample (e.g., bone ash), a big column or splitting sample into aliquots and loading to more Sr Spec. columns are needed [42]. For low-level environmental samples, large sample size is needed for determination of ultra-low level ^{90}Sr, which often contain large amount of stable Sr, Ca, Ba, other interfering elements and radionuclides, the simple extraction chromatography separation using Sr resin may not be suitable.

Chen et al. [100] reported a simple method for the determination of ^{90}Sr in environmental samples containing high Ca and Sr, such as in large volume of seawater samples (45 liters). In this method, strontium is first separated from seawater by co-precipitation of $CaCO_3$-$SrCO_3$ with the addition of stable strontium carrier of 0.3-0.5 g Sr and Na_2CO_3, the sample was heated to 90-95 °C and kept for 2 hour. The precipitation is separated by settling for overnight to remove the supernatant followed by centrifuging the remaining sludge. After dissolution of the $CaCO_3$-$SrCO_3$ using HCl, calcium is separated by hydroxide precipitation by the addition of NaOH to a final concentration of 0.5 M NaOH. In this condition, $Ca(OH)_2$ precipitate is formed, but strontium remains in the solution and separated from large amount of calcium. Strontium in the supernatant is then separated as $SrCO_3$ precipitate by the addition of Na_2CO_3. The formed $SrCO_3$ is dissolved in HNO_3 solution and kept for 2-3 weeks for ingrowth of ^{90}Y from ^{90}Sr. To this solution, yttrium carrier is added, and then strontium is separated by adding H_2SO_4 to form $SrSO_4$

precipitate In this case, Ba and Ra remaining in the sample are precipitated and removed from yttrium. ^{90}Y is then separated by adding oxalic acid to form yttrium oxalate precipitate, and ^{90}Y in the precipitate is measured using low background gas flow G-M counter (Risø detector) or LSC after dissolved in HNO_3. The decontamination factors for most of interfering elements/radionuclides (Ca, Ra, Ba) are higher than 10^3, and a detection limit of 5 mBq was achieved. The main feature of this method is its capacity to handle high calcium samples. Besides water samples (seawater, ground, river and lake water), this method has also been applied for the analysis of milk, bone and large size soil samples for ^{90}Sr [101].

Due to the short half-life, ^{90}Y (64 h) reaches equilibrium with ^{90}Sr in an only few weeks, they are normally in equilibrium in the environmental samples. Direct separation and measurement of ^{90}Y from the samples or separation of the ingrown ^{90}Y from the separated ^{90}Sr can be used to measure ^{90}Sr. Based on high adsorption of Y on an extraction chromatographic resin DGA (Triskem International), it was applied for separation of Y from the sample and separated strontium solution, the obtained Y solution was measured for determination of ^{90}Sr in the samples [96].

In addition, solvent extraction and ion exchange chromatography are also used for separating radiostrontium from various environmental matrices [94]. Tributyl phosphate (TBP) and bis-2-etytlhexyl-phosphoric acid (HDEHP) have been the most commonly used organic extractants to separate ^{90}Y from liquid samples, which is assumed to be in equilibrium with ^{90}Sr. Consequently, rapid assays of ^{90}Sr via ^{90}Y.

Regardless of the separation method, the separated Sr is finally prepared for LSC or Cerenkov counting. At the end of the separation procedure, strontium is precipitated as the carbonate or the oxalate, then dissolved in dilute HCl or HNO_3 acid and mixed with the LSC cocktail. The organic eluates/phase from the chromatographic columns or solvent extraction can be used for LSC measurement. Chemical yields of strontium and yttrium can be determined by gravimetric methods or atomic absorption spectrophotometry, flame photometry or using ^{85}Sr as a yield tracer. Stable Sr and Y originally present in the samples have to be considered in the measurement of the chemical yield, especially for the environmental samples which might contain significant amount of stable Sr and Y.

In the samples, especially shortly collected from a nuclear facilities or its surrounding environment, both ^{89}Sr and ^{90}Sr might present, the simultaneous determination of ^{90}Sr and ^{89}Sr by LSC is possible using several approaches. The separated strontium sample can be measured merely by LSC after mixing with scintillation cocktail or directly by Cerenkov counting or by measuring the sample first by Cerenkov counting followed by adding scintillation cocktail for LSC. Because the overlap of the beta spectra of ^{90}Sr and ^{89}Sr, the strontium sample is often measured twice at various times during the ^{90}Y ingrowth. Thereafter ^{90}Sr and ^{89}Sr activities can be calculated from the two independent counts in consideration of the contribution of ^{90}Sr, ^{90}Y and ^{89}Sr on the counts in different counting windows. The different counting efficiency for ^{90}Sr, ^{90}Y and ^{89}Sr and the time for ^{90}Y ingrowth and the ^{89}Sr decay have to be considered and corrected. When ^{90}Y is separated, its activity is often measured by Cerenkov counting immediately after the separation. If only ^{90}Sr is to be determined, this measurement is sufficient; but in the occurrence of ^{89}Sr, the combined ^{89}Sr and ^{90}Sr activity should be measured in the separated strontium sample.

For low activity samples with high ^{89}Sr/^{90}Sr activity ratios, accurate determination of ^{90}Sr is better to be measured by separation and measurement of the ingrown ^{90}Y using Cerenkov counting or G-M counter. In this method, strontium in the sample solution is first adsorbed onto the Sr Spec column, then waiting for 1-2 days to allow ingrowth of ^{90}Y on the column. The ingrown ^{90}Y is then elated from the column using 8M HNO_3 and used for Cerenkov counting. ^{89}Sr and ^{90}Sr are elated afterwards in the normal way using water or diluted HNO_3 (i.e., 0.05 M HNO_3) and measured by LSA. **Fig. 6** shows the spectra of ^{89}Sr, ^{90}Sr and ^{90}Y in the application where the measurement is based using two LSC windows. The detection limits by the current low-background LSA are typically less than 0.1 Bq (1– 2 hours count time).

Determination of ^{89}Sr and ^{90}Sr by Cerenkov counting is based on the fact that both ^{89}Sr and ^{90}Y can be detected by measuring the Cerenkov radiation (photons) in colourless aqueous solutions with about 40% and 60% counting efficiency, respectively, while the counting efficiency of ^{90}Sr is less than 1.4% because of the low energy of its beta particles. The ^{89}Sr activity is determined almost exclusively from the freshly separated strontium sample. Recounting is performed after some ingrowth of ^{90}Y from ^{90}Sr and the calculation of the concentrations of ^{89}Sr and ^{90}Sr is possible from these two counts.

Alternatively, ^{90}Y can be separated from the purified strontium sample after its ingrowth and counted separately. Although the efficiency of Cerenkov counting of ^{89}Sr and ^{90}Y is lower than that of LSC, the detection limits of Cerenkov counting for them are similar as the LSC because of the lower background in the Cerenkov counting. The Cerenkov counting techniques allow the use of ^{85}Sr as a yield tracer because it decays through electron capture, could not produce Cerenkov radiation; therefore, it is not detected by this counting.

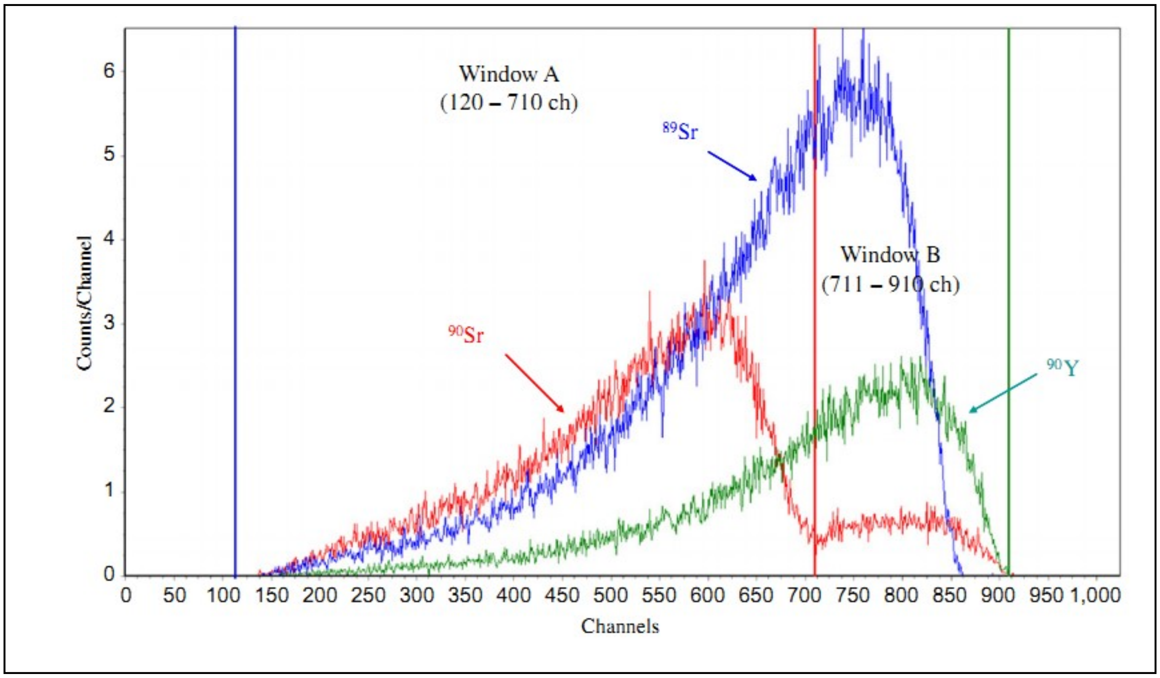

Fig. 6 LSC spectra of ^{89}Sr, ^{90}Sr and ^{90}Y. The spectrum of ^{90}Sr include small contribution of its daughter radionuclides of ^{90}Y.

Technetium-99

^{99}Tc is a fission product of ^{235}U and ^{239}Pu with relatively high fission yields (6.1 % from ^{235}U). ^{99}Tc in the environment mainly originates from nuclear weapons tests and nuclear fuel cycle operations, especially the releases from spent fuel reprocessing plants in Sellfield (UK) and La Hague (France) [102]. The principal reasons for the high interest in the analysis of ^{99}Tc in environmental samples are its very long half-life, high mobility and solubility as the pertechnetate ion (TcO_4^-) in oxidative conditions, and consequently its high transfer rate from soil to edible vegetation and from seawater to seaweeds. Under reducing condition, it can be reduced to Tc^{4+} and strongly bound to sediments. Studies on ^{99}Tc have focused on marine and coastal environments owing to discharges from nuclear reprocessing plants [6, 103-113]. ^{99}Tc is one of the most significant components in the disposal of nuclear wastes. In nuclear medicine, ^{99m}Tc ($t_{1/2}$ = 6 h) is used in high-activity amounts, which decay to ^{99}Tc, and becomes another source of ^{99}Tc in the environment. ^{99}Tc is a long-lived ($t_{1/2} = 2.11 \cdot 10^5$ y) pure beta emitter ($E_{\max}$ = 293.5 keV), and therefore can be measured by LSC after separation from sample matrices and all other radionuclides. It can be also measured by ICP-MS, in this case the chemical separation from the isobaric interference is the main challenge because of serious interference of the isobars (^{99}Ru and ^{98}Mo1H) of stable isotopes.

Chemical separation techniques including anion exchange, solvent extraction, selective precipitation, extraction chromatography and even a combustion technique have been used to assay ^{99}Tc in various environmental samples, nuclear effluent and waste samples. Technetium is a volatile element when presents as heptoxide, loss of technetium might also occur during sample preparation and separation, a caution has to be taken during evaporation or ashing. Shi et al. [105] investigated the stability of technetium in various chemical treatment steps including ashing of solid materials and evaporation of aqueous solution. It was found that no significant loss of technetium occurs in ashing of seaweed under 800ºC for less than 6 hours and under 500 ºC for soil and sediment samples. Evaporation of a solution in different concentration of HNO_3 to dryness at less than 100 ºC does not cause obvious loss of technetium, while significant loss of technetium happens in HCl media, especially in high concentration of HCl. However, if a small volume of solution (more than 0.5 mL) remained after evaporation, the loss of technetium can be highly reduced. Salt presenting in the solution can reduce the loss of technetium during evaporation.

^{99}Tc has no stable isotope to use as a carrier or for chemical yield monitoring. Although the analytical behaviour of rhenium is quite similar to that of Tc, these elements can behave quite differently under certain conditions; precautions need to be taken if rhenium is used as a tracer. ^{99m}Tc, obtained from a ^{99}Mo-^{99m}Tc generator has been used widely as a yield tracer in the radiochemical separation of ^{99}Tc for environmental samples, because it is readily available and its emission of gamma rays. The disadvantage of the ^{99m}Tc tracer is that it may contain ^{99}Tc, ^{99}Mo and ^{103}Ru as impurities, which may cause serious interference in the measurement of ^{99}Tc at low level, requiring correction for each tracer solution used [114]. Hou *et al.* [115] has developed a simple method to produce the ^{99m}Tc tracer solution that is pure enough to be utilized in the analysis of low-level environmental samples. The ^{99m}Tc-^{99}Mo generator was first eluted using saline water (0.9% NaCl) for 3-5 times to remove the accumulated ^{99}Tc in the generator through decay of ^{99m}Tc and ^{99}Mo, the new ingrown ^{99m}Tc is then eluted after a suitable ingrowth time (1 min – 3 hours). The obtained ^{99m}Tc solution is then purified by passing through an activated alumina cartridge to remove any ^{99}Mo and ^{103}Ru leaked from the column. The ^{99m}Tc activity is measured with a gamma spectrometer before preparing the sample for the LSC. Thereafter, the sample is stored for a week to allow ^{99m}Tc to decay completely before measuring the ^{99}Tc activity by LSC. Another possibility for a yield tracer would be to use ^{95m}Tc (half-life = 61 d). ^{95m}Tc decays through electron capture with emission of gamma rays, and can be measured through counting the low-energy auger electrons using LSC. Therefore, ^{99}Tc and ^{95m}Tc can be discriminated and measured by LSA.

Chemical separation methods are mainly based on a combination of selective precipitations, ion exchange and solvent extraction using different extractants like DB18-C6 crown ether (dibenzo-18-crown-6), *tri-n*-octylamine (TnOA) and *tri-n*-butyl phosphate (TBP). Separation of technetium using anion exchange chromatography is based on the very high affinity of TcO_4^- on the strong basic anion exchange resin in either diluted acid, alkaline or neutral media. Chen et al. [116] has reported a method for determination of ^{99}Tc in seawater and other environment samples. ^{99}Tc is first pre-concentrated from large volume of seawater samples (up to 200 L) using anion exchange chromatography. The filtered seawater is spiked with ^{99m}Tc tracer, and then loaded to a big anion exchange column (2.5 cm in diameter and 40 cm in length, AG1×-4 resin, Cl^- form). After rinsing with diluted NaOH and diluted HNO_3 solution, ^{99}Tc is eluted from the column using 8-10 M HNO_3. The eluate is evaporated to small volume (<10 ml), and treated with H_2O_2 and NaClO with heating to remove Ru. Afterwards, the solution is converted to 1M HSO_4 medium, ^{99}Tc in the solution is further purified by solvent extraction using 5% triisooctylamine (TIOA) in xylene. The overall recovery of ^{99}Tc is more than 75% and the most interference can be removed to be able to measure background level ^{99}Tc in seawater samples (0.003mBq/L) using up to 500 L seawater.

$Fe(OH)_3$ precipitation has been used to remove the radionuclides of transition metals, actinide and lanthanides, while Tc as water soluble TcO_4^- remained in the supernatant. In this case, the sample solution is better treated with oxidizing reagents (e.g. $K_2S_2O_8$, H_2O_2, etc.) to ensure all technetium is converted to TcO_4^-. Technetium extracted into tri-n-octylamine (TnOA) in xylene from H_2SO_4 medium was used to purify Tc from Ru, and the extracted ^{99}Tc in TnOA-xylene can be mixed with the scintillation cocktail for LSC measurement of ^{99}Tc [117].

Selective extraction chromatographic methods using TEVA•Spec resin (Triskem International) has become the most popular method for the determination of ^{99}Tc in environmental samples [103-105, 112]. The function group on TEVA resin is similar as anion exchange resin; TcO_4^- also shows a high affinity to TEVA resin. The sample is normally loaded in a neutral solution or in 0.1M HNO_3 solution to a TEVA column, Tc is retained, while most of other elements pass through the column. ^{99}Tc is finally eluted with 4−8 M HNO_3. Shi et al. [105] has reported a method for removing Ru from ^{99}Tc by pretreatment of the loading solution with 30% H_2O_2 in alkaline media, and found a significantly improvement in the removal of ruthenium in chromatographic separation using TEVA column. This might be attributed to the reduction of ruthenium in this process. In addition, TEVA also show a better removal of Mo from Tc. With two sequential TEVA column, Mo and Tc can be remove with a high decontamination factor [105].

Quantitative measurement of ^{99}Tc by LSC is viewed as a practical but also as the main approach, because of the more widespread accessibility of the LSAs, meanwhile it is also tolerance of isobaric ions interference (^{99}Ru and ^{98}Mo^{1}H), which is the major challenge in the ICP-MS measurement of ^{99}Tc. The LSC efficiencies of ^{99}Tc are typically in the range of 70−80% depending on sample composition and quenching. The backgrounds using low-background LSA (e.g. Quantulus LSA) are between 1.6−3.3 cpm and the detection limits of 17 mBq (2 hours count) can be achieved [89].

Tarancon et al. [5] has proposed concept to combine the chromatographic separation with scintillation for the determination of radionuclides using LSC. In this method, a plastic scintillation resin is synthesized, in which extraction reagent and scintillator are grafted on plastic beads. The plastic scintillation resin behaves as both extraction chromatographic resin and scintillator. The resin is prepared and uploaded to a column, the sample solution is loaded to the column, the target radionuclide is adsorbed on the resin, and the matrix and interfering radionuclides are removed by rinsing. The scintillation resin with the analyte radionuclide in the column is directly measured by ordinary LSC. This research group has reported a method for the determination of ^{99}Tc in environmental and waste samples [6]. A specific plastic scintillation resin was synthesized by drafting Aliquat 336 (trioctylmethylammonium chloride) as extractant to plastic scintillation microsphere. Here, the plastic scintillation microsphere (PSm) behaves like liquid scintillation cocktail but in a solid phase. PSm consists of a polymeric solvent and both primary and secondary scintillators, such as the classical PPO, POPOP, p-T or bis-MSB. Fluor molecules remain encapsulated inside the PS solid. **Fig. 7** shows schematic diagram of the determination of ^{99}Tc using the plastic scintillation resin.

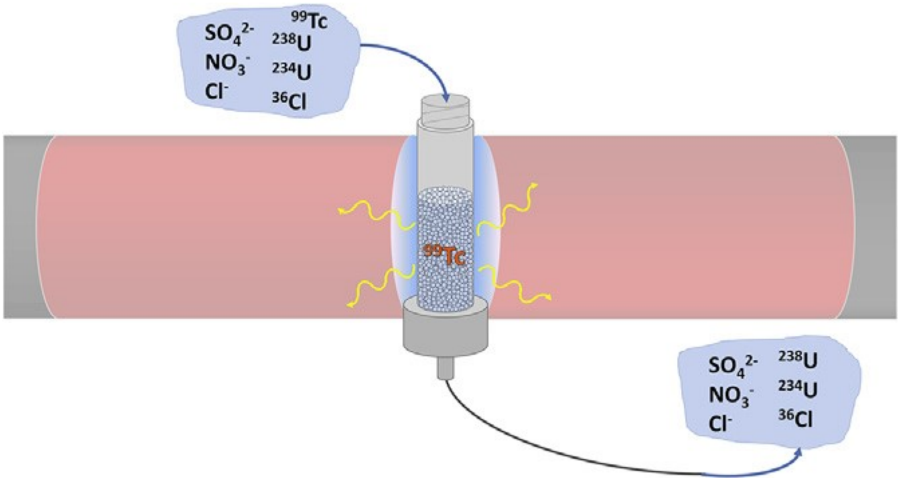

Fig. 7 Schematic diagram of plastic scintillation for determination of ^{99}Tc [6]

Iodine-129

^{129}I decays by beta emission with the maximum beta energy of 150 keV, accompanied with emission of low intensity (7.5%) 39.6 keV gamma ray and some 29.46 keV (20.4%) and 29.78 keV (37.7%) X-rays. It can be therefore measured by LSC and γ spectrometry, while LSC is more sensitive.

^{129}I is naturally present in the environment, generated mainly in the atmosphere from xenon by nuclear reactions induced by cosmic radiation. The concentration of natural ^{129}I in the environment is so low that it is not usually expressed as activity concentration but in proportion to the only stable isotope of iodine as ^{129}I/^{127}I atomic ratio. Before the nuclear age, the ^{129}I/^{127}I atomic ratio was about 10^{-12} in the sea and somewhat higher in terrestrial environment. ^{129}I in the present environment is mainly released from the human nuclear activities, including nuclear weapons tests, nuclear accidents, and emissions from nuclear facilities, the level of ^{129}I in the environment has risen, and the ^{129}I/^{127}I ratio has increased by several orders of magnitude, up to as much as 10^{-4} in the surrounding location of nuclear fuel reprocessing plants. The most extensive releases of ^{129}I to the environment occurred at the spent nuclear fuel reprocessing facilities at Sellafield (UK) and La Hague (France) since the early 1990s [118-120].

The very long half-life of ^{129}I (1.6×10^{7} y) means that its specific activity is very low (6.5×10^{6} Bq/g). Thus, radiometric methods including LSC are suitable only for samples in which the ^{129}I activity is high. Such samples are found in nuclear power plants and fuel reprocessing facilities, or environmental samples around the reprocessing plants. Radiometric methods are not sensitive enough for measuring the very low activity concentrations of ^{129}I in the environment. More sensitive methods are neutron activation analysis and especially accelerator mass spectrometry [118, 121].

Measurement of ^{129}I using LSC is mainly used for the analysis of nuclear waste or environmental samples collected in the contaminated site by nuclear activities (e.g. reprocessing plants or nuclear accident sites) [122-123]. For determination of ^{129}I in the ion exchange resin used in the purification of the primary circuit of nuclear power plants, the iodine in the resin is first extracted using NaOCl. In this case, iodide adsorbed on the exchange resin is oxidized to iodate, which has low affinity to the resin and eluted from the resin. After addition of KIO_3 solution as carrier, the iodate is reduced to I_2 using hydroxylamine hydrochloride in acidic media and extracted into CCl_4 phase. Afterwards, iodine is back extracted into water with $NaHSO_3$, which reduces I_2 to I^-. The iodide is then oxidized to I_2 with $NaNO_2$ in acid condition, which is extracted with toluene or $CHCl_3$. The iodine in the toluene is back extracted into aqueous solution with 0.01 M $NaHSO_3$. Scintillation cocktail is added to the aqueous solution and the activity of ^{129}I is measured by liquid scintillation counting. The detection limit of 0.6 Bq/L was achieved.

For solid samples, such as soil, sediment, vegetation, air particles, ^{129}I has to be separated from the sample matrix and then purified for its measurement using LSC or other techniques. Based on its volatility, iodine is often separated from solid samples by combustion to release iodine as gaseous form [124-126]. The released iodine is trapped in NaOH solution, which is then used to separate iodine by extraction with CCl_4 as described above for its measurement. In addition, alkali fusion can be also used to separate iodine from environmental samples, such as soil, sediment, air particles, vegetation and animal tissues [121, 127]. In this case, NaOH is then mixed with the sample. After dried, the mixture is ashed/fussed at 500-550 °C for 3-4 hours. The ashed/fused sample is leached with hot water, and the leachate is separated from residue by filtration. Iodine in the leachate is finally separated by CCl_4 extraction as described above [121, 127]. **Fig. 3** shows a combined procedure for determination of ^{129}I and ^{36}Cl in soil samples, in which alkaline fusion or acid digestion were applied for decomposition of samples and solvent extraction was applied for separation of ^{129}I from sample matrices and interference radionuclides. For the separation of iodine from water, milk and urine samples, especially large volume of seawater (30-50 liters), an anion exchange chromatographic method has been reported by Hou et al. [119, 120]. In this method, iodine in the water or other liquid samples is first reduced to iodide using $KHSO_3$ at pH<2, the sample is loaded to an anion exchange column (AG1×-4, NO_3^- form), the adsorbed iodine is then eluted with 2 M of $NaNO_3$ solution. The iodine in the eluate is separated by CCl_4 extraction. Iodine is finally obtained in a small volume of back extraction solution, which is used for LSC measurement or prepared in suitable target for neutron activation analysis or AMS measurement for ^{129}I.

Plutonium-241

Plutonium was released to the environment from nuclear weapons tests and nuclear fuel cycle operations particularly from reprocessing plants [89, 128]. There are mainly four isotopes of plutonium, ^{238}Pu ($t_{1/2}$ = 87.74 y), ^{239}Pu ($t_{1/2}$ = 2.41×10^4 y), ^{240}Pu ($t_{1/2}$ = 6563 y) and ^{241}Pu ($t_{1/2}$ = 14.4 y), present in the environment. Among them, only ^{241}Pu is a beta emitter with emission of low-energy β-particles (E_{max}= 21 keV). Although it is less radiotoxic than other alpha-emitting plutonium isotopes, ^{241}Pu decays to more toxic α-emitting ^{241}Am, makes it also an important radionuclides in the radiation protection. Meanwhile, the differences in the Pu isotopic ratios are good fingerprint to trace the origin of the environmental contamination and for nuclear forensics [89, 129, and 130]. Environmental monitoring of ^{241}Pu around nuclear facilities is needed and its determination in activity waste in nuclear fuel reprocessing cycles is important, as it will influence the method of final disposal.

Liquid scintillation is the major method for the measurement of ^{241}Pu, although mass spectrometry (ICP-MS) has also been used for its determination [38, 131]. ^{241}Am is the direct decay daughter of ^{241}Pu, therefore measurement of the ingrown ^{241}Am from ^{241}Pu using alpha spectrometry has also been used for determination of ^{241}Pu.

Many methods have been developed for the determination plutonium in environmental and nuclear samples, as summarized in four comprehensive reviews by [89, 128, and 132]. The chemical separation schemes of ^{241}Pu are normally complicated, because the concentrations of ^{241}Pu is normally very low, its oxidation states have to be considered during the separation, and plutonium has to be purified completely from other radionuclides in advance to avoid the interference. **Fig. 8** shows an often used analytical procedure for determination of plutonium isotopes. In general, plutonium is first released from the solid sample matrix by acid digestion or alkaline fusion followed by acid dissolution. The released plutonium in the sample solution or in liquid samples (water sample) is then pre-concentrated by co-precipitation of hydroxide, florid or phosphate. The precipitate is dissolved and plutonium is converted to Pu^{4+} valence state, which can be implemented by first reduced all plutonium to Pu^{3+} using strong reductant such as $KHSO_3$, and then oxidize Pu^{3+} to Pu^{4+} using $NaNO_2$, concentrated HNO_3 containing HNO_2 can be also used for this purpose. The prepared sample solution is loaded to an anion exchange column (e.g. AG 1x-4, or Dowex 1x-4) or TEVA extraction chromatographic column, followed by rinsing with HNO_3 to remove uranium and all transition elements and HCl for Th removal. Plutonium absorbed on the column is finally eluted by reducing it to Pu^{3+} using $NH_2\cdot OH$-HCl or using diluted HCl or diluted HF. The plutonium eluate is evaporated to dryness and dissolved in a small volume of diluted HCl for LSC measurement of ^{241}Pu.

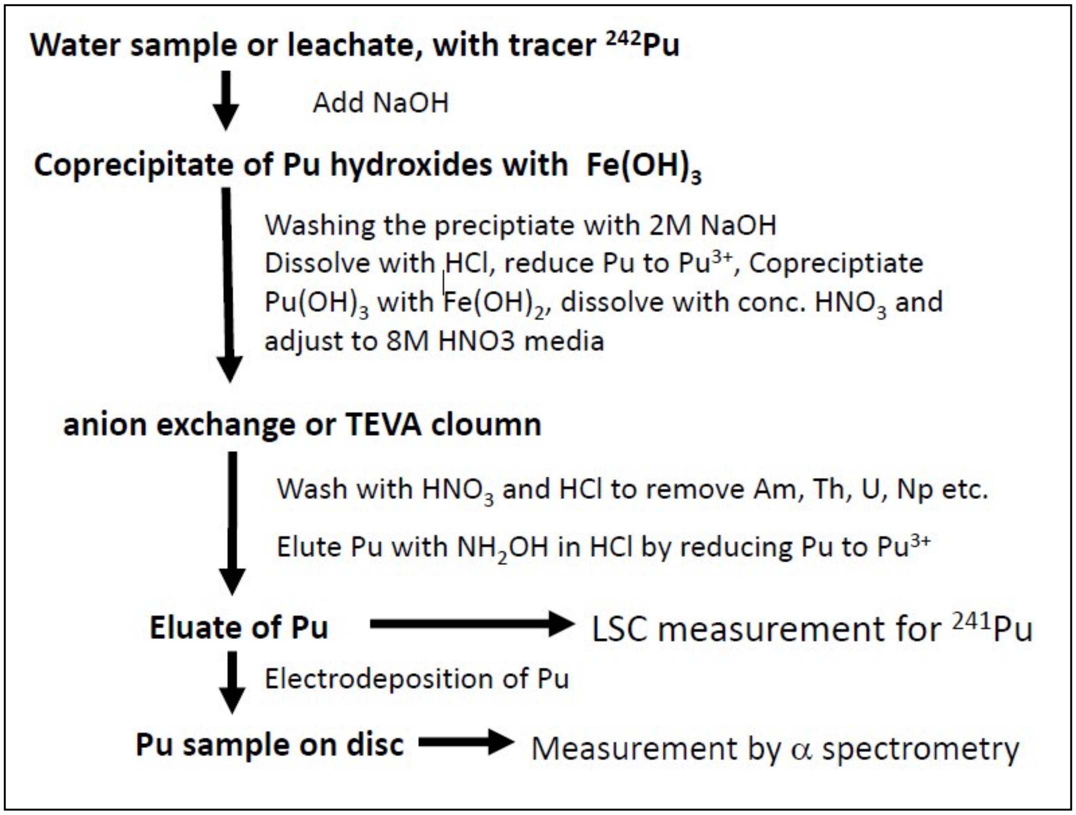

Fig. 8 Diagram of chemical separation procedure for determination of plutonium isotopes

^{241}Pu is a low-energy β-emitter, and LSC is the ideal measurement technique for determining its activity. While, other plutonium isotopes are alpha emitters, and often measured using alpha spectrometry. Therefore, ^{241}Pu and other alpha emitting plutonium isotopes are usually measured separately. This is often implemented that the separated plutonium is first electro-deposited on metal disc or micro-precipitated as NdF_3 co-precipitate on membrane filter and measured for alpha emitting plutonium isotopes (^{238}Pu, $^{239,240\text{Pu}}$ and ^{242}Pu as chemical yield tracer) [132]. Afterwards, the Pu sample on the disk or filter paper is dissolved and measured using LSC for determining the ^{241}Pu activity. The all alpha emitting plutonium isotopes measured by alpha spectrometry can be used as the chemical yield for the ^{241}Pu determination in LSC, which can be measured by using alpha-beta discrimination feature equipped in most of LSA. The Pu on the stainless steel is dissolved in concentrated HNO_3 and then purified by solvent extraction or ion exchange, which is necessary if some interfering elements like Fe and Pt are present in the solution with Pu [131]. They cause quenching and decrease the counting efficiency of ^{241}Pu and increase misclassification. The Pu alpha source prepared as co-precipitation of NdF_3 can be treated by dissolving Pu in a solution of H_3BO_3/HNO_3 and ethanol for LSC measurement of ^{241}Pu. The application of α/β discrimination feature in the LSC can also reduce interferences and background in the low-energy β-region of the ^{241}Pu. A typical β-spectrum of ^{241}Pu with α-peak of other Pu-isotopes is shown in **Fig. 9**. The detection limits for ^{241}Pu are of the order of 10–100 mBq per sample based on a 100–600 minute count time [89].

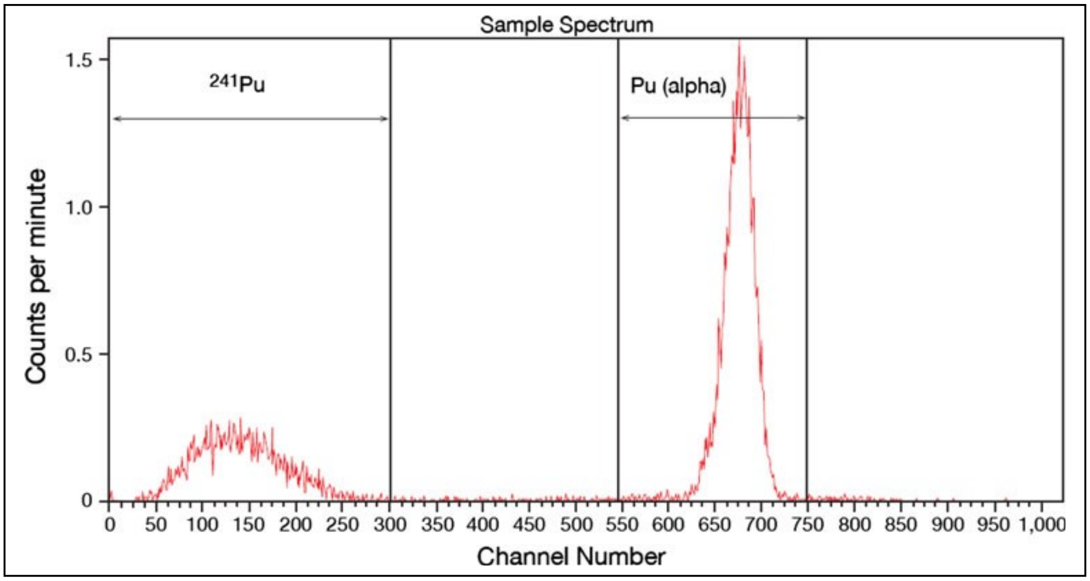

Fig. 9 LSC spectra of a plutonium sample measured by Quantulus [131]

Analysis for nature occurred radionuclides

Naturally occurred radionuclides are mainly decay chain radionuclides of ^{235}U, ^{238}U and ^{232}Th, ^{40}K and some cosmogonic radionuclides. However, the radionuclides measured using LSC are mainly those decay chain radionuclides of uranium and thorium, especially isotopes of Ra, Rn and Pb. In the past decades, LSC is becoming a popular method for measurement of gross alpha and gross beta in water samples for screen purpose.

Radon

There are three natural radon isotopes, ^{219}Rn, ^{220}Rn and ^{222}Rn, all are alpha emitter. The short-lived ^{220}Rn ($t_{1/2}$ = 55.6 s) and ^{219}Rn ($t_{1/2}$ = 3.96 s) are decay products of ^{232}Th and ^{235}U, respectively. ^{222}Rn ($t_{1/2}$ = 3.82 d) is the immediate daughter of ^{226}Ra in the ^{238}U decay series. Uranium and thorium occur in all rocks and soils at varying concentrations, the produced ^{222}Rn and ^{220}Rn in the rock and soil can diffuse from mineral grains into pore spaces and thereafter escape to air and dissolve in water. Because of very short half-life, ^{220}Rn moves much shorter distances before decaying, it is of concern only where the concentration of ^{232}Th is high. ^{219}Rn is not of significant concern for radiation exposure owing to its short half-life and to the low abundance of ^{235}U in natural uranium. Radon-222 is the most significant radon isotope; it presents in air, ground and surface waters. The most important mechanism of exposure is the inhalation of radon and its short-lived decay products with indoor air; ^{222}Rn also accounts for the majority of the human exposure to radiation and presents the largest risk to human health from all natural sources of radiation by increasing the risk of lung cancer [133]. Besides the diffusion from the ground and construction material, releases from radon-rich household water might be also an important reason of high radon in indoor air. Radon in drinking water presents an important risk by radiation exposure of cells in the gastrointestinal tract and in other organs. Radon concentrations in surface waters are typically less than 4 Bq/L, while in ground waters the concentrations vary over a wide range up to 10,000 Bq/L.

As an inert gas, radon is an excellent tracer either alone or together with radium for studying geochemical, hydrogeological and oceanic processes like groundwater discharge rates, groundwater seepage, vertical turbulent mixing, gas exchange across the air-water interface, mixing processes between ground- and seawater and submarine groundwater discharges [134-137]. In these studies, the radon concentration is determined in the field using an extraction method and a portable LSA or by bringing the sample into the laboratory for measurement with a low-background LSA.

For measurement of Ra in air using LSC, radon is first adsorbed on activated charcoal in a small vial during a few days. Afterwards, radon is extracted from the charcoal into toluene or directly into an organic scintillation cocktail to be measured using LSC [138-139]. Radon emanation rates from soil can be also measured by LSC [140-141]. In this case, dried soil is weighed into a glass vial, and wetted with distilled water; an organic scintillation cocktail is then added. The vial is closed tightly and stored for a month to attain the constant radon level emanated from soil before the measurement. Alternatively, radon can be trapped from the dried soil sample directly into the scintillation cocktail in a glass vial for measurement. This is performed in a tightly closed glass bottle where the soil is located at the bottom and the vial is hanging from a hook fixed into the stopper of the glass bottle [141]. The in situ measurement is performed by hanging an open LSC vial containing the cocktail inside a test hole or tube sunk into the soil [142].

Radon in water originates from the decay of ^{226}Ra, which is either dissolved in water or localized in rock or soil minerals in contact with water. Most of the radon in water originates from ^{226}Ra in minerals from where radon gas diffuses into pore spaces and dissolves in soil or ground water. Hence, most of radon in water is unsupported and therefore its concentration in water is often orders of magnitude higher than that of ^{226}Ra dissolved in the same water. However, radon will not be transported far from its place of birth owing to its short half-life. Special attention should be paid to sample collection and its transport when undertaking radon measurements. Radon can easily escape from water during the sampling as well the sample transport and storage if the sampling vials are not gas-tight, because radon is not highly soluble in water. Samples should also be collected into glass bottles, because some radon will be lost by adsorption onto the surface of polyethylene bottles and escaped from the bottle by migration through the polyethylene wall. The bottle caps should be equipped with rubber or Teflon™ septum to prevent radon leakage from the bottle. As a noble gas, ^{222}Rn is therefore difficult to be measured by alpha spectrometry. The most widely used methods for determining radon in water are radon emanation, gamma counting and LSC. Among these methods, the detection limit of gamma spectrometry (1-9 Bq/L) is quite high [143], a lower detection limit of 0.04−1.0 mBq L^{-1} can be reached by emanation method when using a big sample up to 19 L [144]. LSC is a popular method for measurement of ^{222}Rn in water; it is based on the detection of radon gas and its short-lived α-emitting daughters, whose decay properties are shown in Table 1.

Table 1. Members of ^{226}Ra subseries and their most significant decay properties.

Radio-nuclide	Half-life	α - decay energy (MeV) and intensity (%)	β-decay energy (MeV) and intensity (%)	γ-emission energy (keV) and intensity (%)
^{226}Ra	1600 y	4.784(93.8), 4.601(6.2)	-	186.2 (3.64)
^{222}Rn	3.82 d	5.489 (99.9), 4.986 (0.1)	-	510 (0.076)
^{218}Po	3.11 min	6.002 (100)	-	-
^{214}Pb	26.8 min	-	0.667 (45.9), 0.724 (40.2), 1.019 (11.0)	351.9 (35.6), 295.2 (18.4), 242.0 (7.3)
^{214}Bi	19.9 min	-	3.270 (19.1),1.540 (17.6), 1.505 (17.0) 1.423 (8.1), 1.892 (7.4), 1151 (4.4)	609.3 (45.5), 1764,5 (15.3), 1120.3 (14.9), 1238.1 (5.8), 2204.1 (4.9), 768.4 (4.9)
^{214}Po	164.3 µs	7.687 (100)	-	-

The LSC methods for measurement of ^{222}Rn are based on the high solubility of radon in organic solvents such as toluene and xylene or organic scintillation cocktail. Water samples can be prepared by introducing a small amount of water (10-12 ml) directly into the LSC vial containing the organic scintillation cocktail (8-10 ml). A low detection limit of (0.04–0.2 Bq L^{-1}) can be achieved by direct LSC methods by applying more than 60 minutes counting time and α/β discrimination [145]. This is because the counting efficiency of radon with its daughters (^{218}Po, ^{214}Po) in equilibrium can be as high as

270% and α backgrounds using α/β discrimination is also very low (<0.1 cmp) in a narrow energy alpha window. The main advantages of the LSC methods are their simple methodology, high sensitivity and automatic sample counting. If higher sensitivities are required, radon can be extracted from a larger water volume directly into the LSC scintillation cocktail or into toluene to be mixed with the cocktail. In this case, ^{222}Rn is usually extracted from 0.5−1 L water sample with 20−40 mL of extractant. After shaking and allowing the layers to separate, a known proportion of the extractant is transferred into the scintillation vial for the measurement. The detection limits obtained by these methods are 0.0015−0.02 Bq L^{-1} depending mainly on the count time and the sample volume.

Emulsifying cocktail (e.g. Ultima Gold XR) can be also used for the measurement of ^{222}Rn. In this case, two alpha (^{218}Po, ^{214}Po) and two beta decay daughters (^{214}Bi and ^{214}Pb) with ^{222}Rn are measured, a counting efficiency up to 500% can be obtained. However, due to the increased background level, the detection limit of ^{222}Rn by this method is not better than by using organic scintillation cocktail and alpha-beta discrimination method.

The glass vials equipped with urea screw caps and Al foil liners is often used in this measurement to be radon gastight. Low diffusion polyethylene vial with Teflon lined and Al lined cap was also used for this work. However, a long time storage should be avoid, otherwise a slow diffusion of Ra into the Teflon lined wall of the vial might be happened and cause a high analytical uncertainty.

Radium

Radium has four naturally occurred isotopes, ^{226}Ra ($t_{1/2}$ = 1600 y), which belongs to the ^{238}U decay series, ^{228}Ra ($t_{1/2}$ = 5.75 y) and ^{224}Ra ($t_{1/2}$ = 3.66 d), which belong to the ^{232}Th decay series and ^{223}Ra ($t_{1/2}$ = 11.43 d), which belongs to the ^{235}U decay series. Among these isotopes, ^{228}Ra is a beta emitter with maximum energy of only 39.6 keV, while other three are alpha emitters. Radium is widespread in soil, minerals, foodstuffs, surface and ground waters and many common materials. Radium-226 is considered as one of the most hazardous long-lived α emitters in the environment with respect to internal radiation exposure. As an alkaline earth element, radium is accumulated in the skeleton through a process similar to calcium. Food consumption is the main source of ^{226}Ra to man, but the radiation exposure through drinking water can be also an important source, or even be extremely high, if the drinking water originates from ground water sources in contact with uranium rich minerals like granites or phosphates. The regulations limit the maximum contaminant level in public water supplies for combined ^{226}Ra and ^{228}Ra to 0.19 Bq L^{-1} in the USA [146].The primary health concerns of radium have been directed to ^{226}Ra and ^{228}Ra and little attention has been given to the short-lived ^{224}Ra and ^{223}Ra. However, ^{224}Ra can make a significant contribution to elevated measurements of gross α-activities in some case. ^{226}Ra, ^{228}Ra, ^{224}Ra and ^{223}Ra in ground and surface waters have proven useful as natural tracers to study geochemical processes, particularly in the marine environment [135].

There are a variety of methods for determining one or more radium isotopes in environmental and food samples using different chemical separation and measurement methods [27, 146-147].

Radium isotopes can be determined by LSC, radon emanation, alpha and gamma spectrometry. The chemical separation methods are mainly based on precipitation, cation exchange, extraction, adsorption or a combination of these techniques. Several comparison studies have been made on the commonly used methods for determination of ^{226}Ra and ^{228}Ra [89, 148].

Alpha spectrometry is the most sensitive radiometric method because of its low background. In this method, radium must be separated carefully from the sample matrix and from other elements, including barium. Thereafter, radium is electrodeposited as a thin layer on a stainless steel disk or co-precipitated with $BaSO_4$ and/or $PbSO_4$, which is collected on a membrane filter, in order to avoid impairing the resolution and chemical yield, [86, 149]. The high resolution of alpha spectroscopy for low mass samples is enable to directly measure the concentrations of ^{226}Ra, ^{224}Ra and ^{223}Ra. ^{228}Ra can be measured directly from the same disk either by gamma spectrometry via the γ-emitting daughter, ^{228}Ac, after 2 days ingrowth or by alpha spectrometry via its α-emitting grand-daughter, ^{228}Th, after 6−12 months of ingrowth. The detection limits of ^{226}Ra and ^{228}Ra in environmental samples by alpha spectrometric methods are 0.1−0.5 mBq and 0.2–0.3 mBq, respectively, and 0.1–1 Bq and 0.1−0.3 Bq, respectively, by gamma spectrometry

[89, 150-151].

Radon emanation method is based on the separation and measurement of the radon and its daughters from radium isotopes. For large volume of water samples, radium isotopes can be first pre-concentrated on MnO_2 resin, followed by the emanation of their radon daughters (^{219}Rn, ^{220}Rn, ^{222}Rn) and measurement of these radon isotopes. A low detection limit can be obtained if a large size of sample is analysed.

Low background LSA with α/β discrimination is the most popular technique for determining ^{226}Ra activity. This is due to the high counting efficiency, easy sample preparation and automatic sample counting. The typical detection limits are between 0.3−1.4 mBq for a 6 hours count [89]. ^{226}Ra is generally determined indirectly through ^{222}Rn and its short-lived daughters or together with them by LSC. In this method, radium has to be separated from the sample matrices and concentrated. Ashing, acid digestion are the often applied method for pre-treatment of solid samples. The conventional method to separate ^{226}Ra from a sample matrix is the so-called barium sulphate method. The Pb- and Ba-carriers are first added into the water or sample solution to co-precipitate radium with $BaSO_4$ and $PbSO_4$ at pH 1 with H_2SO_4. The precipitate is washed a few times with HNO_3 and then dissolved in alkaline EDTA. For further purification and separating radium from lead, radium is precipitated again as sulphate using an acetic acid solution at pH 4.5 while lead remains in solution to be removed. The nitric acid wash and the re-precipitation of $RaSO_4$ in EDTA solution ensure high purification of radium from most interfering radionuclides. The chemical yield can be determined gravimetrically or by using ^{133}Ba (if only ^{226}Ra is measured) as a yield tracer. The Ra-$BaSO_4$ precipitates are prepared for the LSC measurement by suspending fine precipitates into a scintillation gel or by dissolving the precipitates in warm alkaline EDTA solution. $BaSO_4$ precipitate can be also converted to the more soluble $BaCO_3$, which is dissolved in HNO_3 and then mixed with the LSC cocktail. Measurement of the samples shortly after the separation using its own alpha peak can obtain the results rapidly after the sampling. In that case, the ^{228}Ra activity can be calculated from the β-counts with the least amount of corrections owing to minor ingrowth of ^{214}Pb and ^{214}Bi. The detection limits for ^{226}Ra, ^{228}Ra and ^{210}Pb are 0.5−2 mBq, 4 mBq, and 2−5.2 mBq, respectively. A better detection limit for ^{226}Ra can be obtained by using organic scintillation cocktail. In this case, the separated Ba-RaSO4 precipitate is dissolved in EDTA solution, which is transferred to LSC vial and filled with organic scintillation cocktail (e.g. Opti-Flour O). After 3-10 days ingrowth of ^{222}Rn, the vial was shaken to extract Rn to organic phase, and then measured by LSC using alpha-beta discrimination by counting its three alpha daughters (^{222}Rn, ^{218}Po and ^{214}Po).

Selective adsorption is also used for radium separation. One of them is the Empore™ Radium Rad Disk, which selectively adsorb radium from water with recoveries ranging from 90−100% for 1−3 L sample. In this method, water samples are first acidified with HNO_3 to a 2M and then passed through the disk. After washing the disk with 2M HNO_3, radium is eluted from the disk with 0.25M EDTA solution, which can be concentrated prior to mixing with the LSC cocktail. Lead, strontium and barium are co-separated with radium. High barium in the samples will reduce radium recovery considerably, and the interfering ^{210}Pb should be separated from radium either before or after the elution. The detection limits reported for the Empore™ Radium Rad Disk extraction method vary between 1−2 mBq, 4−8 mBq and 2−6 mBq for ^{226}Ra, ^{228}Ra and ^{210}Pb, respectively.

MnO_2-impregnated acrylic fibre cartridge and MnO_2 resin (impregnated MnO_2 on a modified polyacrylonitrile (PAN) supporting material) column are also used to concentrate radium from large volume of water samples. The sorption of Ra was especially favourable for low-salinity waters; it is also highly dependent on pH, with the best range of pH 4 to 8. At higher salinities, other alkaline earth elements (Mg, Ca, and Sr) compete with Ra for the free sorption sites in the MnO_2 resin. For determination of low-level ^{226}Ra in large volume saline water (seawater) samples, a MnO_2 co-precipitation method can be used. Water sample (>10 L) is first acidified using HCl to pH<2, followed by addition of $KMnO_4$ solution. After adjusting the pH to 9.0 using ammonia, $MnCl_2$ is added during stirring for forming MnO_2. MnO_2 precipitate which adsorbed radium is separated by settling and centrifuge. After washing with water, MnO_2 is then dissolved by addition of HCl and H_2O_2 [152]. Radium in the solution can be further purified by $Ba(Ra)SO_4$ precipitation for the measurement of ^{226}Ra by LSC.

Solvent extraction method was also applied for determination of radium. A commercial extractive scintillation cocktail RADAEX® was developed specifically for LSC measurement of radium [153]. The extraction of radium with RADAEX needs to be carried at alkaline media (pH10-12), large amount of metals in high salt content water will be precipitated in this condition. Therefore, this method cannot be directly applied for analysis of high saline water samples.

^{228}Ra is a low-energy beta emitter (39.6 keV), it is often measured indirectly through its daughter, ^{228}Ac and ^{228}Th. For high-level samples, ^{228}Ra can be simply measured through the gamma lines of ^{228}Ac by gamma spectrometry, or the beta spectrum of ^{228}Ac using LSC. While for the low-level samples with relative high ^{226}Ra, the daughters of ^{226}Ra (^{214}Bi, ^{214}Pb) presented in the samples might seriously interferes with the measurement of ^{228}Ac due to the low resolution of LSC. A method for pre-concentration and separation of ^{228}Ac was reported for reliable determination of low-level ^{228}Ra [154]. In this method, radium is first separated from the sample matrices by co-precipitation of radium with MnO_2, and then Ra is separated from other radionuclides (U, Th, etc.) by extraction chromatography using Diphonix resin, which effectively retains actinides and lanthanides while divalent cations like Ra and Ba pass through. Radium presented in the effluent and wash solutions from the Diphonic column are set aside for ingrowth of ^{228}Ac. Thereafter the solution is loaded to the second Diphonix resin column, the ingrown ^{228}Ac is retained on the column and separated from radium, which is then eluted using 1 M HEDPA (1-hydroxyethane-1,1 diphosphonic acid) directly into a plastic LS vial and mixed with LSC cocktail for measurement. The detection limit of 23.2 mBq was reported for 60 min counting time. The separated ^{228}Ac can be also measured by Cerenkov counting due to the high beta energy of ^{228}Ac (2.07 MeV)

Lead-210 [Bismuth-210 and Polonium-210]

^{210}Pb ($t_{1/2}$ = 22.2 y) decays by emitting β particles ($E_{\max}$ = 63.5 keV) with γ emission (E_γ = 46.5 keV) and internal conversion to the β-emitting ^{210}Bi ($t_{1/2}$ = 5.01 d, $E_{\max}$ = 1161.5 keV) which decays to the α-emitting ^{210}Po ($t_{1/2}$ = 138.4 d, E_α = 5.3 MeV) (**Fig. 10)**. As radionuclides of ^{238}U decay series ^{210}Pb, ^{210}Bi and ^{210}Po exist widely in rock, soil, atmosphere, waters, and food. ^{210}Pb and ^{210}Po belong to the most toxic radionuclides. The toxicity of ^{210}Po is mainly due to its two alpha-daughters ^{210}Bi and ^{210}Po, 79% of the internal dose following ingestion of uranium and thorium series radionuclides is caused by ^{210}Pb and ^{210}Po. The main intake of ^{210}Pb and ^{210}Po is derived from the food, the ^{210}Po concentrations are high in seafood like fish, molluscs and crabs, and high ^{210}Pb and ^{210}Po concentrations were found in reindeer and caribou meat. Drinking water usually constitutes a minor contribution to the normal intake of ^{210}Pb and ^{210}Po; but it can be significant for some population groups consuming ground water enrich with radon. The guideline value of WHO for ^{210}Pb and ^{210}Po in drinking water is 0.1 Bq L^{-1} [155], therefore, much effort is paid to analyses of ^{210}Pb and ^{210}Po in drinking waters. ^{210}Pb is widely used to date sediments in seas, lakes and estuaries, and most of determinations of ^{210}Pb in environmental studies are used for this purpose.

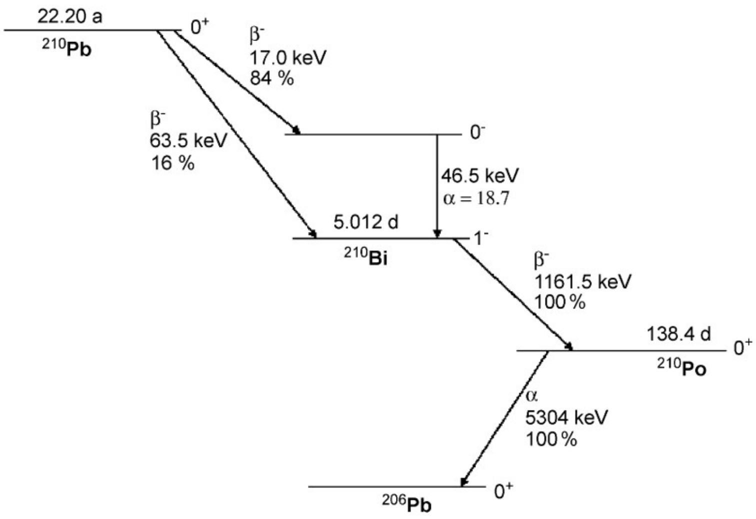

Fig. 10 Decay scheme for the ^{210}Pb subseries [156]

^{210}Pb can be directly measured by gamma spectrometry and LSC or beta counting (e.g. proportional counter), or indirectly measured by α-spectrometry through counting its decay daughter, ^{210}Po. Due to short half-life of ^{210}Bi (5.0 d), it is not often determined separately. The methods based on α and β counting require ^{210}Pb to be separated from the matrix and from other radionuclides. Because ^{210}Pb and ^{210}Po are found often in disequilibrium in biological and most environmental samples, they have to be analysed individually.

Due to the low intensity (4.25%) of low energy (46.5 keV) gamma ray of ^{210}Pb, the direct gamma spectrometric method requires to analyse large size of samples, long counting time, corrections for self-absorption and interference from other γ- and X-rays. The detection limit for ^{210}Pb was reported to be up to 0.4 Bq/sample for a 1000 min counting time, therefore not suitable for determination of ^{210}Pb in low-level samples.

Alpha spectrometric measurement of ^{210}Pb and ^{210}Po is based on two spontaneous depositions of ^{210}Po onto a silver (also Ni, Cu, steel) disc and on measuring the ^{210}Po activity, and the second deposition is implemented after a few months ingrowth of ^{210}Po from ^{210}Pb. Although the detection limit (0.1-0.2 mBq) is quite low, but a long analytical period is needed.

The energy of beta particles of ^{210}Pb (17.0 keV (84%) and 63.5 keV (16%)) is very low, the counting efficiency of LSC is low for directly counting the beta emission of ^{210}Pb, and sensitive to sample quenching. LSC measurement of ^{210}Pb is often carried out via its high beta energy daughter, ^{210}Bi (1161.5 keV) after some days ingrowth. However, Pb has to be separated form sample matrices and other radionuclides before LSC measurement. Precipitation of Pb as the sulphate, extraction chromatography and solvent extraction are the often used method for its separation.

The separation of ^{210}Pb by co-precipitation as Ba(Ra,Pb)SO_4 is a traditional method, by which radium isotopes and ^{210}Pb can be separated simultaneously. After the sample pre-treatments by ashing, acid digestion or alkali fusion, the chemical separation is started by adding stable Pb and Ba carriers as the yield tracers, followed by precipitation as the sulphate, the formed sulphate is then dissolved in alkaline EDTA. The separation of Pb from Ra is achieved by adjusting the EDTA solution of sample to pH4.2−4.5 of with acetic acid. The Ra precipitates with $BaSO_4$, while Pb remains in the solution. Afterward, the solution is further acidified to precipitate Pb as $PbSO_4$. The precipitate is washed with distilled water to remove other interfering radionuclides. The $^{210}PbSO_4$ can be prepared for LSC counting by suspending it in a scintillation gel or dissolving it in alkaline EDTA solution and then mixing with the LSC cocktail. The sample is often counted using LSC with α/β-discrimination, ^{210}Pb is determined from the spectrum of ^{210}Pb or the ingrown ^{210}Bi. ^{210}Pb can be also measured by Cerenkov counting of the ingrown ^{210}Bi, the potential interferences from alpha and soft beta emitters can be eliminated in this case, but the counting efficiency of Cerenkov counting is comparatively low (20%). An increased Cerenkov counting efficiency up to 75% was achieved through the use of Triton X-100 and sodium salicylate as enhancers. Under these conditions, ^{210}Po caused some interference, which was not present in the absence of the enhancers. When Cerenkov counting was used for measurement of ^{210}Pb through

^{210}Bi, no scintillation cocktail is needed; the EDTA dissolution of $PbSO_4$ is directly applied for measurement.

Extraction chromatography using Sr Spec resin have been applied for separation of ^{210}Pb and ^{210}Po for their determination in various environmental and biological samples [157-159]. This is based on the high adsorption of Pb and Po on this resin in diluted HCl solution, while ^{210}Bi does not retain on the column. In this method, the decomposed and pre-concentrated sample is prepared in 2M HCl and loaded to a Sr Spec column; ^{210}Po and ^{210}Pb absorbed on the column were eluted sequentially using 6M HNO_3 and 6M HCl, respectively. The HCl elute was evaporated to dryness followed by converting lead from chloride to nitrate and by precipitating it as the oxalate for the yield determination. ^{210}Po was determined by alpha spectrometry using ^{208}Po as the yield tracer after spontaneous deposition on a metal disc. The separated ^{210}Pb was determined by LSC after dissolving PbC_2O_4 into 1 mL of 6M HNO_3 and mixing with scintillation cocktail. In this method, ^{210}Po and ^{210}Pb were efficiently separated from other elements and interfering radionuclides [157].

Gross alpha and gross beta measurements

Gross alpha and gross beta activity measurement is often used for screening analysis in monitoring of environment, diet and contamination. Particularly, drinking water supplies are screened by the gross alpha and beta analysis method, which is a highly useful control measure for the radiological characterization of water and as a factor in the decision as to whether further analyses by radionuclide-specific methods will be required. Urine samples from the workers who potentially exposed to radioactive contamination is also often screened by gross alpha and gross beta measurement to obtain an overview on internal exposure of radiation. The guideline activity concentrations of water by WHO [155] are 0.5 Bq L^{-1} for gross alpha and 1 Bq L^{-1} for gross beta, respectively. Whereas the European Union [160] has set the screening values of 0.1 Bq L^{-1} for gross alpha and 1 Bq L^{-1} for gross beta.

Some volatile radionuclides are easily lost during the sample preparation, e.g. ^{3}H, ^{14}C and radon, these nuclides, as well as short-lived daughters of radon, are excluded from the gross alpha and gross beta screening analyses, which have to be determined by specific methods. In the normal situation, most important radionuclides to be screened by gross alpha and beta analyses in drinking water sources are the long-lived radionuclides, ^{234}U, ^{238}U, ^{226}Ra, ^{228}Ra and ^{210}Pb and ^{210}Po, from uranium and thorium decay series. ^{40}K occurs in variable amounts in all natural waters; and its contribution to the gross beta counts can be significant. However, its determination is not important, because potassium is under homeostatic control in the body and its amount remains constant in healthy people. Gross alpha and beta measurements are also used to screen transuranic elements and gross beta for fission products in the case related to the nuclear faculties and exposures.

The commonly used methods for gross alpha and beta analysis in drinking water are based either on the gas proportional counting (GPC) or on LSC techniques. In the GPC method, water sample is evaporated to near dryness, and then quantitatively transfer the residue to a planchet for measurement. The GPC method is tedious and labor-intensive, and the results are not precise owing to the inherent variability of the sample preparation technique and water composition. Meanwhile sample size is strongly limited due to the total dissolved solids (TDS) in the sample, which cause self-absorption of α-and β-particles, and the counting efficiency is affected by TDS and the chemical composition of water. The small sample size combined with the relatively low counting efficiency of the GPC makes it difficult to attain low detection limits even by applying very long counting times. The reported detection limits of the GPC methods are 0.8 Bq L^{-1} for the gross alpha and 3 Bq L^{-1} for gross beta using a 22 h counting time [161], which could not meet the requirement of the regulation for screening of the gross alpha in drinking water (0.1-0.5 Bq/L). In the LSC method, the water sample is directly or after some pre-concentration taken to a LSC vial, and mixed with the scintillation cocktail for LSC counting using α/β-discrimination. This avoids most of the difficulties typically in the GPC methods, although dissolved minerals or organics in water may cause variable quenching, which must be considered in the calibrations [161]. If the sample is pre-concentrated, the residue is often dissolved into a few mL of dilute HCl, HNO_3 or H_3PO_4 prior to the addition of the LS cocktail.

The calibrations of gross alpha and beta analyses include the optimization of the α/β discrimination performance and the determination of α- and β- counting efficiencies and spillovers in the selected α- and β-windows. The calibrations become more complicated if variable quenching is corrected, because the optimum pulse decay setting (optimal PSA value), as well as efficiencies, backgrounds and spillovers, depend on quenching. Hence, each sample should be measured at its optimum SPA setting, which is not a practical approach in routine measurements. Another drawback for performing precise calibrations is because the optimum SPA setting and alpha and beta spillovers depend on particle energies. The real samples may contain several α- and β-emitters with largely variable particle energies compared to those used for calibrations including the setting of the optimum SPA. The optimum SPA setting is highly effected for higher-energy α- and β-emitters than for lower-energy emitters. The β-spillover increases with β-particle energy while α-spillover decreases with α-particle energy. With increasing quench, the higher energy β-particle produces a higher spillover compared to the lower-energy particles, while the higher-energy α-particle produces a lower spillover compared to the low-energy particles at the same PSA level. In summary, the calibrations with appropriate quench corrections are necessary, although they would not provide accurate results for variably quenched samples with variable radionuclide composition. The calibrations would be simplest if the samples were unquenched and as similar as possible to the nuclides used for SPA instrument calibration. It is preferable to perform the calibrations with α- and β-emitters with the energies equal to the averages of the nuclides expected to be in actual samples to be analysed.

In a similar manner, gross alpha and gross beta activities may be determined for a range of other environmental matrices. A filter sample is simply placed in the LSC vial with the scintillation cocktail [162] for LSC measurement. Urine samples have been prepared by mixing urine directly with the cocktail [163] or after some processing which involves oxidation of organic substances, co-precipitation of actinides as phosphate, wet ashing using HNO_3 and H_2O_2, conversion of the nitrates to the chlorides, dissolution of the white residue in 0.2 M HCl followed by the addition of the cocktail [164].

Conclusion and perspectives

As a conventional radiometric method, LSC has been widely used for measurement of various radionuclides for different applications. Although this method has been used for more than 60 years, a continuous development and new applications still progress. The major progresses discussed in this paper with the perspective challenges are summarized below:

1) Communization of TDCR based LSA instrument makes this technique one of the popular LSC methods, and used in many radiochemical and environmental laboratory for the determination of radionuclides of beta emission, electron capture and alpha emitters, and in alpha/beta discrimination model and Cerenkov counting model as those in ordinary LSC.

2) With the rapid increased requirement in the decommissioning of nuclear facilities, a number of analytical methods for determination of radionuclides mainly occurred in decommissioning waste have been developed using LSC as measurement technique. This includes the methods for the determination of ^{36}Cl, ^{41}Ca, ^{55}Fe, ^{63}Ni, ^{99}Tc, ^{129}I, ^{241}Pu in various types of samples.

3) LSC is still a competitive method for the determination of pure beta emitting radionuclides including those decay by electron capture, especially for the short-lived ($t_{½}$<100 years) radionuclides, e.g. ^{3}H, ^{241}Pu, ^{89}Sr and ^{90}Sr. It can provide relative rapid and precise measurement compared to other methods,

4) LSC has been well used for determination of naturally occurred radionuclides, and still an attractive method for the determination of ^{222}Rn, ^{228}Ra and ^{210}Pb because of its easy operation, short analytical time, and reliable analytical results. LSC has also becoming more popular method for the determination of gross alpha and gross beta activity for screening purpose.

5) More LSC methods are still needed for the determination of other uncommon radionuclides for the decommissioning of nuclear facilities, e.g. ^{93}Mo, ^{93}Zr, ^{79}Se, ^{126}Sn, ^{151}Sm, etc. A challenge in this aspect will be the calibration and standardization of the LSC for the measurement of these radionuclides, because of luck of standard solution of these radionuclides, and not well established decay properties of these radionuclides.

6) Although an increased number of TDCR based LSA instruments have been installed

in many laboratories, the analytical methodology is still limited, and more method developments are still needed. With the introduction of the low background TDCR based LSA instrument, it is expected that this method will become a more popular LSC method in many application fields, e.g. environmental radioactivity and trace studies.

7) Plastic scintillation resins based LSC method has been proposed in the past years, and a number of such resins have been synthesized and tested for determination of different radionuclides, such as ^{99}Tc, ^{90}Sr and ^{210}Pb. This method can highly simplify the separation procedure and avoid the utilization of scintillation cocktail, and consequently reduce the organic waste. However, such scintillation resins are still limited and the methods need to be further validated for analysis of real environmental and nuclear samples with complicated components and matrices.

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