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Review article

Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples

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ABSTRACT

The radiometric methods, alpha (α)-, beta (β)-, gamma (γ)-spectrometry, and mass spectrometric methods, inductively coupled plasma mass spectrometry, accelerator mass spectrometry, thermal ionization mass spectrometry, resonance ionization mass spectrometry, secondary ion mass spectrometry, and glow discharge mass spectrometry are reviewed for the determination of radionuclides. These methods are critically compared for the determination of long-lived radionuclides important for radiation protection, decommissioning of nuclear facilities, repository of nuclear waste, tracer application in the environmental and biological researches, these radionuclides include ^{3}H, ^{14}C, ^{36}Cl, ^{41}Ca, ^{59,63}Ni, ^{89,90}Sr, ^{99}Tc, ^{129}I, ^{135,137}Cs, ^{210}Pb, ^{226,228}Ra, ^{237}Np, ^{241}Am, and isotopes of thorium, uranium and plutonium. The application of on-line methods (flow injection/sequential injection) for separation of radionuclides and automated determination of radionuclides is also discussed.

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Abbreviations: AMS, accelerator mass spectrometry; CPM, counts per minute; DMG, dimethyl glyoxime; DRC, dynamic collision/reaction cell; EC, electron capture; ETV, electrothermal vaporization; FIA, flow-injection/sequential injection analysis; FWHM, full width at half maximum; GDMS, glow discharge mass spectrometry; GFM, gas-filled magnet; Ge(Li), lithium drift germanium; GM, Geiger-Müller; HDEHP, 2-ethylhexyl phosphoric acid; HpGe, high pure germanium; HPLC, high performance liquid chromatography; ICP-MS, inductively coupled plasma mass spectrometry; ICP-QMS, inductively coupled plasma quadrupole mass spectrometry; ICP-SFMS, inductively coupled plasma sector field mass spectrometry; IISD, ion implanted silicon detector; LSC, liquid scintillation counter; MS, mass spectrometry; My, million years; NAA, neutron activation analysis; REEs, rare earth elements; RIMS, resonance ionization mass spectrometry; SIMS, secondary ion mass spectrometry; TIMS, thermal ionization mass spectrometry; TIOA, tri-isooctylamine; TOF-MS, time of flight mass spectrometry; TOPO, tri-*n*-octylphosphine oxide; TTA, thenoyl trifluoroacetone.

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Liquid scintillation counting
Gamma spectrometry
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Accelerator mass spectrometry
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Glow discharge mass spectrometry
Neutron activation analysis

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1. Introduction

There are many radionuclides naturally occurring in the environment, including the isotopes of uranium and thorium and their decay products, ^{40}K, and those produced from the cosmic ray reactions, such as ^{3}H, ^{7}Be, ^{10}Be, ^{14}C, ^{26}Al, ^{14}C, and ^{129}I. The interest in the determination of these radionuclides mainly comes from the application of them in geochronology (^{14}C, ^{10}Be, ^{210}Pb, etc.) and using them as environmental or paleoclimate tracers. In environmental samples with a high concentration of uranium and thorium, determination of radionuclides, such as ^{222}Rn, ^{226}Ra in air and drinking water is important in the view of radiation protection. Besides the naturally occurring radionuclides, a large number of radionuclides have been produced and released to the environment by human nuclear activity, including nuclear weapons testing, operation of nuclear power plants, research

Table 1 – Radionuclides interest in biological, environmental, and waste samples and their application

Nuclides	Atom mass	Half-life	Decay mode	Specific activity (Bq g^{-1})	Application fields
^{3}H	3.0161	12.3 y	β^-	3.57×10^{14}	EM, DN, MT
^{14}C	14.0032	5730 y	β^-	1.65×10^{11}	Dating, DN, EM
^{36}Cl	35.6983	0.301 My	β^-	1.22×10^{9}	DN, WD, TE
^{41}Ca	40.9623	0.103 My	EC	3.14×10^{9}	DN, WD, MT
^{55}Fe	57.9383	2.73 y	EC	8.36×10^{13}	DT, MT
^{60}Co	59.9338	5.27 y	β^-	5.88×10^{13}	EM, DM, WD
^{59}Ni	58.9343	76400 y	EC + β^+	2.94×10^{9}	DT, WD
^{63}Ni	62.9297	100.1 y	β^-	2.10×10^{12}	DT, MT, WD, ET
^{79}Se	78.9185	1.13 My	β^-	2.08×10^{8}	DT, WD
^{89}Sr	88.9075	50 d	β^-	1.09×10^{15}	EM
^{90}Sr	89.9077	29.1 y	β^-	5.06×10^{12}	EM, DN, WD
^{99}Tc	98.9063	0.211 My	β^-	6.34×10^{8}	EM, ET, WD
^{129}I	129.9050	15.7 My	β^-	6.49×10^{6}	ET, MT, WD
^{135}Cs	134.9060	2.3 My	β^-	4.26×10^{7}	ET, WD
^{137}Cs	136.9071	30.2 y	β^-	3.20×10^{12}	EM, WD, DN
^{210}Pb	209.9842	22.3 y	β^-	2.83×10^{12}	Dating, EM
^{226}Ra	226.0254	1600 y	α	3.66×10^{10}	EM, ET
^{228}Ra	228.0311	5.75 y	β^-	1.01×10^{13}	EM, ET
^{229}Th	229.0318	7340 y	α	7.87×10^{9}	ET
^{230}Th	230.0331	75380 y	α	7.63×10^{8}	EM
^{232}Th	232.0381	14050 My	α	4.06×10^{3}	EM
^{234}Th	234.0436	24.1 d	β^-	8.56×10^{14}	ET, EM
^{233}U	233.0396	0.1492 My	α	3.80×10^{8}	EM
^{234}U	234.0410	0.2455 My	α	2.30×10^{8}	EM
^{235}U	235.0439	703.8 My	α	8.00×10^{4}	EM, WD
^{236}U	236.0456	23.4 My	α	2.40×10^{6}	EM
^{238}U	238.0508	4468 My	α	1.24×10^{4}	EM, WD
^{237}Np	237.0482	2.144 My	α	2.60×10^{7}	EM, ET
^{238}Pu	238.0496	87.7 y	α	6.34×10^{11}	ET, EM
^{239}Pu	239.0524	24110 y	α	2.30×10^{9}	EM, ET, DN,WD
^{240}Pu	240.0538	6563 y	α	8.40×10^{9}	EM, ET, DN,WD
^{241}Pu	241.0568	14.35 y	β^-	3.82×10^{12}	EM, ET
^{242}Pu	242.0587	0.3733 My	α	1.46×10^{8}	EM
^{244}Pu	244.0640	80.8 My	α	6.71×10^{5}	EM
^{241}Am	241.0568	432.2 y	α	1.27×10^{11}	EM, ET, DN,WD

My: million years; d: day; EC: electron capture, β^+: positron emission; EM: environmental monitoring; DN: decommissioning of nuclear facilities; MT: medical tracer; ET: environmental tracer; WD, nuclear waste depository.

reactors, and nuclear fuel reprocessing. Nuclear accidents, such as the Chernobyl accident, have also released a large amount of radionuclides to environment [1]. Radionuclides applied in industry and hospital may also be released to environment, although most of them are short lived. For the radiation protection purpose, the level of these radionuclides in various environmental and biological samples needs to be determined. Meanwhile radionuclides released from the reprocessing plants can also be used as environmental tracer for the investigation of transport of water mass (^{134,137}Cs, ^{99}Tc, ^{129}I) and atmospheric circulation (^{129}I). In decommissioning of nuclear facilities and repository of nuclear waste, invitatory of radioactivity or concentration of various radionuclides in the waste samples need to be determined. Table 1 lists radionuclides with a half-life longer than 10 years (except ^{55}Fe, ^{60}Co, ^{234}Th and ^{89}Sr) which are often required to be measured in environmental, biological and waste samples, the application fields of these radionuclides are also presented. Table 2 lists the sources and the production reactions of these radionuclides except the naturally occurred ones. For great number of radionuclides with half-life of less than 10 years, the radiometric methods are exclusively used for their determination, which are therefore not discussed in this article.

Radionuclides are normally determined by their characteristic radiation, i.e. radiometric methods. In these methods, the decay rate (A, number of decays per unit of time) of the radionuclide of interest is measured, the atom number (N) of radionuclide of interest is calculated based on the statistical property of the decay of the radionuclide using its half-life ($T_{1/2}$): $N = A/\lambda = A/(\ln 2/T_{1/2})$. Mass spectrometric methods, which are normally used for determination of isotopes of elements, can be also used for the determination of radionuclides (radioactive isotopes of elements). In these methods, the atom numbers of the radionuclide of interest are directly measured.

Fig. 1 plots the specific radioactivity (Bq g^{-1}) vs. half-life of the radionuclide listed in Table 1. From this figure, it can be seen that the shorter the half-life of the radionuclide is, the higher the specific radioactivity of the radionuclides. It means that compared with the mass spectrometric method, the shorter the half-life of the radionuclide is, the more sensitive the radiometric method. In the other words, radiometric methods are generally sensitive for short-lived radionuclides,

Table 2 – The sources and main production reactions of radionuclides interest in the biological, environmental, and waste samples

Nuclides	Sources	Nuclear reactions for the production of radionuclide
$^{3}\mathrm{H}$	NWT, ONF, RP	$^{2}\mathrm{H}(n, \gamma)^{3}\mathrm{H}$; $^{3}\mathrm{He}(n, p)^{3}\mathrm{H}$; $^{6}\mathrm{Li}(n, \alpha)^{3}\mathrm{H}$
$^{14}\mathrm{C}$	CRR, NWT, ONF, RP	$^{14}\mathrm{N}(n, p)^{14}\mathrm{C}$; $^{13}\mathrm{C}(n, \gamma)^{14}\mathrm{C}$; $^{17}\mathrm{O}(n, \alpha)^{14}\mathrm{C}$
$^{36}\mathrm{Cl}$	CRR, NWT, ONF, RP	$^{35}\mathrm{Cl}(n, \gamma)^{36}\mathrm{Cl}$; $^{40}\mathrm{Ar}(p, n\alpha)^{36}\mathrm{Cl}$; $^{36}\mathrm{Ar}(n, p)^{36}\mathrm{Cl}$; $^{39}\mathrm{K}(n, 2n2p)^{36}\mathrm{Cl}$; $^{40}\mathrm{Ca}(n, 2n3p)^{36}\mathrm{Cl}$; $^{40}\mathrm{Ca}(\mu^{-}, \alpha)^{36}\mathrm{Cl}$; $^{39}\mathrm{K}(n, \alpha)^{36}\mathrm{Cl}$
$^{41}\mathrm{Ca}$	NWT, ONF	$^{40}\mathrm{Ca}(n, \gamma)^{41}\mathrm{Ca}$
$^{59}\mathrm{Ni}$	NET, ONF	$^{58}\mathrm{Ni}(n, \gamma)^{59}\mathrm{Ni}$
$^{63}\mathrm{Ni}$	NET, ONF	$^{62}\mathrm{Ni}(n, \gamma)^{63}\mathrm{Ni}$; $^{63}\mathrm{Cu}(n, p)^{63}\mathrm{Ni}$
$^{79}\mathrm{Se}$	ONF, RP	$^{78}\mathrm{Se}(n, \gamma)^{79}\mathrm{Se}$; $^{235}\mathrm{U}(n, f)^{79}\mathrm{Se}$
$^{89}\mathrm{Sr}$	NWT, ONF, RP	$^{235}\mathrm{U}(n, f)^{89}\mathrm{Sr}$; $^{88}\mathrm{Sr}(n, \gamma)^{89}\mathrm{Sr}$
$^{90}\mathrm{Sr}$	NWT, ONF, RP	$^{235}\mathrm{U}(n, f)^{90}\mathrm{Sr}$
$^{99}\mathrm{Tc}$	ONF, RP, NOR	$^{235}\mathrm{U}(n, f)^{99}\mathrm{Tc}$; $^{98}\mathrm{Mo}(n, \gamma)^{99}\mathrm{Mo}(\beta)^{99}\mathrm{Tc}$
$^{129}\mathrm{I}$	NWT, ONF, RP	$^{129}\mathrm{Xe}(n, p)^{129}\mathrm{I}$; $^{235}\mathrm{U}(n, f)^{129}\mathrm{I}$; $^{127}\mathrm{I}(2n, \gamma)^{129}\mathrm{I}$
$^{135}\mathrm{Cs}$	NWT, ONF, RP	$^{235}\mathrm{U}(n, f)^{135}\mathrm{Cs}$
$^{137}\mathrm{Cs}$	NWT, ONF, RP	$^{235}\mathrm{U}(n, f)^{137}\mathrm{Cs}$
$^{237}\mathrm{Np}$	ONF, RP	$^{238}\mathrm{U}(n, 2n)^{237}\mathrm{U} \rightarrow {}^{237}\mathrm{Np}$; $^{235}\mathrm{U}(n, \gamma)^{236}\mathrm{U}(n, \gamma)^{237}\mathrm{U} \rightarrow {}^{237}\mathrm{Np}$
$^{238}\mathrm{Pu}$	ONF, RP	$^{235}\mathrm{U}(n, \gamma)^{236}\mathrm{U}(n, \gamma)^{237}\mathrm{U}(\beta^{-})^{237}\mathrm{Np}(n, \gamma)^{238}\mathrm{Np}(\beta^{-})^{238}\mathrm{Pu}$, $^{238}\mathrm{U}(n, 2n)^{237}\mathrm{U}(\beta^{-})^{237}\mathrm{Np}(n, \gamma)^{238}\mathrm{Np}(\beta^{-})^{238}\mathrm{Pu}$
$^{239}\mathrm{Pu}$	ONF, RP	$^{238}\mathrm{U}(n, \gamma)^{239}\mathrm{U}(\beta^{-})^{239}\mathrm{Np}(\beta^{-})^{239}\mathrm{Pu}$
$^{240}\mathrm{Pu}$	ONF, RP	$^{238}\mathrm{U}(n, \gamma)^{239}\mathrm{U}(\beta^{-})^{239}\mathrm{Np}(\beta^{-})^{239}\mathrm{Pu}(n, \gamma)^{240}\mathrm{Pu}$
$^{241}\mathrm{Pu}$	ONF, RP	$^{238}\mathrm{U}(n, \gamma)^{239}\mathrm{U}(\beta^{-})^{239}\mathrm{Np}(\beta^{-})^{239}\mathrm{Pu}(n, \gamma)^{240}\mathrm{Pu}(n, \gamma)^{241}\mathrm{Pu}$
$^{242}\mathrm{Pu}$	ONF	$^{238}\mathrm{U}(n, \gamma)^{239}\mathrm{U}(\beta^{-})^{239}\mathrm{Np}(\beta^{-})^{239}\mathrm{Pu}(n, \gamma)^{240}\mathrm{Pu}(n, \gamma)^{241}\mathrm{Pu}(n, \gamma)^{242}\mathrm{Pu}$
$^{241}\mathrm{Am}$	ONF, RP	$^{238}\mathrm{U}(n, \gamma)^{239}\mathrm{U}(\beta^{-})^{239}\mathrm{Np}(\beta^{-})^{239}\mathrm{Pu}(n, \gamma)^{240}\mathrm{Pu}(n, \gamma)^{241}\mathrm{Pu}(\beta^{-})^{241}\mathrm{Am}$

NWT: nuclear weapons testing; ONF: operation of nuclear facilities; CRR: Cosmic ray reaction; NOR: normal occurring radionuclide; RP, reprocessing plants.

while mass spectrometric methods are sensitive for long-lived radionuclides.

Several informative review articles on the mass spectrometric determination of long-lived radionuclides have been published in recent years [2–9], in which the performance, progress, and interferences of mass spectrometric methods have been discussed in detailed. A few review paper on brief evaluation of radiometric method and mass spectrometry is also available [10]. Rosenberg [11] reviewed the non-conventional measurement techniques for the determination of several long-lived radionuclides in nuclear fuel in 1993. In this article, the authors compared the radiometric methods and neutron activation analysis with mass spectrometric methods. With the significant progress of mass spectrometric techniques, especially inductively coupled plasma mass spectrometry (ICP-MS), the mass spectrometric techniques become more and more popular method for the determination of long-lived radionuclides. An overview review of traditional radiometric techniques with the recently improved mass spectrometric methods can help the analysts and researchers to choice more suitable techniques and also improve the analytical capacity and analytical quality, while such a work is not available. This articles aims to compare the radiometric methods with various mass spectrometric methods for the determination of radionuclides in biological, environmental and waste samples. In which, different radiometric methods, such as gamma (γ)-spectrometry, alpha (α)-spectrometry, and beta (β) counting, and mass spectrometric methods, such as ICP-MS, accelerator mass spectrometry (AMS), thermal ionization mass spectrometry (TIMS), resonance ionization mass spectrometry (RIMS), secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) and their application for the determination of radionuclides are compared. Neutron activation analysis (NAA) method is discussed for the determination of some radionuclides. In addition, the application of on-line methods (flow injection/sequential injection) for separation of radionuclides and automated determination of radionuclides is also discussed.

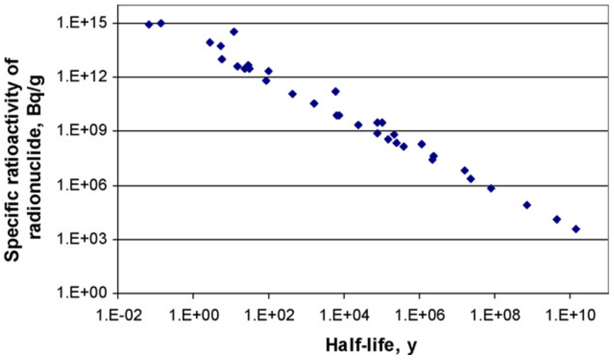

Fig. 1 – Plot of the specific radioactivity (Bq g^{-1}) vs. half-life of the radionuclides listed in Table 1.

2. Radiometric methods

Radionuclides are unstable, they de-excite to stable state by radioactive decay with a specific rate (half-life, $T_{1/2}$). The radioactivity of radionuclide (A) can be expressed as: $A = N \times (\ln 2/T_{1/2}) = N_0 \exp(-0.693 \times t/T_{1/2}) \times (\ln 2/T_{1/2})$, here N is atoms number at time t; and N_0 is atoms number at beginning. There are several types of processes in the de-excitation of radionuclides, i.e. α decay, β decay, electron capture, internal conversion, γ-ray emission, and spontaneous fission. In α decay, the radionuclide is de-excited by emitting an α-particle ($^{4}_{2}\mathrm{He}^{2+}$) with specific energy. The α radionuclide (decay by emitting α-particles) can be measured by α-spectrometry. β decay is a de-excitation process of the radionuclide by emitting an electron (β^-) or a positron (β^+), meanwhile, an antineutrino or neutrino is also emitted, they share the energy with the beta particle in the radioactive decay. Therefore, the resulting beta particles have a continuous distribution of energies from 0 to maximum decay energy. A beta emitter (emitting β^- particles) can be measured by beta counter, such as Geige-Müller (GM) counter or a liquid scintillation counter (LSC). While radionuclides decay by β^+ emission can be measured by γ-spectrometry, because β^+ decay is followed by emitting two annihilation photons each having energy of 511 keV. Electron capture (EC) is a decay process where an atomic-shell electron is captured by the nucleus, this can be considered as an inverse of β^+ decay, but the electron spectrum is discrete, because the energy of the captured electron has a well-defined value. EC is followed by X-ray and/or Auger electrons emission. The radionuclides with EC decay can therefore be determined by measuring their specific X-ray using X-ray spectrometry or by measuring Auger electrons using a liquid scintillation counter. The excited nucleus which formed as a consequence of α or β decay of radionuclide can de-excite by emitting γ-rays with specific energy. The radionuclides with emission of γ-rays can be determined by γ-spectrometry. A radionuclide may have more than one decay process, in this case it can be measured by more radiometric methods, for example, ^{129}I is a β-emitter, but also emitting γ-rays with a energy of 39.6 keV, which can be measured by both beta counting as well as γ-spectrometry. The advantages of three main radiometric methods are discussed below.

2.1. *Alpha spectrometry*

There are several types of detector that can be used for the measurement of alpha-emitting radionuclides; examples are Frisch grid ionization chambers, proportional counters, plastic- and liquid scintillation detectors and semiconductor detectors. Ionization chambers normally have a high counting efficiency, but have very poor energy resolution unless equipped with a shielding Frisch grid preventing induction from the positive ion-cloud and thereby enabling fast collection of the generated electrons. Frisch grid ionization chambers are therefore only used ionization chamber for total alpha activity measurements. Proportional counters as well as liquid scintillation counters both have the advantage that the alpha emitter can be placed inside the counter, thereby reaching 4π counting efficiency. In both cases energy resolution is generally poor and for spectrometric use these detectors play only a minor role. Semiconductor detectors are normally used for the determination of α-emitting radionuclides in the environmental and waste samples, especially when spectrometric information is needed. Both surface barrier and ion-implanted silicon semiconductor detectors are widely used in α spectroscopy because of the relatively good counting efficiency and their superior energy resolution. The counting efficiency of this detector varies with size of the source and detector as well as with the source–detector distance, and is typically between 10% and 45%. The energy resolution presented as full width at half maximum (FWHM) of a peak ranges normally from 15 to 55 keV depending on the distance of source to detector, and the size and thickness of the source. The high charge (+2) and relatively low speed of alpha particles results in significant energy losses even in very thin absorbers. The longer distance the source to the detector is, the better the resolution (the narrower the FWHM) due to a smaller space angel and therefore a shorter passage through the source of the alpha particles reaching the detector. Table 3 shows the energies of some interesting α emitters in the analysis of environmental and waste samples. Although the resolution of semiconductors for α-spectrometry is good, the relatively small difference in alpha particle energy between some alpha emitters makes it difficult to spectrometrically separate the peaks. This is usually the case with isotopes such as ^{241}Am and ^{238}Pu, and ^{237}Np, ^{233}U, ^{234}U and ^{230}Th. It is therefore that a good chemical separation of radionuclide of interest from the matrix and interfering radionuclides is required; otherwise, the self-absorption of α particles in the source will not only reduce the counting efficiency, but also worsen the energy resolution of the α spectrum. For this reason it is essential that a thin source is prepared in α-spectrometry. This can be carried out by electro-deposition on stainless steel disks. Evaporation, co-precipitation, electrospraying, electrostatic precipitation, spontaneous deposition, molecular plating, and vacuum sublimation are also used to prepare α source [12], but the energy resolution of α-spectrum of the source prepared by many of these methods varies considerably because of the thickness of the source, especially, the evaporation and co-precipitation methods. A recently developed absorption method supplied a simple and thin alpha source, which is based on the sorption of some radionuclides such as radium onto a thin manganese oxide film [13].

The procedure blank contribution to the sample counts is a very important factor affecting the detection limit of any method. In α-spectrometry, with a good chemical separation and source preparation, the blank contribution for artificial radionuclides can usually be kept low (<0.15 count per hour), while corresponding numbers for naturally occurring radioisotopes are somewhat higher but most of all have a much larger variability. In environmental samples, the concentration of radionuclides is normally very low; it requires a long counting time (1–10 days for the activity of radionuclide lower than 10 mBq) to acquire a low counting uncertainty. In the author's laboratory, the procedure blank count rate of α-spectrometry is normally lower than 2 counts per day, the corresponding detection limit is less than 0.1 mBq for a counting efficiency of 30%. Table 3 lists the detection limits of radionuclides of interest in the environmental and waste samples in unit of nanogram. It can be seen that the detection limit of α-spectrometry is very good. For the radionuclides with a half-life shorter than 1 million years (My), the detection limit by α-spectrometry is lower than 10^{-12} g.

The main disadvantage of α-spectrometry is the long analysis time, which is a result of the long chemical separation procedure for the complete separation of the target radionuclide(s) from the matrix as well as from interfering radionuclides, and the very long counting time (1–30 days). This makes the analytical capacity low for this method. Due to the relatively low price of standard alpha spectrometry equipment, the radiochemistry- and environmental radioactivity laboratory is normally equipped with several detector units to meet the required analysis of large number of samples. In addition, it is also cheaper to run and maintain α-spectrometry

Table 3 – Energies of α particles of radionuclides and detection limit of α-spectrometry

Radionuclide	γ-Rays (abundance)	Energy of main α particles (MeV) (abundance)	Detection limits[a] (ng)
^{226}Ra	186.2 (3.65%)	4.78 (94.5%), 4.60 (5.5%)	1.95×10^{-6}
^{229}Th	193.5 (4.5%), 86.4 (2.6%)	4.85 (56.2%), 4.90 (10.2%), 4.81 (9.3%), 5.05 (6.6%), 4.97 (6.0%), 4.84 (5.0%), 4.98 (3.2%)	9.05×10^{-6}
^{230}Th	67.7 (0.37%)	4.69 (76.3%), 4.62 (23.4%)	9.34×10^{-5}
^{232}Th	63.8 (0.26%)	4.01 (78.2%), 3.95 (21.7%)	17.55
^{233}U	97.1 (0.02%)	4.82 (84.4%), 4.78 (13.2%),	1.78×10^{-4}
^{234}U	53.2 (0.12%)	4.77 (71.4%), 4.72 (28.4%)	3.09×10^{-4}
^{235}U	185.7 (57.2%), 143.8 (11.0%)	4.40 (55%), 4.37 (17.2%), 4.21 (5.7%), 4.60 (5.0%), 4.56 (4.2%)	0.89
^{236}U	49.4 (0.078%)	4.49 (73.8%), 4.45 (25.9%)	2.97×10^{-2}
^{238}U	49.6 (0.064%)	4.20 (79.0%), 4.15 (20.9%)	5.73
^{237}Np	29.4 (15.0%), 86.5 (12.4%),	4.79 (47.9%), 4.77 (33%), 4.64 (6.2%), 4.66 (3.3%)	2.74×10^{-3}
^{238}Pu	43.5 (0.039%)	5.50 (70.9%), 5.46 (29.0%)	1.12×10^{-7}
^{239}Pu	51.6 (0.027%)	5.16 873.3%), 5.14 (15.1%)	3.10×10^{-5}
^{240}Pu	45.2 (0.045%)	5.17 (72.8%), 5.12 (27.1%)	8.48×10^{-6}
^{242}Pu	44.9 (0.036%)	4.90 (77.5%), 4.86 (22.4%)	4.87×10^{-4}
^{244}Pu		4.59 (80.6%), 4.55 (19.4%)	0.11
^{241}Am	59.5 (35.9%)	5.49 (84.6%), 5.44 (13.0%)	5.61×10^{-7}

[a] The detection limit of alpha spectrometry was supposed to be 0.1 mBq.

equipment, this makes this method low cost in the view of measurement. However, from the above it is obvious that normal separation procedures for α-spectrometry is not suitable for fast analysis in emergency situations, which requires getting the analytical results in a shorter time (less than 1 day). A number of modified, rapid procedures have therefore been worked out to handle such situations for different radioisotopes in various matrixes.

2.2. *Gamma spectrometry*

Many α and β decay radionuclides also emit γ-rays; they can therefore be determined by γ-spectrometry. A number of detectors can be used for the measurement of γ-rays, such as scintillation counter using NaI, CsF and ZnS as scintillator, gas filled counter, and semiconductor detectors based on lithium doped Si or high purity Ge, CdTe, and GaAs. However, since their introduction to the market in 1970s, mainly Si(Li) and Ge (lithium drift germanium Ge(Li)) semiconductor detector are widely used for the γ-spectrometry measurement of radionuclides in the biological, environmental and nuclear waste samples, because of their high energy resolution. The later development of Ge detector in 1980s by using high pure germanium detector makes the maintenance of the detector easy, because HpGe detector can be kept at room temperature without damage. It is therefore, more Ge(Li) detectors were replaced by HpGe detector in many radioanalytical laboratories, although the performance of both detectors are similar. The recent development in the γ-spectrometry is the introduction of large-volume Ge crystal, which significantly increases the counting efficiency to 100–150% (relative counting efficiency) [14], this is very useful for the analysis of environmental and waste samples.

Si(Li) detector or small planar Ge detector are normally used for the measurement of low energy γ-rays and X-rays (<100 keV) with an energy resolution of 0.15 keV at 5.9 keV, while larger Ge detector are better suited for high energy γ-rays (>25 keV) and normally have an energy resolution better than 2 keV at 1332 keV. Due to the property of electromagnetic radiation, γ-ray can penetrate a long distance in the samples without significant absorption, especially high energy γ-rays. Sample usually does not need any treatment before counting, which makes the analysis quick and easy, and minimizes the risk of contamination during sample preparation. It is therefore that the radionuclides with emission of suitable energy γ-rays are normally measured by γ-spectrometry, such as ^{60}Co, ^{65}Zn, ^{54}Mn, ^{94}Nb, ^{106}Ru, ^{133}Ba, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, and ^{241}Am. However, the counting efficiency of γ-spectrometry is low (<10% for absolute counting efficiency) and varies with the γ-ray energy, distance of source to the detector and the size of the Ge or Si crystal. In addition, the background count rate of γ-spectrometry is normally high (>10 counts per hour for 661.7 keV γ-ray of ^{137}Cs and >25 counts per hour for 59.5 keV γ-ray of ^{241}Am) and varies with the total radioactivity of sample and the shielding of the detector. The detection limit of γ-spectrometry (>50 mBq) is typically a few orders of magnitude higher than β counting and α-spectrometry, but depends on the detector shielding, radionuclide of interest and interfering radionuclides. Due to the often superior detection limits of alpha spectrometry, trace level of the alpha emitting radionuclides listed in Table 1 are determined exclusively by α-spectrometry except ^{241}Am, which can be measured by γ-spectrometry when the concentration is not too low.

2.3. *Beta counting*

Beta- or electron emitting radionuclides are normally measured by gas ionization detector, such as ionization chamber, gas flow GM detector, or liquid scintillation counters (LSC). GM counter is normally used for radionuclides emitting higher energy electrons due to the absorption of low energy electrons in the thin window separating the sample and gas volume. LSC has an advantage in measuring low-energy electron emitters due to the absence of attenuation when the sample is immersed within the scintillator. LSC can thus be used for the measurement of both high and low energy β-emitters. Due to the continuous energy distribution of the emitted electrons in the beta decay, beta particle spectrometry is a poor way for identifying individual contributions in the beta spectrum. Determination of beta particle emitters therefore requires chemical separation of the radionuclide of interest from all other radionuclides before counting. Even so, several radioisotopes may present of one element (e.g. ^{89}Sr and ^{90}Sr) and even if the isotope emits electrons at discrete energies (e.g. from internal transition and/or electron capture decay with subsequent Auger electron emission) the electron cascade emitted due to the subsequent filling of electron shell vacancies still results in a complicated energy distribution which prevents accurate analysis of several electron emitters in parallel. In LSC, the relatively poor energy resolution still enables the identification of foreign activity while for the GM-counter, which lacks energy resolution, any foreign activity in the sample has to be determined by other means, e.g. by checking the half-life of the isotope by repeated counting or by its energy using absorbers of different thickness between sample and counter. The absorption of electrons in matter is less than for α-particles, especially for high-energy electrons. However, in order to minimize self-absorption in the sample and maintain a high counting efficiency, samples for GM counting needs to be prepared as a thin solid source which can be carried out by the same method as used for the α-spectrometry, the very often used method is electro-deposition and/or micro co-precipitation. The counting efficiency of a GM counter varies from 10% to 70% with the energy of the emitted electrons, thickness of the source, and counter properties. For the analysis of environmental and low-level waste samples, a low-level GM counter is required. This is mainly achieved by reducing the background count rate of the detector by using heavy lead shielding and a GM guard detector above the sample detectors, operating in anti-coincidence mode with the sample detector(s). A background count rate of 0.1 counts per minute (CPM) was reported for a commercial low-level GM counter produced at Risø National Laboratory, Denmark, and the detection limit reported is less than 1.5 mBq for ^{99}Tc and ^{90}Sr [15–17].

Table 4 lists radionuclides typically measured by beta counting and their approximate detection limits. The GM counter cannot be used effectively for the determination of radionuclides emitting low energy electrons, such as ^{3}H, ^{14}C, ^{129}I, and ^{241}Pu, because of high absorption of these β-particles in the detector window, LSC has to be used in this case. Besides the capability of being able to measurement low energy β^- emitters, LSC also has the advantage of none or minimal self-absorption, high counting efficiency, homogeneous distribution of the sample in the scintillation cocktail, relative simple sample preparation procedure, and easy standardization using internal or external standard. Another capability of LSC is the determination of isotopes decaying by emitting a high proportion of conversion electrons or by electron capture, such as ^{41}Ca and ^{55}Fe, which is carried out by the measurement of the Auger electrons produced during these decay processes. However, due to the low energy of the Auger electrons (<20 keV), the counting efficiency of LSC for radionuclides decaying by these processes is low (<30%) [18,19]. Comparing with the GM counter, the background count rate is higher in LSC, the lowest count rate measured using the commercial Quantulus^{TM} Ultra low-level LSC produced by Wallac, Perkin-Elmer is around 0.5 CPM for the ^{3}H window and 1.5 CPM for the ^{99}Tc window while the background for the anticoincidence shielded GM counter may be as low as 0.1–0.2 CPM, this makes the detection limit of LSC is worse than using low-level GM counters (Table 4). In addition, the quench correction is another drawback of LSC, which requires an extra work for acquiring accurate results.

3. Mass spectrometry

Inorganic mass spectrometry is extensively used for the determination of element concentrations in the trace and ultra-trace range by measuring the number of atoms of isotopes of the element. It has therefore also been used for the

Table 4 – Energies of β particles of the radionuclides and the detection limits of beta counting methods [15–19]

Radionuclides	Decay	E_{max} (keV) (abundance)	Ld of LSC		Ld of GM detector	
			mBq	ng	mBq	ng
^{3}H	β^-	18.6	12.50	2.50×10^{-8}		
^{14}C	β^-	156.5	17.14	7.41×10^{-5}		
^{36}Cl	β^-	708.6	14.0	8.10×10^{-3}	4	2.33×10^{-3}
^{41}Ca	EC		15.00	3.41×10^{-3}		
^{55}Fe	EC		15.00	1.28×10^{-7}		
^{63}Ni	β^-	66.9	20.00	6.78×10^{-6}	10	3.39×10^{-6}
^{79}Se	β^-	151.1	15.00	0.072	8	0.038
^{89}Sr	β^-	1459.1	22.45	1.47×10^{-8}	4	2.62×10^{-9}
^{90}Sr	β^-	546	18.89	2.66×10^{-6}	4	5.64×10^{-7}
^{99}Tc	β^-	293.7	18.75	0.021	5	5.62×10^{-3}
^{129}I	β^-	154.2	17.14	1.88		
^{135}Cs	β^-	269.3	18.75	0.313	5	0.0835
^{210}Pb	β^-	17.0 (84%), 63.5 (16%)	33.33	8.40×10^{-6}	15	3.78×10^{-6}
^{228}Ra	β^-	39.4 (50%), 25.7 (20%), 12.8 (30%)	20.00	1.41×10^{-6}		
^{234}Th	β^-	199.1 (70.3%), 106.5 (26.8%)	18.57	1.55×10^{-8}		
^{241}Pu	β^-	20.8	30.00	5.59×10^{-6}		

determination of radionuclides (radioisotopes of elements) for more than 25 years [20–22]. Solid-state mass spectrometric methods, such as laser ablation ICP-MS [23,24], GDMS [25–27], and SIMS [28], allow direct determination of radionuclides in solid samples without any chemical preparation. This makes the analysis very simple and minimizes the risk from the contamination due to the limited sample handling. However, the interpretation and quantification of analytical results in solid-state mass spectrometry is a problem due to the complex dependence on signal strength and abundance of polyatomic species on the sample composition and structure. Also luck of suitable (matrix-matched) standard reference materials frequently prevents the quantification of data. In addition, the detection limit for many radionuclides is not sufficient for the direct analysis of environmental samples; chemical separation of the elements of interest from the matrix is one way for increasing the signal strength and limiting interferences (but will increase the blank) but the essential point in techniques like LA-ICP-MS or SIMS is to obtain spatial information of isotopes or elements and chemical modification of the sample is in these cases of limited interest. ICP-MS, TIMS [29,30], AMS [31,32] and RIMS [33,34] are very sensitive mass spectrometric techniques for the determination of ultra trace levels of isotopes, and have been widely used for the determination of ultra-low levels of selected radionuclides and the precise determination of isotopic ratios. Several review articles have addressed the application of mass spectrometric techniques for the determination of radionuclides [2–9,35].

3.1. *Inductively coupled plasma mass spectrometry*

ICP-MS is the most frequently used mass spectrometric technique for the determination of elements and isotope ratios in the trace and ultratrace concentration range. In recent year, it has also increasingly been used for determination of radionuclides in environmental, biological and waste samples [2–7,24,35]. In contrast to conventional inorganic solid mass spectrometric techniques, ICP-MS allows a simple sample introduction in an ion source operating at atmospheric pressure and an easy quantification procedure using aqueous standard solutions [8]. With laser ablation system coupled to an ICP-MS, direct analysis of solid samples can be performed. In ICP-MS, the chemical compounds contained in the sample solution are decomposed into their atomic constituents in an inductively coupled argon plasma at a plasma temperature of approximately 6000–8000 K, and the high temperature ensures a high degree of ionization (>90% for most elements) with a low fraction of multiply charged ions (∼1%). The positively charged ions are extracted from the inductively coupled plasma (at atmospheric pressure) into a high vacuum of the mass spectrometer via an interface. The extracted ions are then separated by mass filters of either quadrupole type time of flight or combination of magnetic and electrostatic sector, and finally measured by an ion detector. The detection limit of ICP-MS varies from 10^{-15} to 10^{-8} g depending on interferences and the sensitivity of the instrument. In low-resolution mode, the sensitivity of double-focusing sector field ICP-MS is generally higher than conventional quadrupole ICP-MS instruments. Similarly the precision for isotope ratio measurements using double focusing sector field ICP-MS with single ion detection is somewhat better than quadrupole ICP-MS (around 0.1% or better vs. 0.1–0.5% for quadrupole). Better precision of isotope ratio measurements (one order of magnitude) can be achieved by use of multi-ion collector device in sector field ICP-MS.

The major problem in determination of radioisotopes using ICP-MS is the appearance of isobaric interferences of other elements at the same mass, such as ^{129}Xe interfering with ^{129}I and ^{238}U with ^{238}Pu. Another important interference is from polyatomic ions, such as ^{238}U^{1}H and ^{204}Pb^{35}Cl which interferes with ^{239}Pu. Some of these polyatomic species may be resolved from the element of interest using double-focusing sector field ICP-MS at a required mass resolution, but in this case the sensitivity will be reduced due to the strong collimation of the ion-beam. In quadrupole ICP-MS, the application of a collision/reaction cell (DRC) can significantly suppress the interfering isobaric ions by choice of an appropriate reaction gas. The low abundance sensitivity (or tailing) of ICP-MS is another drawback which limits its application for the determination of radionuclides. Several review articles have addressed the applications and limitations of ICP-MS for the determination of radionuclides [2–9]. Because of the high sensitivity, short analysis time and relatively easy operation, ICP-MS has been widely used for the determination of isotopes of uranium, thorium, and plutonium, ^{79}Se, ^{90}Sr, ^{99}Tc, ^{129}I, ^{135}Cs, ^{210}Pb, ^{226}Ra, ^{228}Ra, ^{231}Pa, ^{237}Np, ^{241}Am, ^{243}Am, and ^{244}Cm in environmental and waste samples [36–70].

3.2. *Accelerator mass spectrometry*

AMS emerged in the late 1970s from nuclear physics laboratories and soon became used as an ultra-sensitive mass spectrometric technique for measuring isotopes of elements, and is now widely used for the determination of radionuclides, especially long-lived radionuclides, such as ^{3}H, ^{10}Be, ^{14}C, ^{26}Al, ^{32}Si, ^{36}Cl, ^{41}Ca, ^{53}Mn, ^{59}Ni, ^{129}I, ^{182}Hf, ^{210}Pb and actinides [31,71,72]. Almost all AMS facilities can be understood as two mass spectrometers (called “injector” and “analyzer”) linked with a tandem accelerator. The radionuclide of interest is first prepared as a solid target, and then injected to the system as a negative ion by ion sputtering (e.g. using a Cs^+ primary ion source). The sputtered negative ions from the sample is pre-accelerated and mass analyzed by a magnet. Since not all elements form negative ions, isobaric interferences can be effectively suppressed in some important cases. In the case of ^{14}C, ^{41}Ca and ^{129}I, isobaric interferences are eliminated because ^{14}N, ^{41}K, and ^{129}Xe respectively do not form stable negative ions. The mass analyzed negative ions are then accelerated to the positive high-voltage terminal of a tandem accelerator where they encounter either a thin carbon foil or low-pressure gas. Several electrons may be stripped off, converting negative ions to multiply charged positive ions (e.g. $^{129}I^{7+}$). The stripping process has the advantage that it dissociates molecular ions if enough electrons are stripped off which results in a further elimination of interferences. The positively charged ions from the accelerator then pass through a magnetic analyzer, where the ions of interest with a well defined combination of charge state and energy are selected, and directed to a detector. Furthermore, the higher energies of the ions after acceleration allow an additional separation of the wanted ions from possible background ions at the particle detector. A range of ion detectors have been employed in the AMS system, of them, charged particle semiconductor detectors are only used for the measurement of the energy of ion, ionization chambers can measure both total energy of an ion as well as its rate of energy loss in the detector, time of flight systems are normally used for the measurement of energy of heavy ions such as for ^{129}I. In addition, gas filled magnets (GFM) and X-ray detector have also been used in AMS measurement. The above features make this method possible to measure isotopic ratios well below 10^{-10}, where many interesting long-lived radionuclides in the environment are expected. This is one of the reasons why AMS is among the most sensitive measurement methods for many long-lived radionuclides, or even only method for measuring some specific long-lived radionuclides, such as ^{10}Be, ^{26}Al, and ^{32}Si. However, due to high price, there are less than 100 AMS facilities installed worldwide, in which most of them are mainly used for the routine analysis of ^{14}C for dating purpose. Although many installed AMS have the capability for the analysis of many long-lived radionuclides mentioned above, but most of these AMS only determine very few of these radionuclides in routine. The main drawback with AMS is that it is only applicable to those elements that form negative ions during the sputtering process. A further drawback with AMS facilities is the lack of flexibility in changing from one element of interest to another. This usually may require changing sputtering conditions, beam-line set-up and detector configuration which may require several days of work. A comprehensive review of AMS analytical technique has been given by Fifield [31], Skipperud and Oughton [73] reviewed the main application of AMS in environmental research.

3.3. *Thermal ionization mass spectrometry*

TIMS has been used for the determination of isotopic composition and concentration of different elements including radioisotopes of some elements, such as uranium, thorium and plutonium since 1980s [5,29,74–83,22,84–88]. In TIMS a small volume (down to 1 μL) of aqueous solution containing the target nuclides or element in the nanogram to microgram range is deposited on a cleaned filament surface (mostly high-purity Re) and evaporated to dryness. The most frequently applied technique in TIMS works with two heated filaments (one for evaporation of the sample and the other for ionization of evaporated atoms) which are arranged opposite to each another. Due to the low initial energies (0.1–0.2 eV) of the ions formed on the hot thermal surface, mostly single magnetic sector field mass spectrometers are sufficient for ion separation. The introduction of fully automated thermal ionization mass spectrometers with multi-detector system over the last two decades has enhanced the capabilities of TIMS in many aspects. These include the possibility of achieving high internal precisions (0.001% or better on isotope ratios) using internal normalization methodology to correct for the isotope fractionation during analysis, as well as applying interfering element correction methodology to correct for the isobaric interference. The limiting factors for the accuracy of measured isotopic ratios in TIMS are mass discrimination in the TIMS instrument (e.g. ion optical system or ion detector) and mass fractionation effects (caused during the evaporation of sample, where the measured isotope ratio changes with time). These inherent effects limiting the capability of isotope ratio measurements by TIMS can be considered by different internal calibration techniques or by using isotopic standard reference materials with well-known isotopic ratios for an element. Besides, U, Th and Pu, TIMS has also been used for many other radionuclides, such as ^{41}Ca, ^{241}Am, ^{242}Cm, ^{126}Sn, ^{226}Ra, ^{228}Ra [82,89–92].

3.4. *Resonance ionization mass spectrometry*

RIMS as a highly selective and sensitive mass spectrometric technique for ultratrace and isotope analysis has been used for the determination of many radionuclides such as ^{41}Ca, ^{90}Sr, ^{99}Tc, ^{135}Cs, ^{210}Pb, ^{236}U, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, and ^{244}Pu in environmental, biological and waste samples [33,34,93–104]. In RIMS the solid or liquid samples are vaporized and atomized by an atomic beam source (e.g. in an atomic beam oven by thermal vaporization on a hot Re filament or by evaporation of sample using an electron beam). One or in most cases more lasers are tuned precisely to the wavelength required for the excited states and ionization of evaporated atoms in order to obtain a highly selective resonance ionization of the element of interest. RIMS offers a number of outstanding properties comparing to other mass spectrometric techniques, such as nearly complete isobaric suppression demonstrated to be better than 10^8, obtained by the uniqueness of optical transitions, especially in multi-step excitations; high overall sensitivity with detection limits in the 10^{-15} to 10^{-18} g range, enabled by the high ionization efficiency, high transmission mass spectrometers, and low background ion detection; high isotopic selectivity with values of 10^{13} and higher, which is achieved by combining isotope abundance sensitivity of the mass spectrometer and optical isotope selectivity in the laser excitation process. Due to these advantages, RIMS has found broad acceptance in various analytical fields, particularly ultratrace determination of long-lived radioisotopes. At present there are no commercial RIMS-instruments available which makes the technique rather rare compared to the other mass spectrometric techniques described.

3.5. *Secondary ion mass spectrometry*

SIMS is a surface analytical technique, and mainly applied for surface mapping and depth profiling of elements and/or isotope ratios. A depth resolution in the low nanometer range depending on sputtering technique may be obtained. In the lateral plans, SIMS are able to perform a microlocal analysis in the sub-micrometer range (e.g. for analysis of local inclusion or impurities). It is quite often used for the characterization of small particles, aerosols, as well as liquid or solid inclusions. SIMS can be applied for the characterization of bulk material with detection limits down to the low nanogram per gram range. SIMS allows precise isotope ratio measurements with precisions between 0.01% and 1%, by the application of multiple ion collectors, a precision of 0.002% can be reached. However, the quantification of analytical results in SIMS is very difficult due to large matrix effects. Nevertheless, if a matrix matched standard reference material is available for SIMS, accurate analytical data can be obtained.

In SIMS, solid sample surface is sputtered by bombardment with a focused primary ion beam (Ga^+, Cs^+, O_2^+ or O^-), the sputtered ions (secondary ions) are separated by mass spectrometer according to their mass-to-charge ratios, the separated secondary ions is then collected for pulse or current measurement, as quantifiable mass spectra, as in-depth or along-surface profiles, or as distribution images of the sputtered surface. SIMS has also been used for the determination of radionuclides, especially radionuclides in environmental "hot" particles and spatial distribution of radionuclides in materials [9,27,28,105–114].

3.6. *Glow discharge mass spectrometry*

GDMS was established as a powerful and efficient analytical method for direct trace element determination and depth profile analysis of solids [26,27,115–117]. In GDMS, an argon gas glow discharge at a pressure of 0.1–10 Torr is used as an ion source. The cathode surface consisting of the sample material is sputtered by Ar^+ ions, which are formed in low-pressure argon plasma and accelerated towards the cathode. Sputtered neutral particles of the sample are ionized in the glow discharge plasma ('negative glow') by Penning and/or electron impact ionization and charge exchange processes. The ionized ions of interest are then detected by mass spectrometry. For the direct analysis of solid samples, the commercial direct current glow discharge mass spectrometer VG-9000 (VG-Elemental, Thermo Instruments, UK) – a double-focusing sector field mass spectrometer with inverse Nier–Johnson geometry – has been available on the analytical market for many years. The analysis of nonconducting materials by d.c. GDMS is difficult due to charge-up effects on the sample surface. Different techniques such as mixing nonconducting powdered samples with a high-purity metal powder (or high-purity graphite) or the use of a secondary cathode have, therefore, been applied for the analysis of electrically insulating samples by d.c. GDMS. Due to the capacity of isotopic analysis, GDMS can be used for the determination of radionuclides, such as uranium, plutonium, ^{237}Np, ^{137}Cs, and ^{90}Sr [115,116]. Since the sample is directly analyzed, the sample preparation is very simple, which minimize the risk of contamination. It is also suitable for fast analysis, where radiometric methods are normally time consuming. However, due to low sensitivity and less accessibility of GDMS, the application of GDMS in the determination of radionuclides is very limited.

4. Comparison of radiometric and MS methods for the determination of radionuclides

For the determination of many specific radionuclides, both radiometric and mass spectrometric method can be used, while their application is directly related with the detection limits, analytical accuracy and capacity, and accessibility of the equipments. In addition, the sample preparation procedure in terms of duration, complexity, the counting time, interferences, the man power and coast are also parameters should be considered in the choice of the analytical method. Due to the high sensitivity and accuracy, and easy access of radioactive measurement equipments in normal radiochemical laboratories, the determination of short-lived radionuclides ($T_{1/2} < 10$ years), especially those with emission of γ-rays is exclusively carried out by radiometric method. Here we focus on the comparison of these two techniques for the determination of some of important radionuclides in the environmental and waste samples, especially long-lived alpha and pure electron emitters.

4.1. *Tritium*

Radiometric methods are sensitive ways for the determination of tritium due to its short half-life (12.3 years), and therefore its high specific radioactivity (3.6×10^{14} Bq g^{-1}). Tritium decays by pure beta particle emission with a low energy ($E_{max} = 18.6$ keV), it is therefore favorably measured by liquid scintillation counting (LSC), a detection limit of 50 mBq (1×10^{-16} g) was reported for the determination of tritium in nuclear waste with low-level LSC for 50 min counting time [118]. In LSC, the sample is normally prepared in a small volume of liquid (<10 mL), which is mixed with a scintillator cocktail for counting. The tritium concentration in environmental samples is normally very low (<1 mBq mL^{-1}), the LSC is therefore not sensitive enough for the direct measurement, an electrolytic method is therefore often applied to enrich tritium from water [119], the enrichment factor of 30–100 can easily be obtained for 100–500 mL water. For the determination of tritium in solid samples, a combustion method is used to convert tritium to THO, which subsequently is measured by LSC [118–120].

Tritium can also be measured by ^{3}He mass spectrometry and AMS. In He-3 mass spectrometry, the sample is first degassed to remove ^{3}He in the sample, and then kept for some period of time for the in-growth of ^{3}He from the decay of tritium. The ^{3}He built from tritium is then measured by the noble-gas mass spectrometer. The ^{3}He mass spectrometry method is more sensitive than LSC, a detection limit of 0.5 mBq mL^{-1} was reported [121,122], the main drawback of the ^{3}He method is its long analysis time, which results from the in-growth of ^{3}He from the decay of tritium, in addition, the sample preparation is also a complicated and time consuming process in this method.

AMS is also a sensitive method for the determination of tritium, a detection limit of 1 mBq (or 10^{-13} to 10^{-15} for ^{3}H/^{1}H ratio) has been reported [123]. The primary benefit of this method is the analysis of small sample (2 mg hydrogen), which is very suitable for the analysis of biological samples. In AMS method, the tritium is first released from the sample, and converted to hydrogen gas which is then absorbed on metal (i.e. Ti), and then measured by AMS. It is therefore the sample preparation of AMS is more complicated comparing to LSC. Combining with the less availability of AMS facility, the application of AMS for the determination of tritium is very limited. In the routine analysis, LSC is still the most often used method for tritium determination in environmental and waste samples.

4.2. Carbon-14

Carbon-14 is a naturally occurring radionuclide produced in the upper atmosphere by reaction of cosmic ray produced neutrons via ^{14}N (n, p)^{14}C, ^{14}C level in the atmosphere was approximately constant before the human nuclear activity (equilibrium between new generated ^{14}C and removal of ^{14}C due to its radioactive decay). After being fixed in living materials (plants, animals), the ^{14}C concentration will decreased due to its radioactive decay with a half-life of 5730 years, ^{14}C is therefore widely used for dating (age determination) purpose. Actually, the most of ^{14}C measurement is used for dating. However, human nuclear activity has released large amount of ^{14}C to the environment. In the nuclear facilities, ^{14}C is mainly produced by neutron capture reactions of ^{14}N, ^{13}C and ^{17}O (Table 2). Therefore, ^{14}C exists in almost all materials exposed to neutron irradiation. ^{14}C is an important radionuclide in the decommissioning of nuclear facilities and repositories of nuclear waste due to its high concentration, long half-life and most of all due to carbon being an essential element for plants and animals.

^{14}C is a pure beta emitter which decays by emitting β-particles with the maximum energy of 156 keV; it can therefore be measured by beta counting, mainly liquid scintillation counting. In this method, ^{14}C is prepared as a liquid sample and then measured. The very often used method for the analysis of waste sample is combustion, in this case all forms of carbon is converted to CO_2 and absorbed in alkaline solution, which is mixed with scintillator cocktail for the LSC. The detection limit of LSC for ^{14}C therefore depends on the count rate of blank, counting efficiency and counting time. A detection limit of 30 mBq was reported for the analysis of nuclear waste and environmental sample such as graphite, concrete, soil, and milk powder, using low-level Quantulus^{TM} 1200 LSC [118]. This is sensitive enough for the waste samples and the present environmental samples [118,124–128]. The traditional sample preparation method for the analysis of solid sample using combustion [124–128] is very time consuming, this makes the analytical capacity of LSC very low (<3 sample per day per person). Hou [118] developed a rapid method for separation of C-14 from solid samples by using a sample oxidizer, using this method the sample preparation time was reduced to only 2–3 min per sample. For the analysis of environmental samples with a low concentration of ^{14}C, such as old materials for dating, the carbon released from the sample is normally converted to benzene in order to get a better counting efficiency and therefore a better detection limit [129,130]. However, due to the high detection limit, the measurement of very low-level ^{14}C for dating requires large samples (>2 g) to get a good analytical accuracy or precision. This feature limits the application of LSC in ^{14}C dating.

Due to the long half-life of ^{14}C, it can readily measured by mass spectrometry techniques. The most sensitive method for the determination of ^{14}C is AMS, which can detect 10^{-7} Bq of ^{14}C (or a $^{14}C/^{12}C$ ratio of 10^{-15}), and the samples up to 60,000 years old have been dated by ^{14}C AMS. Due to the very high sensitivity of AMS, a very small sample (<1 mg carbon) is required for the measurement, which makes it possible to analyze samples with very low carbon content, such as ice, water, ceramics, and metals. Besides good sensitivity, the analytical precision of AMS (<0.2%) is also much better than radiometric method, which is a very important factor in the dating. AMS is therefore very suitable for radiocarbon dating. A large number of papers on the ^{14}C dating using AMS has been published, a journal "Radiocarbon" mainly focus on this field. A compact AMS facility specifically for the radiocarbon dating has been recently developed and introduced to the market [131]. This leads to smaller dimensions, drastically reduced investment and operating costs of AMS facility for radiocarbon dating. In the AMS analysis of ^{14}C, carbon is first released from the samples, mainly by combustion at high temperature, the released ^{14}C as $^{14}CO_2$ is then normally converted to graphite, and used for AMS. But CO_2 samples can also be directly introduced to the AMS for measurement [132,133]. Due to high coast, complicated sample preparation procedure, and less accessibility of AMS, the AMS is mainly used for radiocarbon dating, while the determination of ^{14}C in waste and normal environmental samples is mainly carried by radiometric method.

The ambient levels of ^{14}N in air and the fact that ICP-MS plasmas operate at atmospheric conditions prevent the determination of ^{14}C by this technique. The small mass difference, relatively poor abundance sensitivity, poor ionization in the plasma and normally very large atom number differences ^{14}N:^{14}C makes it impossible to determine ^{14}C even by using sector field ICP-MS in high resolution mode. The presence of nitrogen in nearly all materials makes determination even in solids under vacuum by most of mass spectrometric techniques (e.g. SIMS) a challenge.

4.3. Chlorine-36

In nature, ^{36}Cl is produced mainly by the cosmic ray reactions and thermal neutron reaction of ^{35}Cl in the hydrosphere (Table 2). However, most of ^{36}Cl in the present environment has been produced by human nuclear activities since 1950s via the neutron activation reaction. The interest in the determination of ^{36}Cl in nuclear waste results from the long half-life of ^{36}Cl and its high mobility in the environment, while the purpose of determination of ^{36}Cl in the environmental sample normally focus on the application of this radionuclide as a environmental tracer.

^{36}Cl is a pure beta particle emitter with a high energy ($E_{max} = 708.6$ keV, 98.1%), it is therefore mainly measured by beta counting such as LSC [127,128,134–139]. The reported detection limit of LSC for ^{36}C is 14 mBq using Quantulus^{TM} low-level LSC for 50 min counting time [134]. A complete separation of ^{36}Cl from the matrix and other radionuclides is required in this method. Hou et al. [134] reported a method for the separation of ^{36}Cl from different types of nuclear waste samples, such as graphite, concrete and metals. The ^{36}Cl was first released from the sample by acid digestion or alkaline fusion followed by acid leaching. The chlorine in the decomposed sample was then separated from the matrix by AgCl precipitation. The separated ^{36}Cl was further purified by anion exchange chromatography, and the ^{36}Cl in the NH_4NO_3–NH_4OH eluate was concentrated by evaporation. The separated sample was mixed with scintillation cocktail and measured by LSC. Due to the long chemical separation (4–7 h) and counting time (>30 min), the determination of ^{36}Cl is normally time consuming (one day chemical separation and 1–2 h of measurement).

The concentration of ^{36}Cl in environmental samples is normally very low (<1 mBq g^{-1}, or a ratio of ^{36}Cl/^{35}Cl less than 10^{-9}), it is impossible to determine it by using LSC method. Due to the long half-life of ^{36}Cl (301,000 years), mass spectrometry is a suitable tool for its determination. However, the isobaric interference (^{36}S, ^{36}Ar) and bad abundance sensitivity (>10^{-7}) in the most mass spectrometric techniques limit their application. The only mass spectrometric technique useful for determination of ^{36}Cl in low-level environmental sample is AMS. The reported detection limit of AMS is 10^{-9} Bq (or a ^{36}Cl/^{35}Cl ratio of 10^{-15}) [140–142]. In AMS, ^{36}Cl is normally prepared as AgCl target and the measurement is conducted using ^{36}Cl^{7+} ions. The ^{36}S isobar is the principal challenge in AMS measurement of ^{36}Cl, because sulfur forms negative ions as readily as chlorine and the concentration of ^{36}S is normally much higher in the environmental samples compared to ^{36}Cl. By using a 48 MeV ^{36}Cl^{7+} ion energy and a multi-anode ionization chamber as detector, ^{36}S can be highly suppressed by a factor of 10^4 [141]. In addition, chemical separation of sulfur from chlorine has to be used in the sample preparation, which is achieved by precipitation of sulfur as $BaSO_4$. Remaining sulfur normally exists as sulfate, which can be co-precipitated together with the AgCl as Ag_2SO_4. But the solubility of Ag_2SO_4 is much higher than that of AgCl, and can therefore be separated by washing the precipitate with acidic solution [134].

The separation procedures of ^{36}Cl for both of LSC and AMS analytical methods are similar time consuming, while the detection limit of AMS is a few order of magnitude better than LSC. AMS is the only method for the determination of ^{36}Cl in environmental level, while LSC is still widely used for the analysis of nuclear waste sample, in which the ^{36}Cl concentration is high, because of less cost and easy accessibility of LSC in normal radiochemical laboratory.

4.4. *Calcium-41*

^{41}Ca, a long-lived radionuclide ($T_{1/2} = 1.03 \times 10^5$ years), is produced by neutron activation reaction of ^{40}Ca (Table 2). ^{41}Ca is an important radionuclide in the disposal of radioactive waste, because of its long half-life, high mobility in the environment and high bioavailability. ^{41}Ca is also used as a tracer in the biomedical research [143], which requires a very sensitive determination of ^{41}Ca because of the small sample size normally available.

^{41}Ca decays to the ground state of ^{41}K by pure electron capture, emitting X-rays and Auger electrons of very low energy (3.3 keV, 11.7%), which makes it possible, although difficult, to be measured by X-ray spectrometry [144] and LSC [19,145,146]. X-ray spectrometry is a simple method, but it is insensitive due to the low counting efficiency (<0.08%) of X-ray spectrometry for ^{41}Ca and the low abundance of X-rays from ^{41}Ca (11.4% for 3.31 keV Kα X-ray). A detection limit of 8 Bq for ^{41}Ca was reported by using X-ray counting after chemical separation [144].

The chemical separation is necessary due to possible presence of beta, gamma or X-ray emitters which may either increase the baseline background or directly interfere with the Ca (K) X-rays. A chemical separation of ^{41}Ca from the sample matrix is also needed in many cases due to the self-absorption of X-rays in the sample which varies significantly with sample size and also in the chemically separated sample due to the amount of stable Ca presents in the samples. A self-absorption correction must, therefore, be carried out. The most advantage of this technique is its short sample preparation procedure and minimized risk of contamination in the direct measurement.

LSC has been used for the determination of ^{41}Ca by measurement Auger electrons emitted from ^{41}Ca. Due to the relative high counting efficiency compared to X-ray spectrometry, a better detection limit can be obtained. However, due to the poor energy resolution of LSC and the low energy Auger electron spectrum of ^{41}Ca, calcium has to be completely separated from the matrix and all other radionuclides before counting. Hou [19] reported a chemical procedure for the separation of calcium from concrete based on the precipitation of $Ca(OH)_2$ in high concentration of NaOH (>0.5 mol L^{-1}) with a decontamination factor higher than 10^4 for most interfering radionuclides, such as ^{133}Ba, ^{90}Sr, ^{60}Co, and ^{152}Eu. A detection limit of 0.1 Bq was reported using LSC [19]. The drawback of this method is the long chemical separation procedure, and long counting time (>1 h).

Mass spectrometric techniques including AMS [147–150] and RIMS [93,151] have also been used for the determination of ^{41}Ca. Of these methods, AMS is the most sensitive method. AMS of ^{41}Ca requires the injection of a molecular ion of Ca, because the formation of the Ca^- ion is very low in a sputter source, $CaH_3{}^-$ is normally the ion of choice to eliminate the ^{41}K isobar because the $KH_3{}^-$ ion is not stable [150]. $CaF_3{}^-$ has also been used to inject Ca to the AMS system, since $KF_3{}^-$ ion is instable [149]. In principle, a ^{41}Ca/^{40}Ca ratio as low as 10^{-15} can be measured by AMS, while the detection limit of ^{41}Ca is mainly effected by the procedure blank and ^{41}K interference, the reported detection limit is 10^{-12} to 10^{-13} for Ca/^{40}Ca ratio or 0.1 mBq g^{-1} for ^{41}Ca [147,148].

RIMS is also a sensitive method for the determination of ^{41}Ca. A detection limit of $1–5 \times 10^{-11}$ for ^{41}Ca/^{40}Ca ratio has been reported [93,151,152]. The precision of the isotope ratio determination is dominated by isotope fractionation effects, which may result from small errors in laser spectral or spatial positioning. They limit the precision to about 5% for Ca isotope ratios above 10^{-10} and increase up to 30% near the detection limit due to low counting statistics.

Table 5 compares all four methods for the determination of ^{41}Ca, AMS and RIMS are the most sensitive methods for ^{41}Ca, they can therefore be used for all types of samples, and the samples amount required is small (<2 mg Ca). But both AMS and RIMS are expensive and not easily accessible. X-ray spectrometer is the least sensitive method, but is easy to operator and samples are easily prepared. Low energy Ge- or Si(Li) detectors used for X-ray spectrometry may therefore be a suitable method for the analysis of nuclear waste samples containing higher level activity. LSC is not as sensitive as AMS and RIMS, and sample preparation for LSC is also rather time consuming. But LSC equipment is usually accessible in radiochemical laboratories. Besides X-ray spectrometry, the other three methods require a thorough chemical separation of Ca from the sample matrix and interfering isotopes. In which, a complete separation of other radionuclides is required in LSC, the chemical procedure therefore takes a long time. For AMS

Table 5 – Comparison of X-ray spectrometry, LSC, RIMS, TIMS and AMS for the determination of ^{41}Ca

Sample	Detection method	Target preparation	Detection limit		Sep. time (h)	Count time	Ref.
			Bq	$^{41}Ca/^{40}Ca$			
Concrete	X-ray	CaC_2O_4	8 Bq		0–6	40–70 h	[144]
Concrete	LSC	$CaCl_2$	0.1 Bq		4–6	1 h	[19]
Waste	LSC	$CaCl_2$	0.3 Bq		4–6	4 h	[146]
Concrete	RIMS	$Ca(NO_3)_2$	30 mBq	10^{-10}	2–4	10–20 min	[93]
Concrete	RIMS	$Ca(NO_3)_2$	20 mBq	6×10^{-11}	2–4	~ 1 h	[152]
Iron	RIMS	CaO	1 mBq	5×10^{-11}	2–4	10–60 min	[151]
Snow	AMS	CaH_2	0.1 mBq	5×10^{-12}	4–8	20–60 min	[147]
Iron	AMS	CaH_2	0.1 mBq	2×10^{-13}	4–8	20–60 min	[151]

and RIMS the chemical separation steps are relative simple, Ca is normally separated from the decomposed sample by a simply calcium oxalate precipitation.

4.5. *Nickel-59, 63*

^{63}Ni and ^{59}Ni are produced by neutron activation reactions of Ni and Cu (Table 2), which are released to the environment from the human nuclear activity. The interest in the determination of ^{63}Ni and ^{59}Ni results from the characterization of radioactive wastes for the decommissioning and disposal of nuclear waste, and the use in a number of applications including cosmic radiation studies, biomedical tracing and neutron dosimetry (Table 1) [18,153–156].

^{63}Ni is a pure beta emitting radionuclide (Table 4), the radiometric methods including windowless gas flow GM counters, beta-spectrometry with semiconductor detectors and LSC have been used for its determination. ^{59}Ni decays by electron capture with emission of X-rays, it can therefore be determined by X-ray spectrometry. The AMS has also been used for the determination of these two radioisotopes of nickel [153,154,157–160].

In the determination of ^{63}Ni by gas flow GM counter or semiconductor detector, the ^{63}Ni has to be prepared as thin source to minimize self-adsorption. This is usually carried out by electrodeposited of Ni on a metal disk. Due to its low beta energy, the counting efficiencies of ion implanted silicon detector (IISD) (1–6%) and GM counter (8–40%) are low and varies with the thickness of the source (stable Ni). Detection limits of 1 and 8 mBq were reported for GM counter and silicon detector, respectively for 50 h counting [161,162]. LSC has a high counting efficiency for ^{63}Ni (70%), it is therefore widely used for the determination of ^{63}Ni [18,163–167], the reported detection limit of LSC is 14–37 mBq for 30–1000 min counting time [18,167]. A slightly higher detection limit of LSC results from the relatively high background count rate of LSC (3–10 CPM) compared to GM counting and silicon detector (0.2 CPM). Because of the difficulties in identifying radioisotopes from the continuous energy spectrum of pure beta-emitters, they have to completely be separated from the matrix and other radionuclides before counting. Chemical separation of ^{63}Ni is usually carried out by precipitating nickel as a hydroxide and then extracting the Ni-DMG (dimethyl glyoxime) complex using either solvent extraction or extraction chromatography, sometimes combined with an anion exchange step. A decontamination factor of 10^5 or higher was obtained using a combination of these methods [18]. Chemical separation does not separate ^{63}Ni from ^{59}Ni, but since both ^{63}Ni and ^{59}Ni are produced by thermal neutron reactions with stable nickel ^{62}Ni (3.65%) and ^{58}Ni (68.1%), the initial activity ratio of $^{63}Ni/^{59}Ni$ is around 100 or higher, which means that only ^{63}Ni is measured by LSC. In addition, the signal of ^{59}Ni in LSC occurs in the low energy part of the spectrum, which makes the interference of ^{59}Ni to the ^{63}Ni spectrum very limited. The high radioactive ratio of $^{63}Ni/^{59}Ni$ at the same time makes LSC determination of ^{59}Ni impossible.

As all other low-energy X-ray emitters, the determination of ^{59}Ni also requires a separation of Ni from the matrix and other radionuclides because of the low energy of the K-X-rays emitted from ^{59}Ni (6.9 keV, 30.4%), the same separation procedure used for ^{63}Ni can also be used for ^{59}Ni. The separated Ni is normally electrodeposited onto a metal disk for the X-ray counting. Due to the low counting efficiency (<1%) and relatively high background counts in X-ray spectrometry, this method is insensitive. A reported detection limit of X-ray spectrometry for the determination of ^{59}Ni is 1–2 Bq [168].

AMS is a sensitive method for the determination of ^{63}Ni and ^{59}Ni. In this method, isobaric interference from ^{63}Cu and ^{59}Co is the main challenge, because Cu, Co and Ni easily form anions in the ion sputtering source. To minimize these interferences, a combination of chemical separation methods and AMS instrumental settings are used. A characteristic X-ray detector is used for post-spectrometer ion detection and identification. After separation in the AMS spectrometer, the Ni-ions are detected via X-rays emitted when they pass through a thin foil close to the detector. This allows identifying the ions by atomic number and thereby separating the isobars. By this method, a suppress rate of 10^7 for ^{59}Co was obtained [154,159]. Combined with the chemical separation using DMG extraction, a detection limit of 4×10^{-9} for the $^{59}Ni/Ni$ ratio (or 20 mBq) was reported [154]. For improvement of the detection limit, the Ni in the sample should be further purified and the instrumental background should be reduced. McAninch et al. [153] reduced the instrumental background of ^{63}Cu and ^{59}Co in the ion source by fabrication of Cu and Co free target holders, thorough cleaning of the ion source and addition of a cryogenic pumping system to the ion source [153]. The same authors reported a chemical purification method by using volatile $Ni(CO)_4$, the Ni in ammonium solution was mixed with $NaBH_4$ solution in a flask, and a mixture of CO and He_2 was bubbled through the Ni solution to

Table 6 – Comparison of X-ray spectrometry, GM counter, ion implanted silicon detector, LSC, and AMS for the determination of ^{63}Ni and ^{59}Ni determination of ^{59}Ni and ^{63}Ni

Sample	Nuclide	Method	Target preparation	Detection limit (Bq)	Sep. time (h)	Count time	Ref.
Waste	^{59}Ni	X-spectrometry	Deposited on disk	1–2 Bq	5–6	7 h	[168]
Biological sample	^{59}Ni	AMS	$Ni(CO)_4$-Ni	0.05 mBq	7–8	15 min	[153]
Waste	^{63}Ni	LSC	Ni-DMG	14 mBq	4–6	30 min	[18]
Sludge	^{63}Ni	LSC	$NiCl_2$	37 mBq	4–6	17 h	[167]
Lichens	^{63}Ni	GM counter	Deposited on disk	1 mBq	6–8	50 h	[162]
Fucus	^{63}Ni	IISD	Deposited on disk	8 mBq	4–8	50 h	[161]
Copper wires	^{63}Ni	AMS	$Ni(CO)_4$-Ni	45 mBq	7–8	15 min	[153]
Copper	^{63}Ni	AMS	$Ni(CO)_4$-Ni	0.12 mBq	7–8	10–30 min	[160]

produce volatile $Ni(CO)_4$, which was collected in a cold trap. The collected $Ni(CO)_4$ was heated and transferred to the AMS holder by He_2 flow, where it was thermally decomposed to Ni. By this process, a Cu/Ni ratio of less than 2×10^{-8} in the sample was obtained, corresponding to a detection limit of 2×10^{-11} for ^{59}Ni/Ni ratio or 0.05 mBq of ^{59}Ni and 45 mBq of ^{63}Ni [153]. Rugel et al. [160,169] reported an AMS method by using a cesium sputter ion source dedicated exclusively to ^{63}Ni AMS measurements, the isobaric ^{63}Cu background from this ion source is a factor of 100 less than that from the ion source usually used for other AMS measurements. In addition, the gas-filled magnet (GFM) was chosen in a way that most of the ^{63}Ni ions could still enter the detector (about 80%), but the ^{63}Cu ions were blocked by the aperture due to their higher mean magnetic rigidity in the gas. This resulted in a reduction of the copper count rate in the detector by a factor of about 3000. The final detector was a Frisch-grid ionization chamber with five ΔE sections, enabling independent total energy measurements, position sensitivity and angle sensitivity in the vertical and horizontal plane. This combination improved the detection limit for ^{63}Ni/Ni ratios down to 6×10^{-14} (or 0.12 mBq of ^{63}Ni) and a total isobaric suppression of about 5×10^9.

Table 6 compares different methods for the determination of ^{59}Ni and ^{63}Ni, the detection limit of radiometric methods (LSC, GM counter and ion implanted silicon detector) for ^{63}Ni is similar to the initial AMS technique because of the relatively high specific activity of ^{63}Ni and the interference of ^{63}Cu. But detection limit of later developed AMS technique is much better than the radiometric method. All methods require a long chemical separation procedure, the counting times for LSC and AMS are similar, while a longer counting time is used by GM counter and ion implanted silicon detector. The radiometric methods are easily accessible and cheaper than AMS. Activity levels of ^{63}Ni in nuclear waste samples are often sufficiently high to be determined by radiometric methods, while environmental samples are better analyzed by the more sensitive AMS method. The detection limit of AMS for ^{59}Ni is more than 4 orders of magnitude lower than the radiometric methods even with a simple purification procedure. Radiometric method (in principal only X-ray spectrometry) can only be used for the determination of ^{59}Ni in nuclear waste samples with high level (>1 Bq g^{-1}). The detection of ^{59}Ni in environmental and most nuclear waste samples has to be carried out by AMS.

4.6. *Stronium-89, 90*

Both ^{90}Sr and ^{89}Sr can be produced by neutron fission in nuclear reactor and weapons testing and released to environment, while ^{89}Sr can also be produced by neutron activation of stable strontium (Tables 1 and 2). ^{90}Sr is one of important radionuclides in the views of radiation protection, environmental monitoring, radioecology, and radioactive waste management due to its relative high radioactive level in environmental and nuclear waste samples. The interest in the determination of ^{90}Sr and ^{89}Sr comes also from utilization of them as environmental tracers (Table 1).

Both ^{90}Sr and ^{89}Sr are pure β^- emitters, the radiometric methods, such as gas flow GM counting and liquid scintillation counting are normally used for direct measurement of ^{90}Sr and ^{89}Sr or alternatively via ^{90}Y (also pure β^- emitter), a short-lived ($T_{1/2} = 2.67$ days) daughter of ^{90}Sr. All these radiometric methods require previous chemical separation and pre-concentration in order to avoid interference from other radionuclides and problems with self-absorption due to the presence of calcium or stable strontium in the sample. Several techniques for the separation of strontium from matrices have been reported, such as solvent extraction using crown ether [170,171], liquid membrane extraction [172], extraction chromatography [173] using Sr-Spec resin [174,175], ion-exchange [176,177] and strontium rhodizonate and $CaHPO_4$ precipitation. One general method based on the insolubility of strontium nitrate in strong nitric acid is still widely used for separation of Sr from Ca [178]. Recently a simple method based on $Ca(OH)_2$ precipitation in alkaline solution and $Ba(Ra)SO_4$ precipitate was applied to the separation of Sr from sample matrices and interfering radionuclides [16,179]. A detection limit of 5 mBq for ^{90}Sr was reported by using an anticoincidence shielded gas flow GM counter [16]. When using gas flow GM detector, ^{90}Sr is normally measured through its daughter ^{90}Y, because of the low beta energy of ^{90}Sr ($E_{max} = 546$ keV) and a consequence of low counting efficiency. In order to reach secular equilibrium between ^{90}Sr and ^{90}Y, the separated Sr-samples need to be kept for more than 2 weeks for the in-growth of ^{90}Y before counting. The generated ^{90}Y is then separated from ^{90}Sr, which also enables observing the ^{90}Y decay ($T_{1/2} = 2.67$ days) by using repeated counting. This increases the confidence of the radiochemical purity of the sample. A direct separation of ^{90}Y from the samples has also been reported for the determination of ^{90}Sr, this method can significantly shorten the time used for sample preparation by avoiding the waiting for the in-growth of ^{90}Y from the separated ^{90}Sr [180]. However, the decontamination factors for many interfering radionuclides, especially the short-lived activation and fission products, are not good. A detection limit of 10–30 mBq for ^{89}Sr and ^{90}Sr was reported by using LSC [180,181]. Due to the different beta energy of ^{90}Sr and ^{89}Sr ($E_{\max}$ = 1495 keV), they can be simultaneously measured by LSC via measuring Cherenkov radiation. The energy threshold of the fast moving electrons to produce Cherenkov radiation in water is 256 keV. Cherenkov radiation is emitted in the optical and UV parts of the electromagnetic spectrum, which means that it can be detected by the photomultipliers of an ordinary LSC. Due to the relatively low beta energy of ^{90}Sr, very small fraction of the emitted beta particles give rise to Cherenkov radiation. In a recently separated Sr-sample, the Cherenkov counts mainly originates from ^{89}Sr, but with the in-growth of ^{90}Y ($E_{\max}$ = 2280 keV) by decay of ^{90}Sr, the contribution from the ^{90}Y (^{90}Sr) increases. By measuring the sample two times, shortly after Sr-separation and after 3 weeks (when ^{90}Sr and ^{90}Y have reached equilibrium), both ^{89}Sr and ^{90}Sr can be determined. The main drawback of the radiometric methods is a long analytical time (5–20 days) because of the long chemical separation procedure and the waiting time for in-growth of ^{90}Y from ^{90}Sr.

Mass spectrometric techniques such as AMS, RIMS, ICP-MS and GDMS have also been used for the determination of ^{90}Sr in environmental and waste samples [26,36–40,94,95,102,103]. In AMS determination of ^{90}Sr, SrH_3^- molecular ion is chosen as injection ion because Sr^- ion formation in sputter source is extremely weak. A similar method described above for ^{41}Ca can be used for the preparation of the SrH_2 target. The principal difficulty in the AMS measurement of ^{90}Sr arises from the stable isobaric interference of ^{90}Zr. Higher energies are therefore required in order to be able to discriminate ^{90}Sr from ^{90}Zr. Paul et al. [182] using a energy of 131 MeV, reported a suppression ratio of 1×10^5 for ^{90}Zr, and a detection limit of 3×10^{-13} for ^{90}Sr/Sr ratio or 40 mBq for ^{90}Sr.

RIMS in collinear geometry has been used for the determination of ^{90}Sr [94]. After chemical separation, the Sr sample is placed in a conventional ion source. The Sr-ions are accelerated to 10–60 keV beam energy, mass separated and then neutralized. In quasi-collinear geometry, the atoms in the metastable state are selectively excited with 363.8 nm light emitting from an Ar-ion laser in the $5s^4d^3D_3 \rightarrow 5s^23f^3F_4$ transition and subsequently field ionized, selected in an energy filter, and counted. A selectivity of $>10^{11}$ in suppression of ^{88}Sr and a detection limit of 2×10^6 atoms (or 1.5 mBq) have been reported. The high experimental expense is a main drawback of RIMS in collinear geometry. The coherent multi-step RIMS has also been applied for the determination of ^{90}Sr by using a double resonance excitation $5s^2\ ^1S_0 \rightarrow 5s5p^3P_1 \rightarrow 5s6s^3S_1$ with $\lambda_1 = 689.5$ nm, $\lambda_2 = 688.0$ nm, and subsequent photo-ionization at 488 nm [90]. This method gives an isotopic selectivity of 1.4×10^{10} against stable strontium and a detection limit of 4 mBq.

^{90}Sr has also been determined by ICP-MS [36–38,70]. The main interference in the measurements of ^{90}Sr by ICP-MS is the isobar ^{90}Zr which has a natural abundance of 51%. An ETV system was investigated in order to discriminate against zirconium which has a very high boiling point [39]. By selecting an appropriate temperature, relative Sr/Zr ratio was improved by a factor of 50 as compared to the conventional liquid mobilization. In spite of the improvements, detection limit reported for ^{90}Sr was still around 10 Bq mL^{-1} (equivalent to 2 pg mL^{-1}). Sector field ICP-MS has also been used for the determination of ^{90}Sr [37,38]. By using cold plasma and medium mass resolution, the Zr signal is significantly reduced, and a detection limit of 10 mBq mL^{-1} was achievable in a pure water sample. However, the detection limits in urine was increased to 0.4 Bq mL^{-1} due to the presence of stable strontium. Zoriy et al. [37] used a similar operation condition with further optimization, and determined ^{90}Sr in ground water samples, a detection limit of 55 mBq mL^{-1} was obtained when low stable Sr concentration (<6 ppb, or a ^{90}Sr/^{88}Sr ratio > 2×10^{-6}) presents. For suppression of the isobaric interference from ^{90}Zr, a dynamic reaction cell technique by employing oxygen gas was used in a quadrupole ICP-MS. This resulted in a significant removal of ^{90}Zr, in addition, this method also suppress the interference from other molecular ions such as $^{50}Ti^{40}Ar^+$ and $^{50}Cr^{40}Ar^+$. Combined with a chemical separation, a detection limit of 0.5 Bq mL^{-1} was obtained for water sample [70]. Besides the isobaric interference, abundance sensitivity (tailing of stable ^{88}Sr) is another problem in the ICP-MS measurement of ^{90}Sr. The abundance sensitivity of ICP-MS for ^{90}Sr/^{88}Sr is normally about 10^{-6}, which makes the detection of ^{90}Sr/^{88}Sr ratios less than 10^{-7} very difficult. While the concentration of Sr normally is high in the environmental samples (7–9 mg L^{-1} for seawater, 20–300 mg kg^{-1} soil), the ICP-MS measurable ^{90}Sr in seawater will be higher than 450 Bq L^{-1}, which is much higher than the present ^{90}Sr level in the environmental seawater (<50 mBq L^{-1}). This makes ICP-MS difficult to be used for the determination ^{90}Sr in environmental samples.

As a directly analytical method, GDMS is a very attractive method for rapid analysis of ^{90}Sr. However, the isobaric interference of ^{90}Zr has to be removed which requires a very high MS resolution of around 2×10^6. It is therefore very difficult to determine ^{90}Sr in environmental samples by this technique. Betti et al. [26] investigated application of GDMS for the determination of ^{90}Sr in soil and sediment. The sample was fist mixed with silver powder and then pressed in a disk for GDMS analysis. A detection limit of 50 mBq g^{-1} was reported when no Zr was detected in the sample. However, for real environmental samples, the ^{90}Zr concentration is much higher than that of ^{90}Sr, which makes it impossible to directly determine ^{90}Sr by this technique.

Table 7 compares the radiometric and mass spectrometric methods for the determination of ^{90}Sr. The reported detection limit of radiometric methods such as gas flow GM counting and LSC is similar to that of AMS and RIMS. The detection limit of ICP-MS for real samples is a few orders magnitude higher than radiometric method, while GDMS require a Zr free sample, which makes it unsuitable for the analysis of real environmental sample. Radiometric method normally requires a complete separation of Sr from the matrix and other radionuclides; a long and time consuming separation procedure is therefore needed. In addition, a very long in-growth time (2–3 weeks) is needed in the radiometric method by measuring ^{90}Y. A simple separation method, mainly focused on the sep-

Table 7 – Comparison of radiometric and mass spectrometric methods for the determination of ^{90}Sr

Sample	Detection method	Target preparation	Detection limit	Sep. time[a]	Count time	Ref.
Water	GM counter	$Y_2(C_2O_4)_3$ precipitation	5 mBq	1–2 days/20 days	3–5 h	[16]
Water, milk	LSC by Cerenkov	Sr solution	10 mBq	1–2 days/20 days	2.5–3 h	[180]
Environmental samples	LSC	Sr solution	10 mBq	1–2 days/20 days	3–4 h	[179]
Water	AMS	SrH2	40 mBq	6–8 h	0.5–1 h	[184]
Water	DR-RIMS	$Sr(NO_3)_2$ (pure Sr)	4 mBq		0.5 h	[102]
Aerosol	Collinear RIMS	$Sr(NO_3)_2$	1.5 mBq	5–8 h	0.5 h	[94]
Environmental samples	DRC-ICP-MS	Sr solution	5 Bq or 0.5 Bq mL^{-1}	5–8 h	5–10 min	[70]
Urine	ICP-SFMS	Sr solution	400 mBq mL^{-1}	2–4 h	5–10 min	[38]
Water	ICP-SFMS	Sr solution	55 mBq mL^{-1}	1–3 h	5–10 min	[37]
Soil, sediment	GDMS	No sep./Zr free	50 mBq g^{-1}	No	<30 min	[26]

[a] For the radiometric methods, if ^{90}Y is measured, a 2–3 weeks in-growth time is needed to get generation of ^{90}Y from the separated ^{90}Sr.

aration of Sr from the matrix and Zr, is required for AMS and RIMS, which therefore makes them suitable for rapid analysis. However, the analytical expense is normally much higher than using radiometric methods, and the AMS and RIMS instrumentation set-up for Sr-analysis is very rare. Based on these considerations, radiometric methods is still the main approach for the routine analysis of ^{90}Sr. While a rapid analysis is required, mass spectrometric method, such as AMS and RIMS is a potential choice.

Due to the short half-life of ^{89}Sr, radiometric method is the only suitable method for its determination. In recent years, a big effort was given to develop a rapid analytical method for the determination of ^{90}Sr, which is stimulated by the requirement for the emergency action of the accident and terrorist attack. By solvent extraction, extraction chromatography separation, flow injection technique for the separation of ^{90}Sr from the matrix, and direct measurement of ^{90}Sr by LSC, ^{90}Sr can be determined in a short time (<1 day) [183].

4.7. *Technitium-99*

^{99}Tc in environment is dominated by the releases from the nuclear fuel cycle and nuclear bomb tests, of which the most of them (>90%) was discharged from reprocessing plants in Europe. The interest in determination of ^{99}Tc results partly from the absence of any stable technetium isotope, ^{99}Tc as the completely dominating isotope of Tc is thus the only isotope available for studying the unknown environmental and biological behaviors of this element. In addition, the application of ^{99}Tc as an environmental tracer is also an interest in its determination.

^{99}Tc is a pure beta emitter with maximum beta particle energy of 294 keV. Radiometric methods using beta counting by gas flow GM counters or liquid scintillation is therefore the main techniques used for its determination. The detection limit of these methods depend on the count rate of blank and the counting time, a value of 1.5 mBq was reported by using an anti-coincidence shielded gas flow GM counter for 4 h counting time [182,185], while a higher value of 17 mBq was reported using 2 h counting by LSC which normally have a higher background count rate [186]. Radiometric methods require a thorough chemical separation of Tc from the matrix and other radionuclides, because of the difficulties of spectrometric isotope identification for beta emitters. Due to the generally low concentrations of ^{99}Tc in the environment, large samples are normally required for the analysis. The method adapted for the chemical separation is thus not only important for obtaining a good decontamination from other radionuclides but also to obtain a high chemical recovery of ^{99}Tc. Technetium exists as the conservatively behaving TcO_4^- ion in oxygenated water, while Tc is reduced to particle reactive Tc(IV) in anoxic conditions. Technetium in water or leachate from solid samples is normally pre-concentrated by anion exchange chromatography, which is based on that TcO_4^- have a very high affinity for the column in alkaline or neutral solutions. By passing the solution through the column and washing with different solvents, such as low concentration NaOH, HNO_3, EDTA and NaClO solutions, most of the matrix elements and other radionuclides can be removed. The absorbed TcO_4^- is then eluted using concentrated HNO_3 (12 mol L^{-1}). For further purification, solvent extraction using tri-isooctylamine (TIOA) in xylene has been used to extract TcO_4^-, which can then be back-extracted using NaOH solution. By this procedure, a decontamination factor of more than 10^5 relative to most interfering radionuclides was obtained [184–187]. Based on the insolubility of the reduced Tc, co-precipitation method has also been used for pre-concentration of Tc from aqueous solutions. In this method, technetium is first reduced by $Na_2S_2O_5$, then co-precipitated with $Fe(OH)_2$ to separate it from a large volume of water [188,189]. The precipitate needs to be dissolved in a short time after separation for further chemical separation, otherwise the dissolution will become more difficult and recovery of Tc will be low. The separated Tc is normally electrodeposited onto a stainless steel disk for the measurement using an anti-coincidence shielded gas-flow GM counter [15]. Alternatively, the extracted organic phase can be directly mixed with a scintillation cocktail for LSC measurement [186]. Extraction chromatography using Eichrom TEVA column has also been used for the separation of Tc from other radionuclides [49,189]. In this method, TcO_4^- is absorbed on the column by passing through the solution, and the interfering radionuclides are removed by washing with 0.1 mol L^{-1} HNO_3, the TcO_4^- on the column is then eluted using 4 mol L^{-1} HNO_3. This method was proved to be useful especially for removal of ^{106}Ru.

The long half-life of ^{99}Tc (0.211 My) and low specific activity (6.3×10^8 Bq g^{-1}) makes mass spectrometry a sensitive method for the determination of ^{99}Tc, AMS [190–192], TIMS [193,194] and ICP-MS [46–53,195] have been used for the determination of ^{99}Tc. In AMS, the separated TcO_4^- is mixed with

Table 8 – Potential interfering species on mass 99 in ICP-MS

Isobar/tailing	Oxide	Hydride	Argide	Chloride
^{99}Ru (12.7%)	^{83}Kr^{16}O (11.5%)	^{98}MoH (23.8%)	^{59}Co^{40}Ar (100%)	^{62}Ni^{37}Cl (3.6%)
^{98}Ru (1.1%)	^{81}Br^{18}O (49.5%)	^{98}RuH (1.9%)	^{63}Cu^{36}Ar	^{64}Zn^{35}Cl (48.6%)
^{100}Ru (12.6%)	^{67}Zn^{16}O$_2$ (4.1%)		^{43}Ca^{16}O^{40}Ar	
^{98}Mo (24.1%)	^{51}V^{16}O$_3$ (99.8%)		^{40}Ca^{18}OH^{40}Ar	
^{100}Mo (9.6%)				

Al or Nb to prepare a target, the sputtered TcO$^-$ ions is then stripped to TcO^{14+}, separated in mass spectrometry, and measured by a gas ionization chamber. Stable isotope ^{99}Ru is the main isobaric interference, which is suppressed by using the different energy loss of ^{99}Tc and ^{99}Ru in the detector. By optimal settings, >90% of ^{99}Ru can be rejected. However, for environmental samples, ^{99}Ru concentration is normally some orders of magnitude higher than ^{99}Tc, the chemical separation is necessary before the AMS determination. The sensitivity of this method depends very much on the amounts of Ru in the target. A detection limit of 6–10 μBq for water and environmental samples has been reported [190,192]. In TIMS, the separated TcO$_4$$^-$ is transferred to filament and reduced to TcO$_2$ using HI, the iodine is removed by pre-heating to 930 °C and the Tc is then measured using magnetic sector thermal ionization mass spectrometers equipped with ion counter. A detection limit of 0.02 mBq (or 11 fg) has been reported for geological samples [194]. Due to isobaric interferences from Mo and Ru, which have to be completely removed, the detection limit for more realistic samples has been reported to be 65 fg (0.1 mBq) mainly because of interferences from Mo.

ICP-MS as a very convenient mass spectrometric technique has been widely used for the determination of ^{99}Tc [46–53,195,196]. The main challenge for ICP-MS determination is interferences of isobaric and molecular ions. The possible contributors to the 99 peak background are listed in Table 8. Isobaric interferences from the stable isotope ^{99}Ru, abundance sensitivity or tailing of ^{98}Mo and ^{100}Mo, and the ^{98}MoH$^+$ molecular ion are the main interferences in the analysis of environmental samples using ICP-MS [46]. Due to high concentration of Ru (0.7 ng L^{-1} in seawater) compared to ^{99}Tc in environmental samples ($<8–5000 \times 10^{-6}$ ng L^{-1}) and a high isotopic abundance of ^{99}Ru (12.7%), a high decontamination factor (10^6–10^7) for Ru is required. A good chemical separation is normally needed to meet this requirement. Electrothermal vaporization (ETV) as a sample introduction has been used to remove ruthenium due to its lower boiling point [47,195]. The contribution from ^{98}Mo to mass 99 was mainly due to abundance sensitivity and in a less extent due to formation of the ^{98}MoH. The relative contributions from MoH and abundance sensitivity however depend on sample introduction methodology and instrument operation conditions. The high concentration of Mo in environmental samples (10 μg L^{-1} in seawater), and low abundance sensitivity of ICP-MS (10^{-6}) require a high decontamination factor of Mo in the chemical separation ($>10^6$). Sample introduction techniques such as ETV have also been used to remove Mo and reduce the formation of MoH$^+$ ions. A detection limit of 0.18 mBq has been reported by using ETV and ICP-QMS [47]. Normally, both radiometric and mass spectrometric methods have difficulties in performing accurate measurements of ^{99}Tc close to the detection limits, but the procedure blank in the radiometric measurements can easily be kept in the same as the instrument blank and thus the detection limit is governed by the instrumentation background. On the other hand, the detection limit of ICP-MS is often set by the blank contribution from the chemical processing rather than the instrument blank alone. In this respect radiometric techniques have a well-defined detection limit contrary to what is obtained by the ICP-MS technique.

The chemical separation techniques used in radiometric methods can also be used for the mass spectrometric determination of ^{99}Tc. The main difference is that the separation methods used for radiometric determination focuses on the removal of radionuclides, the stable elements in the reagents and apparatus are not of importance. Since the stable isotopes ^{99}Ru, ^{98}Ru, ^{100}Ru, ^{98}Mo, and ^{100}Mo are the main interferences in the mass spectrometric determination of ^{99}Tc, it is necessary to use high purity chemical reagents and operate under clean conditions. In addition, a separation procedure designed for ICP-MS also needs to focus on the removal of Mo and Ru.

Due to lack of stable isotope of Tc, other radioisotopes of Tc or other elements such as rhenium have to be used as yield tracer in both radiometric and mass spectrometric methods. The short-lived radioisotope, ^{99m}Tc, obtained from a ^{99}Mo–^{99m}Tc generator has been widely used as yield tracer in the chemical separation step for determination by radiometric and mass spectrometric methods. The drawback of ^{99m}Tc as yield tracer is the risk of radioactive contaminants of ^{99}Tc. In the generator, ^{99}Mo decays to both ^{99m}Tc and ^{99}Tc, and finally all to ^{99}Tc. Therefore, the generator has to be extensively eluted before use and a short in-growth period for new ^{99m}Tc generation should be applied to reduce the ^{99}Tc in the tracer. However the ^{99m}Tc tracer is still not pure enough for low-level environmental samples [17,187]. Hou et al. [17] have investigated the ^{99}Tc impurity in ^{99m}Tc eluate from a hospital ^{99}Mo–^{99m}Tc generator, and found that a relatively higher contribution to ^{99}Tc in the eluate comes from ^{99}Mo breakthrough and ^{99}Tc remained on the column as reduced form. They developed a simple method by passing the new ^{99m}Tc eluate through two sets of alumina columns to remove the reduced ^{99}Tc and ^{99}Mo in the ^{99m}Tc solution, this procedure produced a pure ^{99m}Tc solution which is good enough for the use as yield tracer for environmental sample. The long-lived ^{97}Tc ($T_{1/2} = 2.6$ My) is an idea tracer for mass spectrometry, but it is very difficult to be obtained. In addition the ^{99}Tc impurity in ^{97}Tc has to be investigated before use. Rhenium has a similar chemical properties as technetium, it has therefore been used as tracer in mass spectrometric determination of ^{99}Tc, However, the behavior of Re in chemical separation has to be well investigated in order to be sure it behaves the same way as ^{99}Tc [46].

Table 9 – Comparison of radiometric and mass spectrometric methods for the determination of ^{99}Tc

Sample	Detection method	Target preparation	Detection limit	Sep. time[a]	Count time	Ref.
Environmental sample	GM detector	Tc on disk	1.5 mBq	1–2 days/7 days	3–4 h	[15]
Environmental sample	LSC	Tc solution	17 mBq	1–2 days/7 days	2 h	[186]
Geological samples	RIMS	TcO_2	20 μBq	1–2 days	30–60 min	[194]
Water	AMS	Tc in Al_2O_3 or Nb_2O_5	6–10 μBq	1 days	20–40 min	[190,192]
Sediment, seawater	ICP-SFMS	Tc solution	0.16–0.29 mBq	1–2 days	10–20 min	[47]
Seawater	ICP-MS with ETV	Tc in solution	0.18 mBq	1–2 days	20–40 min	[47]
Environmental sample	ICP-QMS	Tc in solution	10 mBq	1–2 days	20–40 min	[49]
Environmental sample	ICP-SFMS on-line	Tc in solution	0.05 mBq mL^{-1} or 0.2 mBq	1 h/4–5 h	10–20 min	[196]

[a] For the radiometric methods, if ^{99m}Tc is used as yield tracer, further 5–7 days decay time is needed after separation to remove all ^{99m}Tc which interferes the counting using GM counter or LSC. For on-line ICP-MS, the separation procedure take about 1 h, while the sample preparation takes about 5 h.

Neutron activation analysis can be also used for the determination of ^{99}Tc [200], which based on two reactions, $^{99}\text{Tc}(\text{n},\gamma)^{100}\text{Tc}\xrightarrow{\beta^-,15.8\,\text{s}}{}^{100}\text{Ru}$ and $^{99}\text{Tc}(\text{n},\text{n}')^{99\text{m}}\text{Tc}\xrightarrow{\text{IT},6.0\,\text{h}}{}^{99}\text{Tc}$, when counting ^{100}Tc, which has a very short half-life (15.8 s), ^{99}Tc has to be separated from the sample prior to irradiation; in addition a fast sample transfer system has to be used to shorten the decay time. NAA is theoretically a more sensitive method for ^{99}Tc, and a detection limit of 2.5 mBq has been obtained using pre-separation and radiochemical NAA [197,198]. Compared with ^{100}Tc, ^{99m}Tc, a neutron activation product of ^{99}Tc by (n, n′) reaction, has a longer half-life, it makes the post-irradiation separation becomes easier. However, the low neutron activation cross section (0.24 b) of ^{99}Tc(n, n′)^{99m}Tc reaction limits its analytical sensitivity [199]. The reported detection limit of this method is more than 1 Bq. Up to date NAA was mainly used for the analysis of samples with a high ^{99}Tc concentration, such as radioactivity waste.

Table 9 compares the radiometric and mass spectrometric methods for the determination of ^{99}Tc. AMS and RIMS are the most sensitive methods, their detection limits are 2 orders of magnitude better than radiometric method. These two methods are also rapid due to short counting time. The ICP-MS is comparable to the beta counting using GM detector, by using ETV or ICP-SFMS, the detection limit of ICP-MS may reach 10 times better than radiometric method. Due to the rapid analytical capacity and the installation of more ICP-MS instruments in radiochemical laboratories, many measurements of ^{99}Tc have being carried out by ICP-MS in recent years. However radiometric methods are still the dominating analytical technique for the analysis of environmental samples due to the well controlled blank counts, easy accessible measurement equipment and low cost.

4.8. *Iodine-129*

Iodine-129, a naturally occurring long-lived radioisotope of iodine (15.7 My) formed by cosmic ray reaction with Xe and fission of uranium, exists in the environmental with a low concentration (^{129}I/^{127}I ratio of 10^{-12}). Releases from human nuclear activities dominates the present ^{129}I level in environment (^{129}I/^{127}I ratio of 10^{-10} to 10^{-4}), in which discharges from nuclear reprocessing facilities are responsible for about 90% of the ^{129}I environmental inventory [201,202].

^{129}I decays by emitting β-particle with a maximum energy of 154.4 keV and γ-rays of 39.6 keV as well as X-rays (29–30 keV). It can therefore be measured by γ-spectrometry and β-counting using LSC [203,204]. Gamma spectrometry has been used to measure ^{129}I in thyroid, urine, seaweed, and waste by using HpGe detector [203,216]. Due to the low counting efficiency of gamma detector (<2%), low γ-ray abundance (7.5%), and high background, a high detection limit of 20–200 mBq was obtained [216] depending on the level of interfering radionuclide. The direct measurement is easy operation, but a high detection limit (100–200 mBq). A chemical separation of iodine from the matrix and interfering radionuclides can improve the detection limit to around 20 mBq when using gamma spectrometry. Using LSC and measuring ^{129}I separated from the matrix and other radionuclides results in a slight better detection limit of about 10 mBq [216]. A more sensitive method for the determination of ^{129}I is neutron activation analysis, in this method, the sample is irradiated with neutrons in a reactor to convert ^{129}I to short-lived ^{130}I ($T_{1/2} = 12.36$ h) by reaction ^{129}I(*n*, γ)^{130}I, which is then measured by γ-spectrometry. For removal of the interference, the iodine needs to be separated from the sample before the neutron irradiation; a detection limit of 1 μBq has been reported [201,205].

Mass spectrometric techniques, AMS, SIMS and ICP-MS have also been used for the ^{129}I determination. In AMS, the iodine needs to be separated from the sample and prepared as AgI precipitate, which is then mixed with Ag or Nb powder. I^{-} ions are easily formed in the sputter source, which is then stripped to I^{5+} or I^{7+} in the stripper tank, and separated from the interferences such as ^{128}TeH^{-} and ^{127}IH$_2$$^{-}$. The isobaric interference from ^{129}Xe in AMS is not a problem because the formation of the ^{129}Xe^{-} ion is extremely low. The separated ^{129}I is then detected by a combination of time-of-flight and a silicon charged particle detector. The instrumental background of ^{129}I/^{127}I down to 10^{-14} has been obtained [206–208]. The detection limit of ^{129}I very much depends on the level of procedure blank, by using a low ^{129}I iodine carrier, a $^{129/127}$I ratio of 1×10^{-13} was reported, it corresponds to 10^{-9} Bq ^{129}I for 1 mg ^{127}I carrier, and the analytical uncertainty is lower than 10% for a 1^{29}I/^{127}I ratio of 10^{-12} [208]. Due to the very high sensitive, most of determinations of ^{129}I in environmental samples, especially low-level geological samples, is now carried out by AMS. Actually, AMS is the only method

Table 10 – Comparison of radiometric and mass spectrometric methods for the determination of ^{129}I

Sample	Detection method	Target preparation	Detection limit	Sep. time	Count time	Ref.
Thyroid, seaweed	γ-Spectrometry	Direct measurement	100 mBq or 0.5 Bq kg^{-1}	No	20–60 h	[202]
Waste	γ-Spectrometry	Separated iodine (AgI)	20 mBq	3–4 h	60 h	[216]
Waste	γ-Spectrometry	Direct measurement	200 mBq	No	20 h	[216]
Seaweed	LSC	Separated iodine	10 mBq	3–4 h	1.5 h	[203]
Environmental samples	RNAA	Separated LiI	1 μBq or a $^{129}I/^{127}I$ ratio of 10^{-10}	4–7 h	1 h	[205]
Environmental samples	AMS	AgI	10^{-9} Bq or a $^{129}I/^{127}I$ ratio of 10^{-13}	4–7 h	20–30 min	[208]
Thyroid	SIMS	Direct measurement	5 Bq	No	10–60 min	[214]
Water	DRC-ICP-MS	Direct water measurement	37 μBq mL^{-1}	0.5–1 h	20–30 min	[42]
Sediment	DRC-ICP-MS	Gaseous iodine	2.5 μBq g^{-1} or a$^{129}I/^{127}I$ ratio of 10^{-7}	2–3 h	10–20 min	[41]

for the determination of ^{129}I in the pre-nuclear age samples ($^{129}I/^{127}I < 10^{-10}$) [202,199–212].

ICP-MS has been investigated for the determination of ^{129}I, but the problems associated is low sensitivity, isobaric and molecular ions interferences (^{129}Xe, $^{127}IH_2$, $^{89}Y^{40}Ar$, $^{115}In^{14}N$, $^{113}Cd^{16}O$), memory effects, low abundance sensitivity of ICP-MS (tailing from the ^{127}I peak), especially isobar ^{129}Xe and tailing of ^{127}I. A dynamic reaction cell (DRC) ICP-MS by using oxygen as reaction gas has been found to significantly reduce xenon ions by charge transfer. It was also found that pressurizing the collision cell with helium the tailing of ^{127}I or abundance sensitivity can be improved. By using helium and oxygen in the DRC, and directly introducing gaseous iodine to the ICP-MS system, the detection limit of ICP-MS could be significantly improved to 10^{-6} for $^{129}I/^{127}I$ ratio (25 μBq g^{-1} for ^{129}I at a ^{127}I concentration of 4 μg g^{-1}) [213]. By trapping gaseous iodine thermally released from samples, and then desorbing it to the ICP-MS system, detection limit could be further improved to 2.5 μBq g^{-1} (or 10^{-7} for $^{129}I/^{127}I$ ratio) [41]. By using a similar techniques, but directly introducing water samples in 1% tertiary amine carrier solution, a detection limit of 37 μBq mL^{-1} was reported [42].

SIMS has also been used for the determination of ^{129}I in the thyroid. Due to the low sensitivity of this method, only high level sample can be measured. The animal and human thyroid sample, in which more than 10 μg ^{129}I was administrated, have been directly *in vivo* analyzed by SIMS to map the distribution of ^{129}I in the thyroid [214,215]. The major benefit of this technique is the direct and *in vivo* analysis as well as the ^{129}I spatial information in the sample

Table 10 compares the radiometric and mass spectrometric methods for the determination of ^{129}I. The γ-spectrometry and LSC are the least sensitive and long counting time, while it is cheaper and good accessible. These methods are therefore only suitable for the analysis of waste and high level environmental samples. The sensitivity of SIMS is very low, but it can provide spatial information of ^{129}I and directly used for *in vivo* analysis of high ^{129}I level samples, it is therefore only used in some special samples. By using DRC techniques, ICP-MS can be used for the determination of ^{129}I in relatively low-level samples, but the detection limit for $^{129}I/^{127}I$ is only 10^{-7}, it may only be suitable for the analysis of waste and high level environmental samples. Only NAA and AMS are sensitive enough for the analysis of environmental samples, especially AMS, which is the only method for the analysis of sample with a very low ^{129}I level (<10^{-10} for $^{129}I/^{127}I$ ratio).

4.9. *Cesium-135, 137*

Both ^{135}Cs and ^{137}Cs are fission products of ^{235}U with a similar fission yield to mass 135 and 137 (6–7%). Due to a very high neutron absorption cross section of ^{135}Xe (3.6×10^6 b), the ratios of $^{135}Cs/^{137}Cs$ in irradiated nuclear fuel varies with time of neutron irradiation. Therefore, the $^{135}Cs/^{137}Cs$ ratio may be used as a marker for the source identification. ^{135}Cs and ^{137}Cs in environmental samples may originate from the weapons testing, operation of nuclear faculties such as nuclear power plants and reprocessing plants, and nuclear accidents. ^{137}Cs is one of important radionuclides in the views of radiation protection, environmental monitoring and waste disposal.

^{137}Cs, a short-lived radionuclide (30.07 years), decays by emitting β-particles with maximum energies of 514 keV (94.4%) and 1175 keV (5.4%), it is accompanied by γ-ray emission of 661.7 keV (85.1%). ^{137}Cs can thus be measured by β-counting and γ-spectrometry. The often common choice to use gamma-counting is a consequence of the high abundance of the 661.7 keV γ-ray from ^{137}Cs, little self-adsorption in the sample due to high energy, possibility of direct measurement and a minimum of contamination during sample preparation. These factors together with easy operational instrumentation make γ-spectrometry using HpGe detector an excellent method for the determination of ^{137}Cs in waste and environmental samples. A detection limit for γ-spectrometry of ^{137}Cs can be less than 50 mBq (or 1 mBq g^{-1} for 50 g sample), which is less than present environmental levels in most samples.

^{135}Cs, a long-lived radionuclide (2.3 My), is a pure β-particle emitter with a maximum beta particle energy of 269 keV. ^{135}Cs is therefore suitable to be determined by using a beta counter, such as GM counter and LSC. However, both of ^{135}Cs and ^{137}Cs exist in the sample, and the radioactivity concentration of ^{137}Cs is normally more than 5 orders of magnitude higher than ^{135}Cs due to the significantly different half-life of these two isotopes. The presence of ^{137}Cs makes the detection of ^{135}Cs by beta counting impossible.

^{135}Cs can be also measured by gamma spectrometry by counting its 268.2 keV γ-ray (15.5%). However, the low specific activity of ^{135}Cs (43 mBq ng^{-1}) and low counting efficiency of gamma spectrometry for ^{135}Cs makes its determination by radiometric methods very difficult.

NAA can be also used for the determination of ^{135}Cs based on the reaction: $^{135}Cs \xrightarrow{(n,\gamma)} {}^{136}Cs \xrightarrow{\beta,13.16\,\mathrm{day}} {}^{136}Ba$ [217,218].

Because of the very low concentration of ^{135}Cs in the environmental samples, a pre-irradiation concentration has to be carried out to separate Cs from a large amount of sample. The most used method for the separation and concentration of Cs in water samples is based on its specific absorption on ammonium phosphomolybdate (AMP) and copper ferrocyanide (CFC). However, before irradiation, Cs has to be separated from AMP and CFC to reduce the radioactivity of ^{32}P, ^{99}Mo, ^{59}Fe, ^{64}Cu. Cs concentrated in AMP can be released by dissolution of AMP with diluted KOH, and the released Cs is then absorbed on a cation exchange resin for neutron irradiation [217]. For improvement of the detection limit, a post-irradiation separation of Cs can be carried out, the Cs on the irradiated cation exchange resin can be eluted by 5–8 mol L^{-1} HNO$_3$, and the released Cs is then separated by AMP precipitation or cation exchange chromatography [217]. The separated Cs sample is measured by an HpGe detector; the content of ^{135}Cs can be calculated by counting the radioactivity of ^{136}Cs using its main gamma rays with energies of 818.5 keV (100%), and 1048.1 keV (80.3%). The detection limit of NAA for ^{135}Cs depends on the concentration of other Cs isotopes, especially ^{133}Cs and ^{137}Cs. A detection limit of 10^{-4} Bq (10^{-12} g) of ^{135}Cs has been reported for a sample with a ratio of ^{133}Cs:^{135}Cs:^{137}Cs = 1:1:1 [217].

Mass spectrometry is a good technique for the determination of ^{135}Cs. TIMS, SIMS and ICP-MS have been used for the determination of ^{135}Cs and ^{137}Cs. In TIMS, Cs in the sample is separated from the matrix and interfering element, especially Ba, and the separated Cs is finally loaded onto a Re filament. The main problem in the mass spectrometric determination of ^{135}Cs and ^{137}Cs is the stable isobaric interference of ^{135}Ba and ^{137}Ba, and the tailing of stable ^{133}Cs. By a combination of proper chemical separation and heating the filament to introduce Cs to the system at 700 °C, the contribution of Ba to ^{135}Cs can be removed. By using an additional electrostatic analyzer, the removal of the tailing of ^{133}Cs to ^{135}Cs could be significantly improved. Lee et al. [219] has used a TIMS equipped with a static retarding potential repeller and a static quadrupole lens to determine ^{135}Cs, ^{137}Cs and ^{133}Cs in sediment samples. The tailing of ^{133}Cs at 135 amu was better than 3×10^{-10}, and a ratio of ^{135}Cs/^{133}Cs of 1×10^{-9} was measured.

In RIMS, the separated Cs is loaded into a graphite tube, which is lined with titanium tubing, therefore resistively heated to atomize the sample, exciting using the 6s $^2S_{1/2}$ $(F = 4) \rightarrow$ 6p $^2P_{3/2}$ $(F' = 5)$ transition with an extended cavity diode laser followed by photoionization with the 488 nm line of an argon ion laser in order to obtain an optical selectivity for ^{135}Cs against stable ^{133}Cs. By this method, a ^{135}Cs/^{133}Cs ratio of more than 10^{-8} can be measured [97–99].

The main problem in determination of ^{135}Cs by ICP-MS is the isobar ^{135}Ba and the tailing from the ^{133}Cs, ^{134}Xe and ^{136}Xe. Chemical removal of barium has to be carried out before measurement. Further discrimination against barium may be done by using an ETV sample introduction system. By using different chemical modifiers in the ETV system, the detection limit of ^{135}Cs can be significantly improved. Using KSCN as chemical modifier, the Cs signal was enhanced around 60 times without significantly enhancing the barium signal. By further using a vaporization temperature of 1100 °C most of the cesium was vaporized while only some 0.03 ppm of the barium was vaporized. An absolute detection limit of 0.2 μBq (0.4 fg) for ^{135}Cs has been reported by using this method [220] in an artificial ^{135}Cs solution. Considering the relatively poor abundance sensitivity of ICP-MS instrument, and the very low ^{135}Cs/^{133}Cs ratio in real samples, the practical detection limit will be higher for environmental samples due mainly to the presence of stable ^{133}Cs [221].

4.10. *Lead-210*

^{210}Pb, a short-lived beta emitter (22.3 years), is one of decay products in the ^{238}U decay chain. The interest in the determination of ^{210}Pb mainly comes from its application in geochronology, air flux of radon, and radiation protection in uranium mine. ^{210}Pb decays by emitting soft β-particles of maximum energy of 17.0 keV (84%) and 63.5 keV (16%) accompanying by a 46.5 keV γ-rays (4.25%) to ^{210}Bi (5 days) and then to ^{210}Po (138 days) as shown below:

$$^{210}\mathrm{Pb}\xrightarrow{\beta,22.3\,\mathrm{year}}{}^{210}\mathrm{Bi}\xrightarrow{\beta,5.0\,\mathrm{day}}{}^{210}\mathrm{Po}\xrightarrow{\alpha,138.4\,\mathrm{day}}{}^{216}\mathrm{Pb}\,(\mathrm{stable})$$

The determination of ^{210}Pb can be carried out by γ-spectrometry, beta counting using GM counter through its daughter ^{210}Bi, which emits a high energy beta particles ($E_{\max} = 1.2$ MeV), and by alpha spectrometry of its granddaughter ^{210}Po. γ-Spectrometry is the easiest method, the sample can be directly measured using an HpGe detector. However, due to the low energy of its γ-ray, the self-absorption and interference from other γ-X rays have to be considered. A detection limit of 440 mBq was reported by using γ-spectrometry and a 1000 min counting time [222]. For beta counting, the sample needs to be decomposed and Pb needs to be separated from the matrix and other radionuclides. Solvent extraction, precipitation and ion exchange methods have been used to separate Pb. The separated Pb is kept for 8–9 days for the in-growth of ^{210}Bi, which is then measured using GM detector or LSC [223,224]. A detection limit of 7 mBq was reported using this method [222]. For α-spectrometry, the sample is first decomposed, after removal of the ^{210}Po in the samples by solvent extraction or self-deposition on a silver disk [225], the sample is kept for more than 3 months for the in-growth of ^{210}Po, the newly generated ^{210}Po from ^{210}Pb is then self-deposited onto a silver dick and measured by α-spectrometry using semiconductor detector. Because of the very low background counts and the high counting efficiency (30–40%), detection limits of 0.1–1 mBq, depending on the in-growth time, have been obtained [222,226]. The drawback of α-spectrometry is the long analytical time due to the waiting for in-growth of ^{210}Po. The relatively higher detection limit of γ-spectrometry and the complicated separation procedure for beta counting make the α-spectrometry an attractive technique, especially for the analysis of the very low-level samples [227].

ICP-MS has also been used for the determination of ^{210}Pb, the main problem in this method results from the interference of molecular ions such as ^{209}Bi^{1}H, ^{208}Pb^{1}H$_2$, ^{194}Pt^{16}O, ^{198}Hg^{12}C, and ^{170}Er^{40}Ar, and the abundance sensitivity by the tailing of ^{209}Bi and ^{208}Pb. By converting lead into the volatile tetraethyl lead, and directly introducing this form of Pb to the plasma, most of molecular ions interferences can be significantly removed. Since the ethylated species of bismuth are also volatile, this element is a major problem, chemical removal of this element prior to analysis is therefore imperative. In spite of the improved sample introduction technique and a thorough chemical clean-up of the samples, the detection limits for water sample was not better than 90 mBq L^{-1} (10 pg L^{-1}) after pre-concentration, mainly because of the tailing from the stable lead isotopes [228]. This makes ICP-MS less attractive compared to radiometric methods, although a rapid analysis can be carried out by this technique.

4.11. *Radium-226, 228*

^{226}Ra and ^{228}Ra originate from the naturally decay series of ^{238}U and ^{232}Th. Concentrations of ^{226}Ra and ^{228}Ra in typical soil samples are 1000 and 5 fg g^{-1} (or 30 and 50 mBq g^{-1}), respectively. The interest in the determination of ^{226}Ra and ^{228}Ra comes not only from the radiation protection concern, but also from the application of them as environmental tracers.

^{226}Ra, a long-lived radionuclide (1600 years), decays by emitting alpha particles with energies of 4.60 and 4.78 MeV to ^{222}Rn, accompanied with an emission of 186.2 keV (3.59%) γ-ray. This decay follows by a few short-lived decay daughters as shown below:

$$^{226}\mathrm{Ra}\xrightarrow{\alpha,1600\,\mathrm{year}}{}^{222}\mathrm{Rn}\xrightarrow{\alpha,3.8\,\mathrm{day}}{}^{218}\mathrm{Po}\xrightarrow{\alpha,3.10\,\mathrm{min}}{}^{214}\mathrm{Pb}\xrightarrow{\beta^-,26.8\,\mathrm{min}}{}^{214}\mathrm{Bi}$$

$$\xrightarrow{\beta^-,19.9\,\mathrm{min}}{}^{214}\mathrm{Po}\xrightarrow{\alpha,0.16\,\mathrm{ms}}{}^{210}\mathrm{Pb}(22\,\mathrm{year})$$

^{226}Ra can thus be determined by α-spectrometry and γ-spectrometry. The γ-rays from its granddaughters ^{214}Bi (609.3 keV (46.1%) and 1120.3 keV (15.1%)) and ^{214}Pb (295.2 keV (19.3%) and 351.9 keV (37.6%)) can also be used for the determination of ^{226}Ra. In addition, LSC has been used for the determination of ^{226}Ra by measuring alpha particles of ^{226}Ra, its daughters or ^{226}Ra plus its daughters (^{222}Rn, ^{218}Po, ^{214}Po) by using alpha–beta discrimination mode in LSC equipment. In γ-spectrometric measurement of ^{226}Ra, the interference with the 185.7 keV γ-ray from ^{235}U has to be subtracted because the two gamma lines cannot be resolved using gamma spectrometry. The low abundance of the 186.2 keV γ-ray of ^{226}Ra (3.6%), the interference from ^{235}U and Compton background due to the presence of other radionuclides make this method insensitive, the detection limit varies from 0.1 to 1 Bq depending on the background level [229]. Measurement via the γ-rays of ^{214}Bi and ^{214}Pb can improve the detection limit because of less interference and higher abundance of these γ-rays, however, the leaking of ^{222}Rn gas, the daughter of ^{226}Ra and the mother of ^{214}Bi and ^{214}Pb, is the main problem related to the reliability of analytical results.

LSC is a sensitive method for the determination of ^{226}Ra, which can be carried out by measuring the β-emitting daughter isotopes ^{214}Bi and ^{214}Pb, or the α-emitters ^{226}Ra, ^{222}Rn, ^{218}Po and ^{214}Po. The detection limit by measuring α-emitters is much better than that of β-emitters, because of the low background in the alpha windows of LSC and the high counting efficiency of LSC for α-emitters (>95%). If all four α-emitters (^{226}Ra, ^{222}Rn, ^{218}Po and ^{241}Po) are measured, the counting efficiency will be higher than 380%, which is more than one order of magnitude higher than that of counting beta emitters. In addition only ^{214}Po may be used alone for the determination of ^{226}Ra in LSC, since it is completely separated from the peaks of ^{226}Ra and other daughters (Fig. 2). A spectrum of ^{226}Ra using ^{133}Ba as chemical yield tracer is shown in Fig. 2, in the beta window, the ^{133}Ba tracer, ^{214}Bi and ^{214}Pb are measured, while in the alpha windows, ^{226}Ra and its daughters ^{222}Rn, ^{218}Po and ^{214}Po are measured. In this method, Ra has to be separated from the matrix and other radionuclides. In addition, the measurement of ^{226}Ra can also be carried out by extracting ^{222}Rn to the organic scintillation cocktail and the LSC counting of ^{222}Rn, ^{218}Po and ^{214}Po is thereby done. In this case, chemical separation of Ra from other radionuclides may not be so stringent, because most of radionuclides do not be extracted into the organic cocktail but rather in the aqueous phase. By using this method, a detection limit of 0.3–1.4 mBq has been reported [230,231]. The main drawback of the LSC is the long analytical time which results from a long waiting time (3 weeks) for the in-growth of the ^{226}Ra daughters.

The most sensitive radiometric method for ^{226}Ra is α-spectrometry due to the very low background counts. In this method, Ra has to be separated from the matrix and other radionuclides, and electrodeposited on a disk or precipitated and filtered on a filter. The main problem of electrodeposited

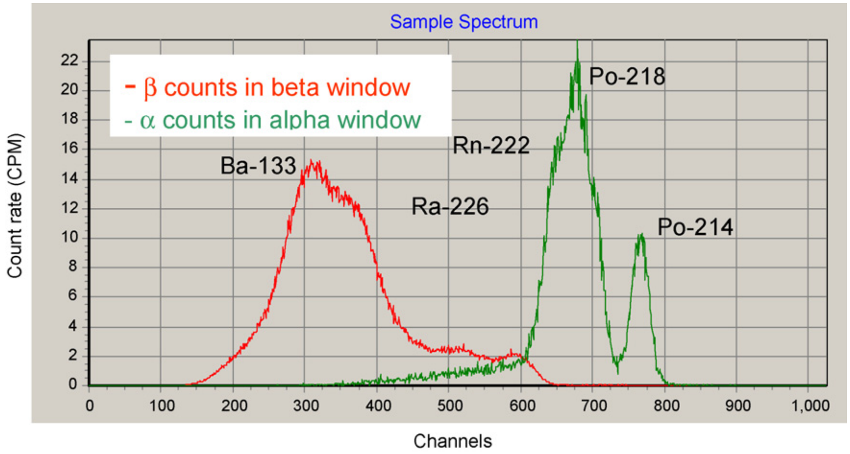

Fig. 2 – Beta spectroscopy of ^{226}Ra measured by α-β separation in Quantulus^{TM} 1220 LSC.

sources for alpha spectrometry of Ra is the interference of Ba, which exists in environmental samples with a much higher concentration than that of Ra. A high Ba concentration in the separated solution prepared for electrodeposition will significantly reduces the chemical yield of Ra in the electrodeposition process and worsening the resolution of α-spectroscopy by increasing the thickness of the source, it is therefore Ba has to be completely separated from Ra before electrodeposition [232]. Co-precipitation of Ra and then filtered on a filter is an easy method for the preparation of the alpha source, but the self-absorption and thereby the reduced energy resolution is the main problem in this method because of the thickness of the source. A new development on the chemical separation and alpha spectrometric determination of Ra is the thin film absorption of Ra from the solution [13]. In this method, polyamide piece was immersed in $KMnO_4$ solution at 60 °C under stirring, a manganese oxide layer was generated on the polyamide substrate. The prepared thin film was then suspended in the sample solution with pH of 4–8 for 40–50 h under stirring at room temperature. Following the sorption step, samples were washed and measured using alpha or gamma spectrometry. The absorption efficiency is higher than 99% for 1 L sample solution using a film of 2.5 cm^2. With the increasing of the sample volume, the absorption efficiency decreases. This method is easy to operate, but not suitable for a large volume sample. Another drawback of the α-spectrometry is the risk of the contamination of the detector, because the release of the ^{222}Rn from the Ra source and deposition of its daughter on the detector, however, this risk is quiet less due to shorter half lives of most daughter radionuclides of ^{226}Ra. A detection limit of 0.2–0.5 mBq has been reported for this method for 2 days counting time [13,233].

Radium-228, a short-lived radioisotope of Ra (5.75 years), decays by low energy β^-emission (12–40 keV) to ^{228}Ac, with emission of 12–17 keV low energy gamma rays (3%) which are difficult to be detected. This decay follows by a few short-lived decay daughters as shown below:

$$^{228}\mathrm{Ra}\xrightarrow{\beta,5.75\,\mathrm{year}}{}^{228}\mathrm{Ac}\xrightarrow{\beta,6.15\,\mathrm{h}}{}^{228}\mathrm{Th}\xrightarrow{\alpha,1.91\,\mathrm{year}}{}^{224}\mathrm{Ra}$$

^{228}Ac, daughter of ^{228}Ra, decays by emitting high energy beta particles (1.16 MeV), accompanying by γ-rays (911.2 keV (25.8%), 969.0 keV (15.8%)). ^{228}Ra is therefore normally determined by γ-spectrometry and beta counting of its short-lived daughter ^{228}Ac or by α-spectrometry of its granddaughter ^{228}Th. Direct γ-counting is the simplest method, but a high detection limit (100 mBq) is normally obtained [236]. In the beta counting method, Ra is first separated from the matrix and Ac, after in-growth of ^{228}Ac from ^{228}Ra for 3–24 h, the generated ^{228}Ac is separated from Ra, which can be carried out by solvent extraction using 2-ethylhexyl phosphoric acid (HDEHP) or extraction chromatography. The separated ^{228}Ac is prepared as a precipitate such as $Ac_2(C_2O_4)_3$ for beta counting. A detection limit of 15 mBq has been reported by using this method and counting by a GM counter for 100 min [236]. The separated ^{228}Ac can be also measured by LSC, in this case a slight higher detection limit of 25 mBq was reported [237]. In the α-spectrometry, the Ra is separated from the matrix and other radionuclides, and prepared as a α source by electrodepositing on disc or precipitating/adsorbing on filter. The ^{228}Th generated from ^{228}Ra is then measured by α-spectrometry. The advantage of this method is the simultaneous determination of ^{224}Ra, ^{226}Ra and ^{228}Ra, and a relatively low detection limit (0.2 mBq) [234]. The drawback is the very long analytical time (1–2 years) due to the long waiting time for the in-growth of the longer-lived ^{228}Th (1.9 years).

Mass spectrometric methods, AMS, TIMS and ICP-MS have also been used for the determination of ^{226}Ra and ^{228}Ra. In AMS, the separated Ra is simply adsorbed in a carbon powder matrix, $RaC_2{}^-$ is normally chosen as injection ion because of the low count rate of Ra^-. The mass separated Ra ions are measured by multi-anode gas ionization detector. A detection limit of 10^7 atoms or 0.1 mBq for ^{226}Ra and 40 mBq for ^{228}Ra has been reported [238], which is comparable to alpha spectrometric method for ^{226}Ra, and beta counting method for ^{228}Ra, but worse than alpha spectrometry for ^{228}Ra (^{228}Th). The major advantage of AMS for radium measurements is the ability to measure both isotopes within a short time. TIMS is a sensitive method for the determination of ^{226}Ra, a detection limit of 37 μBq was reported. While, detection limit of 12 mBq for ^{228}Ra is comparable to beta counting but worse than alpha counting using ^{228}Th [239,92]. The drawback of this method is the interference from Ba, which has to be completely separated from Ra. In ICP-MS, there are no isobaric interferences to ^{226}Ra, while ^{228}Th is a potential isobaric interference to ^{228}Ra. As a short-lived decay product of ^{228}Ra, the mass concentration of ^{228}Th in the samples is normally less than 30% of ^{228}Ra. However, with fractionation in natural process, concentration of ^{228}Th in some samples may be comparable or even higher than that of ^{228}Ra. In addition the polyatomic interferences and signal suppression due to a high salt load to the plasma makes chemical separation of radium necessary before ICP-MS measurement. Since radium is an alkaline earth element, high concentrations of barium, strontium and calcium may be expected to follow in the separation and polyatomic species like $^{88}Sr^{138}Ba$ may appear. Other potential interferences include $^{208}Pb^{18}O$ and $^{146}Nd^{40}Ar_2$ as well as several combinations of molybdenum isotopes with xenon isotopes. A detection limit of 0.1–0.5 mBq for ^{226}Ra has been reported using a SF-ICP-MS combined with an APEX-Q nebuliser [59,240], which is comparable to radiometric method. The main advantage of mass spectrometric method is the short analytical time, normally only some minutes excluding sample preparation.

Table 11 compares the radiometric and mass spectrometric methods for the determination of ^{226}Ra and ^{228}Ra. γ-Spectrometry is the simplest, cheaper and rapid method, but the sensitivity is low, and can only be used for high level or large soil or sediment samples. Mass spectrometric methods including ICP-MS are sensitive for ^{226}Ra, they are comparable to the LSC and alpha spectrometry, and the analytical time is much shorter than using radiometric methods. AMS and TIMS can be used for the determination of ^{228}Ra, the sensitivity is comparable with beta counting, but lower than alpha spectrometry using the daughter isotope ^{228}Th. Due to the restricted availability to AMS and TIMS instrumentation configured for such measurements, radiometric methods are still the most suitable method for the determination of ^{228}Ra.

Table 11 – Comparison of radiometric and mass spectrometric methods for determination of ^{226}Ra and ^{228}Ra

Sample	Detection method	Nuclide	Detection limit	Sept. time	Count time	Ref.
Environmental samples	γ-Spectrometry	^{226}Ra	0.1–1 Bq	No	5 h	[229]
Water	γ-Spectrometry	^{226}Ra (via ^{214}Pb)	80 mBq	No	40 h	[235]
Environmental samples	LSC	^{226}Ra (via its daughters)	0.3–1.4 mBq	2 h/30days*	6 h	[230,231]
Environmental samples	α-Spectrometry	^{226}Ra	0.2–0.5 mBq	2–4 days	2 days	[13,233,234]
Environmental sample	TIMS	^{226}Ra	37 μBq	4–5 h	20–30 min	[239,92]
water	ICP-MS	^{226}Ra	0.1–0.5 mBq	2–4 h	10 min	[240,252]
Water	ICP-MS/flow-injection separation	^{226}Ra	0.34 mBq	20–30 min	20 min	[59]
Water	AMS	^{226}Ra	0.1 mBq	3–5 h	30 min	[238]
Environmental samples	α-Spectrometry	^{228}Ra (via ^{228}Th/^{224}Ra)	0.2 mBq	2–4 days/6–12 months*	2–3 days	[234]
Water	LSC	^{228}Ra	25 mBq	1–2 days	60 min	[237]
Water	GM counter	^{228}Ra (via ^{228}Ac)	15 mBq	4–8 h	100 min	[236]
Water	γ-Spectrometry	^{228}Ra (via ^{228}Ac)	100 mBq	No	40 h	[235]
Environmental sample	TIMS	^{228}Ra	12 mBq	4–5 h	20–30 min	[239,92]
Water	AMS	^{228}Ra	40 mBq	3–5 h	30 min	[238]

* Time of separation and in-growth of ^{222}Rn from ^{226}Ra or ^{228}Th/^{224}Ra from ^{228}Ra.

4.12. *Isotopes of thorium and uranium*

The determination of uranium and thorium isotopes has historically been a subject mostly within the fields of geochronology and geochemistry. Within the fields of environmental sciences and health physics, interest has been widespread although to a lesser extent. In recent years uranium isotopes has also been of major interest within the field of nuclear forensic analysis. Among the naturally occurring uranium and thorium isotopes, there are some very long-lived (^{238}U, ^{235}U and ^{232}Th), some with intermediate half-lives (^{234}U and ^{230}Th) and some with a short half-life (^{228}Th, ^{234}Th, ^{231}Th). When concerning nuclear materials, additional isotopes like ^{236}U and occasionally ^{233}U are of interest. The analytical methods used for these isotopes depends mainly on what isotopes are of interest, their half-lives, decay mode and risk of interferences in the various techniques. Due to the huge span in specific activity (from 19 TBq mg^{-1} for ^{231}Th to 4 Bq mg^{-1} for ^{232}Th), both mass spectrometric and radiometric methods are required in order to be able to analyze all isotopes. In general, the long-lived radioisotopes are best determined by mass spectrometric methods, while the short-lived ones are preferably determined by radiometric methods.

The geochronology and the geochemistry societies mainly seek to obtain high precision isotope ratios (^{234}U/^{238}U, ^{230}Th/^{234}U), while the health physics interest is mainly focused on concentrations. An exception is nuclear forensic groups requiring high precision ^{235}U/^{238}U and ^{236}U/^{238}U ratios. Achieving high precision means counting a sufficient number of events (radioactive decays or ions) which may be done by either a sensitive instrumentation or a large sample mass (activity). Lack of suitable, high abundance gamma lines emitted by the long-lived U and Th-isotopes means that the standard radiometric method is alpha spectrometry where the chemically separated U or Th-isotopes usually have been electrodeposited on stainless steel discs and measured using semiconductor detectors for charged particles [242]. From spectroscopy point of view, alpha spectrometry of the natural composition of either the U or the Th-isotopes presents few problems. This technique has been used for more than 30 years and is well established and very reliable. It should be kept in mind that mass spectrometry often requires considerable skill of the operators to obtain reliable results. For both elements, tracer isotopes (^{232}U and ^{229}Th) are readily available for alpha spectrometry and do not disturb other peaks in the spectrum. In cases where the ^{230}Th/^{229}Th is very low and/or the energy resolution is poor, a correction for ^{229}Th in the ^{230}Th peak must be performed. The major obstacle with alpha spectrometry of the U and Th-isotopes are long counting times (days–weeks) and a limited precision due to the counting statistics. The development of detector hardware for alpha spectrometry during the last 10 years has been very limited and in principle all measurements are being performed using ion implanted planar silicon detectors.

Due to the low specific activity of the long-lived ^{238}U and ^{232}Th isotopes (12.3 and 4 Bq mg^{-1} respectively), there is an upper limit as to how much U or Th that can be accepted on the disc before severe degradation of the alpha spectrum starts due to self-absorption of the alpha particles in the source. This means that there is an upper limit of the count rate that can be achieved in alpha spectrometry for the alpha emitting ^{238}U, ^{235}U, ^{234}U, ^{232}Th and ^{230}Th isotopes. To compensate for the low count rates, long counting times have been necessary in order to obtain sufficiently good counting statistics. Even with counting times in the order of weeks to months, only a very tiny fraction of the U and Th isotopes are detected on the steel disc. The instrumental efficiency may be measured as the count rate relative to the amount of U or Th isotopes present on the disc and is thus extremely small. Although matrix suppression of the signal also occurs in mass spectrometry, counting of the ions instead of their emitted radiation makes mass spectrometric analysis of the long-lived ^{238}U and ^{232}Th around six orders of magnitude more sensitive than the radiometric methods. The development within high-precision isotope ratio mass spectrometry has partly been driven by the geochemical/geochronological society and today multicollector systems both in TIMS and ICP-MS instruments has further manifested mass spectrometry as the main tool for high-precision measurements of the U-isotopes and long-lived Th-isotopes ^{232}Th and ^{230}Th.

At present both MC-ICP-MS and MC-TIMS instruments are considered the ultimate tools for isotope ratio measurement of the longer lived U and Th isotopes. TIMS instruments show the best ion beam stability and better abundance sensitivity due to the lower spread in ion energy than ICP-MS instruments. With the introduction of multi-collectors in ICP-MS instruments, the ion beam instability could be compensated for and the internal precision in TIMS and MC-ICP-MS instruments may typically reach 0.01 per mille [246]. The main factor limiting precision and accuracy in TIMS is the time dependent mass fractionation that arises from the evaporation process at the filament. This means that the isotope ratio changes with time during the analysis. In order to overcome this instrumental-induced mass fractionation, a double-spike technique is required. For uranium a ^{236}U–^{233}U mixture with known atom ratio may be applied or the natural ^{238}U/^{235}U atom ratio of 137.88 may be used, but for thorium isotopes this technique is not possible due to lack of natural occurring isotopes of known ratios and due to lack of other isotopes than ^{229}Th as spike. In order to correct for mass fractionation in Th-analysis by TIMS, external correction factors have to be applied by analyzing suitable thorium standards. An alternative to minimize the influence of the time dependent mass fractionation is to integrate the signal over the complete analysis time until the sample has been consumed. The main advantage with MC-ICP-MS over TIMS is the absence of any time dependence in mass fractionation (although mass-fractionation in ICP-MS typically is an order of magnitude larger than in TIMS) and the significantly less complicated sample preparation, which means a higher throughput of samples during any given time. For thorium in particular, ICP-MS is better than TIMS due to the low ionization efficiency at the TIMS filament. Another advantage with ICP-MS instruments is that other isotope systems than what is intended to be measured may be used to correct for the mass bias. A well-known uranium isotope mixture may thus be used to correct for mass fractionation acting on the ^{230}Th/^{232}Th isotopes. A similar approach is not possible in TIMS due to the temperature dependent element evaporation from the filament. The temperature dependent evaporation is, on the other hand, one of the advantages in TIMS since it means a more element specific input to the instrument and thus a significantly reduced risk of isobaric and polyatomic interferences. Several review articles on radiometric and mass-spectrometric techniques for measuring U and Th isotopes are available [241–244].

Mass spectrometric techniques like MC-ICP-MS and TIMS are presently the standard accepted methods for determination of long- and intermediate half-life U and Th isotopes within the geological sciences, the requirements of high precision measurements are less in the health physics societies which means that alpha spectrometry and/or single collector ICP-MS is the standard techniques used. For ICP-MS instruments the most critical parameter is the abundance sensitivity which determines whether the intermediate half-life isotopes ^{234}U and ^{230}Th can be measured without significant influence of tailing from the more abundant ^{235}U, ^{238}U and ^{232}Th isotopes. In alpha spectrometry this is never a problem. When faced with poor abundance sensitivity of ICP-MS instruments, alpha spectrometry is preferred. The better peak shape in quadrupole based instruments (better defined boundaries) means that despite the absence of flat topped peaks in Q-ICP-MS a more reliable ^{230}Th/^{232}Th ratio may be obtained since no interference corrections needs to be applied for tailing.

Apart from the natural uranium isotopes, ^{236}U (half-life: 2.4×10^7 years) produced through neutron activation reaction of ^{235}U in nuclear reactors, is of interest in nuclear forensic analysis. Due to the very low atom ratio of ^{236}U/^{235}U (ppb–ppm levels) in samples of interest, ordinary ICP-MS is often not sufficient due to the poor abundance sensitivity and the hydride formation (^{235}UH). Boulyga and Heumann [247], using a ELEMENT 2 SF-ICP-MS optimized for improved abundance sensitivity and minimized hydrides, have managed to measure ^{236}U/^{238}U atom ratios down to 10^{-7} which may be sufficient even at very low-levels of contamination of nuclear material. Alpha spectrometry proves difficult in analyzing ^{236}U due to similar alpha particle energies as ^{235}U. TIMS, and in particular AMS, is the best technique suited for this analysis. This is because of the excellent abundance sensitivity achieved by these techniques. A comparison between AMS and MC-ICP-MS for the measurement of ^{236}U and the naturally occurring uranium isotopes was presented by Buchholz et al. [248]. With AMS, measurement of ^{236}U/^{238}U atom ratios down to 10^{-15} is possible using high energy filters, and a detection limits in the order of 10^4 atoms has been reported [245]. Due to the several other measurement techniques available for the analysis of naturally occurring U and Th isotopes these isotopes are rarely analyzed by AMS.

There may be a choice between mass-spectrometric and radiometric methods for U and Th isotopes with long and intermediate half-lives, while for the short-lived Th-isotopes, ^{228}Th and ^{234}Th (half-lives of 1.91 years and 24 days respectively), radiometric methods may be the only possible technique for their determination when present at environmental levels. The alpha-emitter ^{228}Th is most conveniently determined by standard alpha spectrometry, it may also be determined by gamma spectrometry through one of its daughter isotopes when activity levels are sufficient. The beta emitter ^{234}Th has played a major role as a particle tracer in the marine environment, especially a rate tracer for particulate organic carbon (POC) vertical fluxes [250]. Several techniques for direct measurement of ^{234}Th onboard a ship or in the shore based laboratory have been developed. Being a fairly low-abundant gamma emitter (64 keV (4.8%) and 93 keV (5.6%)), a large sample volumes of sea-water is required for the analysis, but significantly smaller volumes, down to a few liters, is enough when using anti-coincidence shielded GM-counters and measuring the combined electron emission of both ^{234}Th and ^{234}Pa which reaches secular equilibrium within some tens of minutes after separation of Th. A recent review article on the methodology for analyzing ^{234}Th in marine systems has been presented by Van der Loeff et al. [249].

4.13. Neptunium-237

Neptunium-237 presenting in environment has been produced by $^{238}U(n, 2n)^{237}U \rightarrow {}^{237}Np$ reaction through fast neutrons in nuclear bomb testing and reactors and $^{235}U(n, \gamma)^{236}U(n, \gamma)^{237}U \rightarrow {}^{237}Np$ reaction in nuclear reactors followed by releases from spent fuel reprocessing. It is also produced as a consequence of the decay of ^{241}Am. The interest in the determination of ^{237}Np results from tracer applications and in connection to repositories of nuclear waste because of its relatively high mobility in the environment and as a consequence the most hazardous radioisotopes in spent nuclear fuel.

^{237}Np is an α-emitting long-lived radionuclide (2.144 My), α-spectrometry has therefore traditionally been used for its measurement. Due to the low concentration encountered in environmental samples, a pre-concentration and completely separation from interfering radionuclides are necessary. Ion exchange, extraction chromatography and solvent extraction, are normally used for the separation of ^{237}Np [251–259]. Control of the valence state of Np plays an important role in the chemical separation procedure. Neptunium can exist as Np^{3+}, Np^{4+}, $NpO_2{}^+$, and $NpO_2{}^{2+}$, among these, $NpO_2{}^+$ is the most stable form in the environment. For pre-concentration of neptunium from the matrix, hydroxide co-precipitate method is widely used. However, $NpO_2{}^+$ cannot be completely co-precipitated with $Fe(OH)_3$, it has to be therefore reduced to Np^{4+} before hydroxide precipitation. Solvent extraction using tri-*n*-octylphosphine oxide (TOPO) in toluene or thenoyl trifluoroacetone (TTA) in oxylene has been used to separate Np from metals, uranium, thorium and other transuranics. In this step, Np is adjusted to Np^{4+} and extracted into organic phase in low concentration of HNO_3 (1–2 mol L^{-1}) or high concentration of HCl (8–12 mol L^{-1}), and back-extracted using high concentration of HNO_3 (8 mol L^{-1}) [255,258]. However, due to the insufficient decontamination from some elements, an anion exchange method is normally followed after solvent extraction. Based on the formation of anionic complex of Np^{4+} with $NO_3{}^-$ and Cl^- in high concentration of HNO_3 and HCl media, Np is first adjusted to Np^{4+} and absorbed onto an anion exchange column, uranium, which do not form a stable complex anion in HNO_3 solution, passes through the column and Th, which does not form complex anion in HCl solution, is removed from the column by washing with 12 mol L^{-1} HCl. The Np remained on the column is finally eluted from the column by 4–6 mol L^{-1} HCl with $NH_2OH{\cdot}HCl$, or 4 mol L^{-1} HCl—0.1 mol L^{-1} HF. By this method, decontamination factors of 10^6 for U and 10^5 for Th, and a detection limit of 0.1 mBq have been reported [254,255].

Due to the long half-life of ^{237}Np, mass spectrometric methods are sensitive for its determination, AMS [256], ICP-MS [257], and GDMS [115] have been used for the determination of ^{237}Np. In AMS, the separated Np is mixed with Fe_2O_3 and used as a target; NpO^- ions are sputtered by ion source, separated in the mass spectrometer and counted by an ionization chamber. A sensitivity of 0.024 μBq was measured, considering the procedure blank count rate; a detection limit of 7 μBq was reported [256]. A GDMS method was reported for the direct determination of ^{237}Np in sediment from the Irish Sea [115]. Since the sample was non-conducting, secondary cathode of Ti was used. The main interference from the molecular ion $^{181}Ta^{40}Ar^{16}O$ can be avoided by choosing a high resolution of 1700. A detection limit of 2.1–7.9 mBq g^{-1} was reported [115]. ICP-MS is the most often used mass spectrometric method for the determination of ^{237}Np, the main interference is the tailing of ^{238}U. Due to the much higher concentration of uranium in almost any type sample compared to Np, a good chemical separation of Np from uranium is required. Several polyatomic interferences such as $^{197}Ag^{40}Ar$, $^{181}Ta^{40}Ar^{16}O$, $^{183}W^{40}Ar^{14}N$, combinations of thallium and mercury isotopes with sulfur and chlorine isotopes, and palladium isotopes with xenon as well as $^{153}Eu^{84}Kr$ are possible interferences. With a through chemical separation, most of these interferences can be removed. Detection limit for ^{237}Np is more dependent on procedure blank levels (uranium and polyatomic interferences) than on instrument sensitivity. Sector field instruments and quadrupole instruments equipped with guard electrode using high-efficiency nebuliser may be tuned to have signal intensities of 10–20 MHz ppb^{-1} while still maintaining instrument background count rates at mass 237 below 1 cps. A detection limit of 1 nBq was reported by using SF-ICP-MS [159]. While, detection limits of 0.01–0.1 μBq of ^{237}Np are easily obtained by present ICP-MS systems and a chemical removal of uranium, this level is impossible to be detected even with the best radiometric systems available. It is therefore ICP-MS is becoming more common used method for the determination of ^{237}Np in the environmental samples. An inter-comparison of ^{237}Np determination in artificial urine samples was carried out using alpha spectrometry and ICP-MS by Lee et al. [260], they concluded that based on the analytical accuracy, the best results obtained by ICP-MS were comparable with but not better than the most accurate results obtained by alpha-particle spectrometry. Alpha spectrometry measurements overall gave consistently better agreement with known values.

NAA can be also used for the determination of ^{237}Np based on the reaction: $^{237}Np \xrightarrow{(n,\gamma),\sigma=169b,I=600b} {}^{238}Np \xrightarrow{\beta^-,2.1\,day} {}^{238}Pu$. Uranium may interfere with the analysis by the following reactions: $^{238}U(n, 2n)^{237}U \xrightarrow{\beta^-} {}^{237}Np(n, \gamma)^{238}Np$ and $^{235}U(n, \gamma)^{236}U(n, \gamma)^{237}U \xrightarrow{\beta^-} {}^{237}Np(n, \gamma)^{238}Np$. Although these interferences are said to be small, uranium has to be separated from the sample prior to the neutron irradiation. In addition, the pre-irradiation separation can also be used to concentrate Np from a large sample, and to avoid working with high activity. The chemical procedure used for alpha spectrometry of ^{237}Np can be also used for the pre-concentration of Np in NAA. A post-irradiation chemical separation is also necessary in order to achieve adequate decontamination from other gamma and beta emitters produced by activation of remaining impurity elements. A detection limit of ^{237}Np as low as 0.01 mBq (0.5 fg) in environmental and biological samples has been reported [261], and NAA has been successfully used for the determination of ^{237}Np in various environmental samples, such as soil, sediment, seawater, seaweed and fish [261,251,252,262].

One of the main problems in determination of ^{237}Np, either by radiometric or mass spectrometric methods, is the lack of a suitable tracer. Both the gamma emitting short-lived ^{239}Np ($T_{1/2}$ = 2.35 days) and ^{235}Np (half-life of 396 days) may be used to trace the separation chemistry [258]. While ^{242}Pu is mainly used as tracer in many laboratories [255,259] because ^{242}Pu isotope is relatively close to ^{237}Np with respect to mass and ionization potential, can be obtained very pure (essentially free from ^{237}Np), and has a chemistry similar to that of plutonium.

4.14. *Plutonium isotopes*

The interest in determining plutonium isotopes in environmental samples results from dosimetric reasons in the case of accidents or releases, interest in its biogeochemical behaviour in the environment, and tracing the source of the plutonium using the isotopic composition as a fingerprint. The most interest isotopes of Pu in environmental and waste sample are ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Pu. ^{241}Pu is a beta emitter with maximum energy of 20.8 keV, while the other isotopes are alpha emitters (Tables 1, 3 and 4). Alpha spectrometry is normally used for the determination of ^{238}Pu and $^{239+240}$Pu. Due to the similar energies of alpha particles from ^{239}Pu (5.16 MeV) and ^{240}Pu (5.17 MeV), α-spectrometry can only measured the sum activity of ^{239}Pu and ^{240}Pu. Spectrometric interferences for the α-spectrometric determination of ^{238}Pu and $^{239+240}$Pu are mainly from ^{214}Am and ^{210}Po, ^{224}Ra, ^{229}Th, ^{231}Pa, ^{232}U, and ^{243}Am, respectively. In addition, the matrix elements have to also be removed to improve the resolution. It is therefore that plutonium has to be separated from the matrix and other interfering radionuclides before measurement. Co-precipitation, solvent extraction, ion exchange chromatography and extraction chromatography are often used for the separation of Pu. The separation of Pu by ion exchange chromatography is based on the formation of anionic complexes of Pu(IV) with NO_3^- or Cl^- in concentrated HCl or HNO_3. Pu is first adjusted to Pu(IV) by first reducing all Pu to Pu(III) using sulphite and then oxidized to Pu(IV) by nitrite. The Pu(IV) in 8 mol L^{-1} HNO_3 is loaded onto an anion exchange column, which is then washed by 8 mol L^{-1} HNO_3, and 12 mol L^{-1} HCl, so americium, uranium and thorium are moved. Pu remained on the column is finally eluted by reducing Pu to Pu(III) by using 2 mol L^{-1} HCl–$NH_2OH{\cdot}HCl$ solution [255]. In extraction chromatography, Eichrom UTEVA and TRU columns are used. Plutonium is first reduced to Pu(III) and then passed through an Eichrom UTEVA column, U and Th are absorbed onto the column, while Pu(III) and Am(III) are passed through. The effluents containing Pu is loaded to an Eichrom TRU column and converted to Pu(IV) using nitrite, the column is then washed with 3 mol L^{-1} HNO_3 and 9 mol L^{-1} HCl to remove Am, Pu remained on the column is finally eluted by 0.1 mol L^{-1} $NH_4HC_2O_4$ solution [263]. Due to the very low concentration of Pu in environmental samples, pre-concentration of Pu from a large samples (such as 100–1000 L seawater) is necessary, which is normally carried out by $Fe(OH)_3$ or CaC_2O_4 co-precipitation or absorption onto MnO_2 impregnated fibers filter [255,263–265]. The separated Pu is normally electrodeposited onto a disk for α-spectrometric measurement. Micro-precipitation using LnF_3 has also been used to prepare the Pu source, but the resolution is not as good and electrodeposition. A detection limit of 0.05 mBq for ^{238}Pu and $^{239+240}$Pu was obtained in the authors' laboratory by α-spectrometry and counting for 3 days [265]. Besides α-spectrometry, X-spectrometry has also been used for the determination of ^{239}Pu and ^{240}Pu, which is based on the somewhat different intensities of the emitted L_x-rays from the ^{239}Pu and ^{240}Pu isotopes. A detection limit of 2–4 mBq for ^{239}Pu and ^{240}Pu has been reported by using L_x X-ray spectrometry and counting in underground laboratory [266].

The determination of ^{241}Pu can be carried out by direct measurement of ^{241}Pu using LSC or α-spectrometry by measuring its decay daughter ^{241}Am. In the direct LSC method, Pu has to be separated from the matrix and all other radionuclides, especially interfering beta emitters. The chemical procedure used for alpha isotopes of Pu can also be used for ^{241}Pu. Actually, the separated Pu used for determination of ^{238}Pu and $^{239+240}$Pu is normally used for LSC of ^{241}Pu after the α-spectrometric measurement. A detection limit of 11 mBq has been reported [267] using LSC. In the α-spectrometry method, the separated plutonium have to be kept for more than half year for the in-growth of ^{241}Am, the generated ^{241}Am is then separated from plutonium and measured by α-spectrometry, in this case, the detection limit varies with the in-growth time, a detection limit of 0.3 mBq can be obtained using α-spectrometry and 13 years in-growth time [268].

Mass spectrometric techniques such as TIMS [269], AMS [270,271], RIMS [96,272], and ICP-MS [64,273,274,276,277] have also been used for the determination of Pu isotopes. During the last decade, the use of ICP-MS has gained a increased interest as an alternative to alpha spectrometry because of the good sensitivity, short analytical time and ^{239}Pu–^{240}Pu–^{242}Pu isotopic information which are difficult to obtain through alpha spectrometry due either to overlapping peaks of ^{239}Pu and ^{240}Pu or to the low specific activity of ^{242}Pu (1.4×10^8 Bq g^{-1}). The mass spectrometric techniques should be seen as a complement rather than a replacement to ordinary alpha spectrometry since the latter technique is still very suitable for the analysis of ^{238}Pu and the ^{238}Pu/$^{239+240}$Pu ratio, which in some cases is more informative than the ^{240}Pu/^{239}Pu ratio obtained by mass spectrometry. The ^{238}Pu in environmental samples is very difficult to be determined by mass spectrometric techniques due to its low mass concentration and serious isobaric interference from ^{238}U which is much more abundant in environmental samples. Furthermore, mass spectrometric techniques are also insufficient to accurately analyse the short-lived ^{241}Pu (14.4 years) in normal environmental samples unless the ^{241}Pu/^{239}Pu ratio is large like in samples contaminated by material from the Chernobyl accident. Measuring ^{241}Am by solid-state alpha spectrometry or direct analysis of ^{241}Pu by low-level liquid scintillation counting are more sensitive ways than using ICP-MS, but may necessarily not be more accurate due to problems with cross-calibration of tracers (^{242}Pu–^{243}Am), imprecise detector efficiency or unknown blank contribution and calibration problems (LSC). Due to the high sensitivity of many ICP-MS instruments, it is possible to determine Pu-isotopes at very lower level. There are however a number of problems that have to be addressed and dealt with before being able to trust the weak signals provided by the instrument when measuring Pu at low-levels (fg–pg range). Some of these are the relatively low abundance sensitivity, the risk of interferences from polyatomic species, blanks, background and sensitivity.

The most important problem when measuring low-level samples for Pu by ICP-MS is the interference from uranium, because the mass concentration of uranium is usually 10^6–10^9 times higher than that of Pu. The tailing and formation of UH^+ thus represent a major disturbance at mass 239 unless uranium is removed prior to analysis. This particular problem is seldom encountered in alpha spectrometry due to the low specific activity of uranium and that the alpha energies of U and Pu isotopes do not overlap. A partial overlap of ^{234}U (4.77 MeV) and the ^{242}Pu (4.90 MeV) tracer may occur at situations when the U concentration on the electrodeposited steel disc is high enough to affect the energy resolution. In this case, the low energy side of the ^{242}Pu peak may tail into the ^{234}U peak. However, problems with uranium are much less severe in alpha spectrometry which therefore sets much lesser demands on the degree of removal of uranium from the sample. While in the alpha spectrometric determination of ^{238}Pu (5.50 MeV), the interference from the ^{228}Th peak (5.42 MeV) may be a severe problem. A thorough removal of thorium prior to analysis is necessary to obtain a reliable result when analysing low-level samples. The contribution of ^{228}Th to ^{238}Pu can also be corrected for by measuring ^{224}Ra (5.65 MeV), the decay daughter of ^{228}Th. In this case, the sample after electrodeposition needs to be kept for about 3 week for the in-growth of ^{224}Ra (5.65 MeV), so that the daughter product, to reach secular equilibrium with ^{228}Th. Varga et al. [274] compared alpha spectrometry and ICP-SFMS, a comparable detection limits were obtained for $^{239,240}Pu$ by two techniques (0.1–0.2 mBq).

In TIMS, problems with uranium are less severe since uranium and plutonium have different ionisation potentials and thus are emitted from the filament at different temperatures (plutonium leaves the filament before uranium). The dry sample introduction furthermore reduces UH^+ species considerably and abundance sensitivity is generally orders of magnitude better in TIMS instruments than in ICP-MS. The stability of the ion beam also permits $^{239}Pu/^{240}Pu$ ratios of a precision in ppm range rather than at percentage range typical for single detector ICP-MS. Recent multicollector ICP-MS instruments have however an isotope ratio precision and sensitivity that surpasses most commercial TIMS instrument. In ICP-MS, matrix suppression of the signal occurs when the sample introduced to the mass spectrometer is not pure enough. In TIMS this suppression is normally more severe than in ICP-MS and this therefore sets a higher demand on the chemical isolation of the Pu before loading onto the filament. Using ordinary commercial TIMS instruments (e.g. Finnigan MAT 262) a detection limit of around 1 fg (2 μBq) ^{239}Pu has been reached [30].

Alpha spectrometry is more straightforward than any of the mass spectrometric methods and the risk of interfering signals is less than ICP-MS. In alpha spectrometry there is no interference from the presence of microgram amounts of stable elements on the disc after separation and electrodeposition. While in ICP-MS, several polyatomic species may appear in the mass range 230–245 when micrograms of lead, mercury, thallium and REEs remain in the sample after separation. This makes the evaluation of mass spectra from samples weak in plutonium more critical than alpha spectrometry. It is possible to reach better detection limits by ICP-MS for ^{239}Pu when a thorough quality control is followed. The main drawback of alpha spectrometry is the very long counting times for low activity samples, weeks to months.

RIMS is a sensitive mass spectrometric method for determination of Pu-isotopes. The method also enables an ultrahigh selective determination of the element with almost completely elimination of interferences from other elements. These instruments are however not commercially available and are designed for one element due to the specific laser tuning used and adaptation to a new element requires elaborate development. This method had been used for the determination of Pu isotopes in environmental sample, a detection limit of 10^6–10^7 atoms corresponding to 1–10 μBq ^{239}Pu has been reported. Comparing to radiometric method, a similar chemical separation is needed for RIMS, but the counting time (1–2 h) is remarkable shorter than alpha spectrometry [96]. AMS similarly offers a very good sensitivity and abundance sensitivity well suited for ultra trace detection of plutonium, a detection limit of 0.5–2 μBq for ^{239}Pu has been reported by using AMS [270,275]. However, commercially available AMS instruments are expensive and normally not developed for heavy ion detection. Analysis of heavy elements like the actinides is still only performed at physics laboratories where larger instrument are available. Contrary to RIMS, which can be interfaced to a TOF-MS and therefore analyse the Pu-isotopes simultaneously, AMS needs to do peak hopping since only one ion mass can be transported through the analyser ion optics at any time. This results in less precise isotope ratios.

A new pre-concentration technique was recently developed to separate plutonium from as large as 10 m^3 of seawater sample by solid phase extraction using MnO_2 impregnated fibres [264]. This is very useful for the determination of ultra low-level samples by alpha spectrometry or ICP-MS.

Table 12 compares the radiometric method and mass spectrometric methods for the determination of plutonium isotopes, AMS, TIMS and RIMS are more sensitive than alpha spectrometry method for the determination of $^{239,240}Pu$, ICP-MS is comparable with alpha spectrometry and LSC for $^{239,240}Pu$ and ^{241}Pu. All mass spectrometry methods are able to measure ^{239}Pu, ^{240}Pu and ^{241}Pu, but not ^{238}Pu because of isobaric interference of ^{238}U. While alpha spectrometry can measure $^{239,240}Pu$ and ^{238}Pu, but can not separate ^{239}Pu and ^{240}Pu. Mass spectrometric methods are comparable to LSC for the determination of ^{141}Pu respect to the sensitivity. The chemical separation procedures are similar for both radiometric and mass spectrometric methods, while the counting time of mass spectrometric methods are much shorter than that of radiometric methods. Lee et al. [276] compared alpha spectrometry, LSC, AMS, ICP-MS and TIMS techniques by analysis some environmental reference materials, they concluded that the analytical results of $^{239,240}Pu$ by alpha spectrometry are in general in good agreements with ICP-MS and AMS, and the results of ^{241}Pu by LSC and ICP-MS are reasonable good agreement, radiometric methods are still a powerful techniques because of simplicity of measurement, good resolution and reasonable sensitivity, ICP-MS and AMS have proved to be high sensitive techniques which will be used more frequently in the future for the determination of Pu isotopes. However, mass spectrometry cannot replace radiometric methods, because mass spectrometry cannot supply a reliable measurement of

Table 12 – Comparison of radiometric and mass spectrometric methods for the determination of isotopes of plutonium

Sample	Detection method	Nuclide	Detection limit	Sept. time	Count time	Ref.
Environmental samples	X-spectrometry underground counting	^{239}Pu, ^{240}Pu	4.4 mBq, 2.0 mBq	3–5 days	57 days	[266]
Environmental sample	α-Spectrometry	$^{239+240}$Pu, ^{238}Pu	0.05 mBq	2–3 days	3 days	[265]
Environmental sample	α-Spectrometry	$^{239+240}$Pu, ^{238}Pu	0.02 mBq	3–4 days	5 days	[274]
Environmental sample	LSC	^{241}Pu	11 mBq	2–3 days	5 h	[267]
Environmental sample	α-Spectrometry	^{241}Pu (via ^{241}Am)	0.5 mBq	3–5 days (13 year)[a]	3 h	[268]
Urine	TIMS	^{239}Pu, ^{240}Pu ^{241}Pu	1.4 μBq 0.9 μBq 0.4 mBq	2–3 days	20–30 min	[30]
Environmental sample	ICP-SFMS	^{239}Pu ^{240}Pu ^{241}Pu	0.021 mBq 0.014 mBq 11.9 mBq	3–4 days	20 min	[274]
Environmental sample	RIMS	^{239}Pu ^{240}Pu ^{241}Pu	10 μBq 30 μBq 20 mBq	2–4 days	1–2 h	[96]
Seawater	ICP-MS	^{239}Pu ^{240}Pu	0.78 mBq mL^{-1} 3.6 mBq mL^{-1}	3–4 days	20 min	[264]
Urine	AMS	^{239}Pu	0.5 μBq	2–3 days	20–40 min	[275]

[a] In-growth time for the generation of ^{241}Am from the decay of ^{241}Pu.

^{238}Pu and alpha spectrometry is still the most sensitive and reliable method for ^{238}Pu.

4.15. *Amerium-241*

^{241}Am as an anthropogenic radionuclide has been released into environment from the weapons testing, reprocessing plants and nuclear accident. Since ^{241}Am is a decay daughter of ^{241}Pu ($T_{1/2} = 14.35$ years), its concentration will increase in the future in the environment and it is estimated to reach its maximum activity in the middle of the 21st century [278]. The interest in the determination of ^{241}Am results from its high specific activity and dose contribution, and application as a unique tracer in oceanographic and sedimentation studies.

^{214}Am decays by emitting α-particles of 5.44–5.49 MeV, accompanying by emission of 59.5 keV (35.9%) γ-ray. ^{241}Am can therefore be measured by γ-spectrometry and α-spectrometry. Gamma spectrometry is an easy and direct method for the determination of ^{241}Am, but care must be taken to properly correct for the attenuation of γ-ray in the samples in order to obtain accurate results. In addition, the sensitivity of γ-spectrometry is also low because of the generally low counting efficiency of HpGe detector and the small (or thin layer) sample have to be used for reducing the self-adsorption of γ-ray in the sample. A detection limit of 0.1–1 Bq kg^{-1} has been reported for the direct measurement of soil and biota (Byrne 1993) by γ-spectrometry using HpGe detector. Chemical separation before γ-counting can significantly improve the detection limit by using a large sample and reducing the self-absorption. In the author's laboratory, a detection limit of 50 mBq has been obtained for the direct γ-counting of solid sample, which is therefore suitable for the screen of the sample. Alpha spectrometry is a more sensitive method for the determination of ^{241}Am. In this case, ^{241}Am has to be separated from matrices and interfering radionuclides, especially Pu, Th, Ra, and Po because of close α-energies of ^{210}Po, ^{238}Pu, ^{224}Ra and ^{228}Th to ^{241}Am. Co-precipitation of hydroxides or oxalate, solvent extraction using TIOA/xylene, anion exchange and extraction chromatography are used for the separation. The solvent extraction using TIOA/oxylene is based on the extraction of Pu, Po, U, and Fe to organic phase, while Am remain in the aqueous phase. The anion exchange chromatography is based on absorption of the Pu(IV) and U(IV) to the column in high concentration of HCl and Th(IV) and Pu (IV) in high concentration of HNO_3 medium, while Am does not form anionic complex in neither HNO_3 nor HCl and could not be absorbed on the column. For removal of most rare earth elements (REEs) which may interferes with the α-spectrometric determination of ^{241}Am due to increased self-absorption in the source and thus poor resolution, extraction chromatography using Eichrom TRU column and anion exchange chromatography have been used. In anion exchange chromatography, Am is prepared in a 1.0 mol L^{-1} HNO_3–93% CH_3OH solution and loaded to the anion exchange column, the column is then washed with 0.1 mol L^{-1} HNO_3–0.5 mol L^{-1} NH_4SCN–80% CH_3OH, in this case, REEs pass through the column, Am on the column is then eluted by 1.5 mol L^{-1} HCl–83% CH_3OH. The separated ^{241}Am is normally electrodeposited on a disc for measurement using α-spectrometry, a detection limit of 0.1–0.2 mBq has been reported depending on the counting time and count rate of the procedure blank [278–280].

ICP-MS has also been used for the determination of ^{241}Am in environmental samples. In the ICP-MS, the main problem comes from the isobaric and molecular ions interferences, such as $^{241}Pu^+$, $^{240}Pu^1H^+$, $^{209}Bi^{32}S^+$, $^{209}Bi^{16}O_2{}^+$, $^{206}Pb^{35}Cl^+$, $^{205}Ti^{36}Ar^+$, $^{204}Pb^{37}Cl^+$, $^{207}Pb^{34}S^+$, and $^{201}Hg^{40}Ar^+$. Using SF-ICP-MS in high resolution mode can solve some of these problems with molecular ions, while this will cost at a lower sensitivity. The ^{214}Pu isobaric interference requires a very high resolution (10,800,000), which cannot be solved by SF-

ICP-MS. Since ^{241}Am is a decay product of ^{241}Pu, in some samples the mass concentration of ^{241}Am is much lower than ^{241}Pu, which therefore requires a through chemical separation of Am from Pu before measurement. In addition, chemical separation can also remove most of the stable elements, which forms the interfering molecular ions [281–283]. The chemical separation procedure used in the α-spectrometry can also be used for the ICP-MS analysis of Am. Although less demand on removal alpha emitters, a relatively through removal of the stable matrix elements is required for low-level samples. A detection limit of 0.1 mBq has been reported by using SF-ICP-MS with chemical separation [278], which is comparable with α-spectrometry, but the analytical time (1 days chemical separation and 2 h measurement) is much shorter than α-spectrometry (3–4 days separation with 3–5 days measurement). The drawback of ICP-MS compared with α-spectrometry is the analytical reliability of ultra-low-level of ^{241}Am measurement, the contribution of noises and interfering ions to the small signal is difficult to identify. The rapid analytical capacity of ICP-MS makes it however an attractive method, especially for the emergency analysis.

5. Application of on-line methods (flow injection/sequential injection) for separation of radionuclides

In the traditional analytical procedure for radionuclides, the target radionuclides have to be pre-concentrated and separated before measurement because of their low activities in environmental samples and the presence of interfering elements and radionuclides. Co-precipitation, solvent extraction, ion exchange and extraction chromatography are commonly used techniques, of which ion exchange chromatography and extraction chromatography are the dominant techniques for the separation of target radionuclide from the interfering elements and radionuclides. These methods are tedious, time consuming, and labor-intensive. For example, the determination of plutonium and americium normally takes up to 3–4 days per sample. Moreover, the methods require large volumes of organic solvents or mineral acids, and embody the risk of cross-contamination.

Flow-injection (FI)/sequential injection analysis (FIA) has been widely used for the determination of trace elements since its introduction in 1975 [284] and made a significant progress not only in terms of efficiency, but also in reliability, rapidity and robustness [285]. However, this technique has not been applied for the determination of radionuclides until 1996 [183]. With the requirement of rapid analysis of radionuclides for emergency purpose and the increased application of ICP-MS, the automated analysis of radionuclides by hyphenation of flow injection/sequential injection for on-line separation with ICP-MS measurement has becoming more attractive for waste and environmental radioactivity analysis.

The automated analysis using FI on-line separation is normally composed of a multi-port valve, a solvent distributor which can divert solution to different direction, peristaltic pump, and chromatographic column (one or more). The operation of the system is controlled by a PC and automated running, Fig. 3 shows the schematic diagram of this system. The prepared sample in a suitable solution is first loaded to a loop, which is then loaded to the column. The column is then washed with different solvent to remove the interfering elements and radionuclides. The target radionuclide is finally eluted from the column, which can be directly introduced to the detector or collected by a fractionation collector for measurement later. The main advantages of the sequential injection system compared to the traditional separation method include: (1) rapid separation; (2) directly connection to the detector such as ICP-MS for the measurement; (3) automated operation, so less manpower and less cost; (4) less consumption of the chemical regents; (5) less cross contamination; (6) less risk of exposure of chemicals to the laboratory staff because of less contact with the chemical reagents. In recent years, this method has been used for the determination of ^{90}Sr, ^{99}Tc, and actinides, some examples are given below.

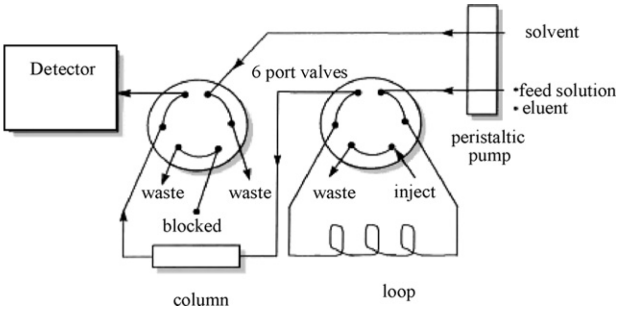

Fig. 3 – Schematic diagram of the sequential injection manifold interface with the detector (modified from Truscoot et al. [297]).

Grate et al. [183,286] described a automated method for the determinations of ^{90}Sr in nuclear waste by using a sequential inject separation and a flow through liquid scintillation counter for on-line detection. In this method, an Eichrom Sr-Spec resin was used for the extraction chromatographic separation, which can efficiently separate the interfering radionuclides, such as ^{137}Cs and ^{90}Y from ^{90}Sr. The analytical time can be reduced to 40 min, while the traditional method normally requires 1–3 days. A HPLC using ion chromatography was also used for the automated separation of ^{90}Sr [287], with the on-line detection using LSC, and waste water sample can be rapid analysis.

In the determination of ^{99}Tc, an anion exchange column was used for the separation of ^{99}Tc from other radionuclides. In this method, all technetium in the sample has to be converted to TcO_4^- before the separation. Combined with an on-line flow through scintillation detector, the ^{99}Tc in waste samples was determined. The analytical time was only less than 13 min per sample [288]. A method by using extraction chromatography (TEVA) in the sequential injection system and direct ICP-MS detection has been reported for the determination of ^{99}Tc in environmental samples [196]. Due to the interference of ^{99}Ru and ^{98}MoH in the ICP-MS determination of ^{99}Tc, the high concentrations of Mo and Ru in environmental samples have to be removed. For this purpose, two TEVA column was used, and a decontamination factor of 10^4 to 10^5

for Ru and Mo was obtained. An analytical time of 3–5 h for soil sample, and a detection limit of 0.05 mBq mL^{-1} was reported [196].

Benkhedda et al. [59] reported an automated analytical method for the determination of ^{226}Ra by combining sequential injection and ICP-MS. In this method two extraction columns containing Eichrom Ln and Sr-Spec resin were used. The sample solution was first loaded on the Ln column, where Ra, Sr, and Ba were absorbed and separated from the matrix elements. Ra, Sr and Ba were then eluted from the Ln column and passed through Sr-Spec column, where, Sr and Ba are absorbed, while Ra was passed through the column and directly introduced to the plasma of the ICP-MS instrument. The entire analysis took only 20 min per sample, a detection limit of 0.34 mBq for a 20 mL water sample was obtained.

There are many works have been carried out on the development of an automated method for the determination of actinides [286,289–297]. An HPLC with mix bed ion exchange column has been used to separate actinides and employing ICP-MS for the detection. CS10 column was used for the separation of Pu, U and Am, but the separation of Pu from U was not sufficiently good. While, CS5A column gave a good separation of U, Pu, Am and Cm from each other. Neither column could separate Pu from Np, but it does not effect the ICP-MS detection of the isotopes of these two elements. The method has been successfully used for the analysis of spent nuclear fuel [294]. For the separation of Np from Pu, an extraction chromatographic column (UTEVA) was investigated. After adjusting Pu to Pu(IV) and Np to Np(V), these two elements can be completely separated by this method [295]. Extraction chromatographic resin TRU in the sequential injection system has been used for the separation of Am and Pu from the matrix and from each other. In this method, the Pu is adjusted to Pu(IV) before the loading to the column, in this case, Pu is absorbed on the column while Am pass through the column. The main problem is the decontamination of U from Pu which is not very good; the method has been used for the analysis of waste sample. For the analysis of environmental sample which contains high uranium and lead, two extraction chromatographic columns using Sr-Spec and TEVA resin in the sequential injection system has to be used [196,289,290]. In this method, the sample in 5 mol L^{-1} HNO$_3$ solution was loaded to the Sr-Spec column, Pu on the column is then eluted by 0.8 mol L^{-1} HNO$_3$ and loaded onto the TEVA column, while Pb is retained on the Sr-Spec column. The uranium absorbed on the TEVA column is washed out by 1 mol L^{-1} HNO$_3$, the Pu retained on the column is then eluted by 1 mol L^{-1} HCl, and injected to the detector for measurement. A decontamination factor of 10^6 for U and 10^4 for Pb and a detection limit of 1.5 μBq mL^{-1} for 5 L seawater have been obtained, an analytical time of 4 h per sample was reported [196]. The application of sequential injection systems can significantly shorten the analytical time. For waste water sample it is possible to complete a full automated analysis [286]. However for the analysis of environmental sample and solid waste sample, an off-line pre-concentration step is necessary. The solid sample has to be decomposed to release the target radionuclide from the sample to solution, the traditional co-precipitation can be used for pre-concentration of target radionuclide from large volume of water sample or pre-separation of target radionuclide from a large amount of matrix elements which may worse the column separation. Although the SI system has been used for the automated determination of radionuclides for more than 10 years, the application is still limited to a few laboratories, most of radiochemical laboratories still use the traditional method. This may results from a few reasons: (1) a pre-concentration is still needed for the environmental samples; (2) the developed system are normally small scale, which is not enough for the analysis of the low-level environmental samples; (3) the decontamination factor is not high enough; (4) less robust of the SI system, especially the column part, which may cause a much longer time for reparation. However, the automated SI system is still very attractive for the determination of radionuclides because of its remarkable advantages. With the development of the extraction chromatographic techniques and new generation of flow inject technique; this technique will become more and more popular in radiochemical laboratories for the determination of radionuclides in environmental and waste samples.

6. Conclusion

Radiometric methods, as the traditional analytical methods, are still the unique techniques for the determination of short-lived radionuclides ($T_{1/2} < 10$ year), and dominating analytical techniques for the determination of most long-lived radionuclides in waste and environmental samples. Mass spectrometric techniques such as AMS, TIMS and RIMS, especially AMS, are very sensitive techniques for the determination of many very long-lived radionuclides, such as ^{14}C, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{129}I, and ^{135}Cs, they can not only measure the very low-level of these radionuclides, but also significantly reduce the sample amount needed for the analysis, they are therefore better than radiometric techniques, especially for the biological and low-level environmental samples. SIMS and GDMS are not sensitive enough for the determination of radionuclides in low-level, however they are useful techniques for surface and profile analysis for some radionuclides, especially characterization of hot particles and spatial distribution analysis of radionuclides in the biological tissues. With the improvement and popularity of ICP-MS analytical techniques, it is becoming a competitive technique for the determination of many long-lived radionuclides, such as ^{99}Tc, ^{237}Np, and isotopes of U, Th, and Pu because of its comparable detection limits to the radiometric methods and rapid analytical capacity. Regardless the application, it is desirable that the techniques for determination of a radionuclide are sensitive, accurate, rapid and low cost. Unfortunately no single analytical technique can meet all of these goals for all application. Each technique has its own strengths and weaknesses. In general, mass spectrometric techniques are good complementary to the radiometric techniques for the determination of most of long-lived radionuclides, which has been used for the investigation which previously required too large sample or were not possible due to lack of sensitivity of radiometric techniques. However, mass spectrometry cannot replace the radiometric techniques for the determination of many radionuclides because of the isobaric interference, stability, less accessible, high cost and noise of equipment. In addition, radiometric methods do not require extensive equipments or infrastructure, and can be scaled down and even portable for field measurement.

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