

# Present status and perspective of radiochemical analysis of radionuclides in Nordic countries

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**Abstract** Radiochemical analysis plays a critical role in the determination of pure beta and alpha emitting radionuclides for environmental monitoring, radioecology, decommissioning, nuclear forensics and geological dating. A remarkable development on radiochemical analysis has been achieved in the past decades to meet the increased requirement. In the recent years, mass spectrometric techniques have been considerably improved and are widely employed for measurement of radionuclides. Analytical methods for rapid, automated and simultaneous determination of radionuclides have been extensively developed for emergency analysis. In Nordic countries, many laboratories are involved in the determination of radionuclides for various purposes, and a series of radiochemical analytical methods have been developed and applied. This article presents the present status and progress on

radiochemical analysis of radionuclides, especially in Nordic countries; some requirements from nuclear industries and research organizations, as well as perspectives on the development of radiochemical analysis are discussed.

**Keywords** Radionuclides · Radiochemical analysis · Extraction chromatography · Automated analysis · Rapid analytical methods · AMS · ICP-MS

## Introduction

In the operation of a nuclear power plant, determination of radionuclides in coolant water, air, filters, liquid discharges and waste samples, as well as environmental samples surrounding the plant is required in order to monitor the corrosion status, integrity of the nuclear fuel, build-up and distribution of radioactivity in the systems, radioactivity level in the environment. In the decommission of nuclear facilities, the determination of various middle and long-lived radionuclides has to be carried out to estimate the contamination level of materials and the inventory of each radionuclides in the waste, to provide accurate information for decision on the treatment/repository of the waste, and to evaluate the radioactive level of the decommissioned place and building to be released for other utilization. Speciation analysis of radionuclides provides the basic information for environmental radioactivity investigation and radioecology studies. In addition, radionuclides released to the environment from the human nuclear activities can be also used in the studies of environmental processes. This requires highly sensitive determination of low level radionuclides, as well as their speciation.

Based on their decay model, radionuclides are often categorized to gamma, pure beta and pure alpha emitters.

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Because of the high energy resolution of gamma spectrometry using HPGe detectors, gamma emitters are often directly measured using gamma spectrometry without chemical separation. Enrichment or chemical separation is only used for determination of gamma emitters that have a low concentration or suffer interference of other strong activity gamma emitters. For pure beta emitters that decay by emitting electrons, positrons and electron capture but without emission of any measurable gamma rays, chemical separation has to be implemented to isolate the interest radionuclide from the matrix material of the sample and to remove all other radionuclides which interfere with its measurement because of the continuous energy beta spectrum. For alpha emitters, the high adsorption of alpha particles in the material matrix and low energy resolution of alpha spectrometry prevent direct measurement of alpha emitters in the samples, chemical separation of alpha emitters from matrix and other radionuclides are required before measurement. Therefore determination of pure beta and pure alpha emitter has to involve chemical separation and purification, they are also considered to be hard to measure, so called hard to measure radionuclides. In addition, chemical separation and purification have to be implemented when mass spectrometric techniques are used for the measurement, because the mass concentration of radionuclides in the samples is normally very low, and spectroscopic and isobaric interferences of stable isotopes in the sample matrix to the measurement of the radionuclides is often very high.

Many organizations including nuclear industries, radiation protection authorities, research institutes and universities are involved in radiochemical analysis of hard to measure radionuclides for various purposes, and a lot of analytical methods have been developed for the determination of radionuclides and their species in various samples. This article aims to review the status and present progress of radiochemical analysis of radionuclides and to summarize the requirements from Nordic industries and research organizations for radiochemical analysis. A perspective on the development of radioanalytical methods in the near future is also discussed.

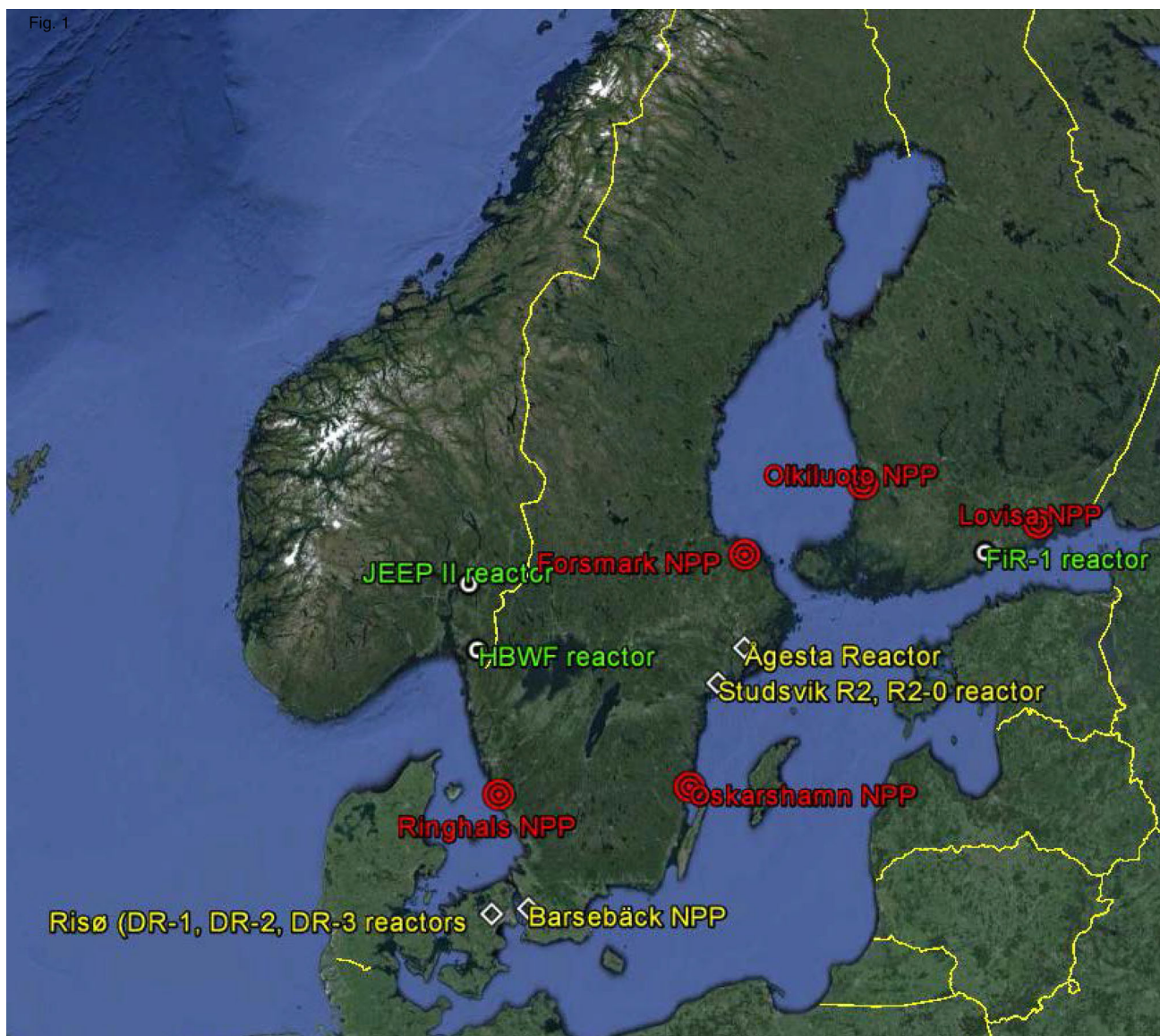
### Requirements of radiochemical analysis in Nordic countries

In the Nordic countries, there are three nuclear power plants in Sweden (Forsmark, Oskarshamn and Ringhals NPPs) and two in Finland (Loviisa and Olkiluoto NPPs) with a total 14 power reactors. Meanwhile there are three research reactors (JEEP II and HBWF reactors in Norway and FiR-1 reactor in Finland) in operation by 2015 (Fig. 1). The monitoring of radionuclides in these nuclear power

plants has to be routinely carried out. Environmental safety of the nuclear installations is a sensitive and critical issue for the public and authorities. In the past years, increased and stricter environmental assessment program are required by the authorities. For this purpose, some hard to measure radionuclides, such as  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{63}\text{Ni}$ ,  $^{55}\text{Fe}$ ,  $^{89}\text{Sr}$ ,  $^{90}\text{Sr}$  and actinides are listed in routine monitoring program of the nuclear power plants and research reactors in Nordic countries as well as other EU countries [1]. During the operation of the reactor, various types of radioactive waste are produced, such as spent ion exchange resins, evaporator of the processing water, dismantled equipment and construction materials. These waste materials need to be characterized before further treatment. The determination of the pure beta (e.g.  $^{14}\text{C}$ , tritium,  $^{36}\text{Cl}$ ,  $^{41}\text{Ca}$ ,  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$ , etc.) and alpha emitting radionuclides (i.e.  $^{238,239,240}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$ ,  $^{234}\text{Cm}$  etc.) in these materials is the major challenge.

A large number of research and power reactors were built in the 1950s–1960s and 1960s–1970s, respectively. These reactors, as well as many other nuclear facilities are reaching their designed age and are going to be decommissioned [2]. In the Nordic countries, some nuclear reactors and nuclear facilities have been closed and a few of them have been decommissioned, while many of them are being decommissioned [3]. In Denmark, two research reactors (DR1 and DR2) have been decommissioned by 2008, and the third reactor (DR-3) is being decommissioned [4]. In Sweden, six nuclear reactors have been closed by 2013 and 4 of the 10 operating units are being closed within the next 5 years. Of them only one (R1 at Royal Institute of Technology) has been decommissioned, and other 5 [two research reactors in Studsvik R2 and R2-0, power reactors in Ågesta and Barsbäck (2 units)] are being decommissioned [5, 6]. In Norway, two small research reactors (JEEP I and NORA) were closed in 1960s and have been decommissioned to stage 2 and 3, respectively [7]. In Finland, a research reactor FiR-1 at Otaniemi, Espoo has just been closed in 2015, and the decommissioning of this reactor is planned [8]. In addition, some nuclear facilities are also under decommissioning, for example hot cells at Risø site in Denmark. During the decommissioning of these nuclear facilities, various radionuclides, especially middle and long-lived radionuclides, are required to be determined for characterization of the produced waste, such as biological shield concrete, ion exchange resins, graphite, metals, etc. Among these radionuclides, determination of the pure beta and alpha emitters (e.g.  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{41}\text{Ca}$ ,  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$ , plutonium isotopes,  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ , etc.) is the major challenge.

Human nuclear activity has released large amounts of radioactive substances to the environment, the investigation of the level, distribution, dispersion, environmental



**Fig. 1** Nuclear facilities in Nordic countries, *red circle* nuclear power plants in operation, *black and white circle* research reactors in operation, *white cube* reactors in decommissioning. (Color figure online)

behavior of the released radionuclides and their transfer in the ecosystem is important for estimating their impact to the human as well as to the ecosystem. Determination of the released radionuclides in various materials and their species is the key issue in this work. Besides fallout radionuclides from the nuclear weapons testing, nuclear accidents and discharges from nuclear facilities are major contribution to the level of anthropogenic radionuclides in the environment. A significant contribution within the Nordic environment is the accident at Thule in Greenland (1968) in which an aircraft carrying four nuclear bombs crashed onto sea ice, causing an explosion and the release of radioactive materials to the local environment, sea and land. A series of investigations on the level, distribution,

composition of radionuclides and their species [9–12] have been implemented in the Technical University of Denmark, Center for nuclear technologies (part of former Risø National Laboratory). Chernobyl nuclear accident that happened on 26 April 1986 is so far the largest nuclear accident. Due to the weather conditions, a significant amount of radioactive debris from the Chernobyl accident was transported to and deposited in the Nordic region, causing the Baltic Sea the most contaminated sea in the world. A big effort has been taken in the Baltic region, mainly in the Nordic countries, to investigate the contamination levels, dispersion, fate and the environmental behavior of radionuclides and their impact to the Nordic ecosystem [13, 14]. Although most of the investigation on



environmental impact of Chernobyl accident in the Nordic region has focused on radiocesium ( $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ ), Chernobyl accident derived plutonium and curium isotopes have also been measured in the Nordic environment [15, 16]. Nuclear fuel reprocessing plants at La Hague (France) and Sellafield (UK) as the largest reprocessing plants in the world have discharged a huge amount of radioactive substance to the English Channel and Irish Sea, respectively. The sea currents carry these radioactive substances and move to the North Sea, and further to the Norwegian Sea and the Arctic, some parts also move to the Skagerrak, Kattegat, and enter the Baltic Sea. This causes a large dispersion of radionuclides in the European water, including the Nordic waters. A lot of investigations on marine radioactivity in the Nordic water, as well as the Arctic have been carried out in the Nordic countries [17–34]. Besides the environmental impact of radioactive substance, most of the work was devoted to the marine tracer studies, to use the radionuclides such as  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^3\text{H}$ ,  $^{99}\text{Tc}$  and  $^{129}\text{I}$  discharged from these two reprocessing plants as oceanographic tracer to trace the water circulation and exchange in the Nordic water, as well as in the Arctic and North Atlantic. For these studies, determination of various radionuclides in different environmental samples, especially in low radioactivity level samples, is the key issue. These studies require effective chemical procedures to separate tiny amount of radionuclides from big sample sizes, for example 100–500 L seawater or 10–100 g sediment or biota. A sensitive measurement method is also needed to reach a sufficient low detection limit to be able to measure these radionuclides in various environmental samples. The major sources of radionuclides in the Nordic environment are summarized in Table 1.

Chemical species of radionuclides are important for their behavior in the nuclear facilities, environment and repository site. Therefore speciation analysis of radionuclides in

various samples is often required in radiological monitoring and radioecology investigation.

### Present status of radioanalytical chemistry for the determination of important radionuclides of hard to measure

In the past decades, a lot of radiochemical analytical methods have been developed for the determination of various natural and anthropogenic radionuclides that are hard to measure in different types of samples. These methods have been successfully used for many years for analysis of various environmental samples such as soil, sediment, aerosol, seawater, fresh water, vegetation, food, and biological samples for environmental radioactivity, radioecology and environmental tracer studies [16, 35–74]. Some methods have also been developed in Nordic laboratories for the analysis of samples from nuclear facilities such as spent exchange resins, waste waters, air, filters, activated graphite, concrete and metals for activation and fission product radionuclides, such as  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{41}\text{Ca}$ ,  $^{55}\text{Fe}$ ,  $^{59}\text{Ni}$ ,  $^{63}\text{Ni}$ ,  $^{99}\text{Tc}$ , and transuranics [63, 75–89] for the purpose of monitoring radioactivity in nuclear power reactors and characterization of nuclear waste for decommissioning. Table 2 lists the major Nordic laboratories where radiochemical analysis of hard to measure radionuclides has been carried out. The major methods developed and applied in determining anthropogenic radionuclides of hard to measure are reviewed below.

### Radiochemical analysis of major fission product radionuclides ( $^{90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{129}\text{I}$ )

Among all fission product radionuclides,  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$  and  $^{129}\text{I}$  are the most often determined radionuclides of hard to

**Table 1** Major sources of radionuclides in the Nordic environment

Source	Environment	Major radionuclides	Contribution
Nuclear weapons testing	Marine and terrestrial	$^{134,137}\text{Cs}$ , $^{90}\text{Sr}$ , Pu, Np, Am isotopes, etc.	Major
Chernobyl accident	Terrestrial and Baltic Sea	$^{134,137}\text{Cs}$ , $^{131}\text{I}$ , $^{129}\text{I}$ , etc.	Major
Reprocessing plants at Sellafield and La Hague	Marine (North sea, Baltic Sea, Norwegian Sea)	$^{134,137}\text{Cs}$ , $^{90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{129}\text{I}$ , actinides, etc.	Major
Thule accident	Thule, Greenland (marine and terrestrial)	Pu isotopes, $^{241}\text{Am}$	Relative high in local environment
Nuclear power plants	Terrestrial and marine	Activation and fission products	Small/negligible
Research reactors	Terrestrial and marine	Activation and Fission products	Negligible
Fukushima accident	Terrestrial	$^{134,137}\text{Cs}$ , $^{131}\text{I}$	Small
Medical applications of radioisotopes	Atmosphere and river	$^{131}\text{I}$ , $^3\text{H}$ , $^{14}\text{C}$ , Tc, etc.	Negligible

**Table 2** Radiochemical analysis of hard to measure radionuclides in main Nordic laboratories

Country	Organization	Purpose of analysis	Main radionuclides
Denmark	Technical University of Denmark	Environmental radioactivity, radioecology, environmental trace, characterization of decommissioning waste, emergency preparedness	$^3\text{H}$ , $^{14}\text{C}$ , $^{36}\text{Cl}$ , $^{41}\text{Ca}$ , $^{55}\text{Fe}$ , $^{63}\text{Ni}$ , $^{89,90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{129}\text{I}$ , $^{210}\text{Po}$ , $^{210}\text{Pb}$ , $^{222}\text{Rn}$ , $^{226,228}\text{Ra}$ , Isotopes of U, Th and Pu, $^{237}\text{Np}$ , $^{241}\text{Am}$ , $^{244}\text{Cm}$ , gross alpha, gross beta
Finland	Radiation and Nuclear Safety Authority (STUK)	Environmental radioactivity, bioassay of radioactivity, emergency preparedness	$^3\text{H}$ , $^{14}\text{C}$ , $^{89,90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{210}\text{Po}$ , $^{210}\text{Pb}$ , $^{222}\text{Rn}$ , $^{226,228}\text{Ra}$ , $^{234}\text{U}$ , $^{235}\text{U}$ , $^{238}\text{U}$ , $^{232,230,228}\text{Th}$ , $^{239,240}\text{Pu}$ , $^{241}\text{Am}$ , gross alpha, gross beta
	University of Helsinki	Environmental radioactivity and radioecology, analysis of nuclear waste	$^3\text{H}$ , $^{14}\text{C}$ , $^{41}\text{Ca}$ , $^{89,90}\text{Sr}$ , $^{210}\text{Po}$ , $^{210}\text{Pb}$ , $^{222}\text{Rn}$ , $^{226,228}\text{Ra}$ , Isotopes of U, Th and Pu, $^{237}\text{Np}$ , $^{241}\text{Am}$ , gross alpha, gross beta
	Loviisa NPP	Monitoring of radioactivity in the nuclear power plant and its discharges and waste	$^3\text{H}$ , $^{14}\text{C}$ , $^{63}\text{Ni}$ , gross alpha, gross beta
	Olkiluoto NPP	Monitoring of radioactivity in the nuclear power plant and its discharges	$^3\text{H}$ , $^{14}\text{C}$ , gross alpha, gross beta
Norway	Institute for Energy Technology (IFE)	Environmental radioactivity, waste management	$^3\text{H}$ , $^{89,90}\text{Sr}$ , $^{210}\text{Po}$ , $^{210}\text{Pb}$ , $^{222}\text{Rn}$ , $^{226,228}\text{Ra}$ , isotopes of U, Th and Pu, $^{237}\text{Np}$ , $^{241}\text{Am}$ , gross alpha, gross beta
	Norwegian University of Life Sciences	Environmental radioactivity, radioecology, environmental trace	$^{89,90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{210}\text{Po}$ , $^{210}\text{Pb}$ , $^{222}\text{Rn}$ , $^{226,228}\text{Ra}$ , isotopes of U, Th and Pu, $^{237}\text{Np}$ , $^{241}\text{Am}$
	Norwegian Radiation Protection Authority (NRPA)	Environmental radioactivity and radioecology, environmental trace, emergency preparedness	$^{89,90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{1210}\text{Po}$ , $^{210}\text{Pb}$ , $^{226}\text{Ra}$ , isotopes of U, Th and Pu, $^{241}\text{Am}$ , gross alpha, gross beta
Sweden	Studsvik Nuclear AB	Waste management, characterization of decommissioning waste, emergency preparedness	$^3\text{H}$ , $^{14}\text{C}$ , $^{55}\text{Fe}$ , $^{63}\text{Ni}$ , $^{89,90}\text{Sr}$ , $^{210}\text{Po}$ , $^{226}\text{Ra}$ , isotopes of U, Th and Pu, $^{241}\text{Am}$
	Forsmark NPP	Monitoring of radioactivity in the nuclear power plant, discharges and surrounding environment	$^3\text{H}$ , $^{14}\text{C}$ , $^{63}\text{Ni}$ , $^{90}\text{Sr}$ , Pu, Am, Cm, gross alpha, gross beta
	Oskarshamn NPP (OKG AB)	Monitoring of radioactivity in the nuclear power plant, discharges and surrounding environment	$^3\text{H}$ , $^{14}\text{C}$ , $^{55}\text{Fe}$ , $^{63}\text{Ni}$ , $^{89,90}\text{Sr}$ , $^{238}\text{Pu}$ , $^{239,240}\text{Pu}$ , $^{241}\text{Am}$ , $^{242,243,244}\text{Cm}$ , gross alpha
	Ringhals NPP	Monitoring of radioactivity in the nuclear power plant, discharges and surrounding environment	$^3\text{H}$ , $^{14}\text{C}$ , $^{63}\text{Ni}$ , $^{89,90}\text{Sr}$ , $^{238}\text{Pu}$ , $^{239,240}\text{Pu}$ , $^{241}\text{Am}$ , $^{242}\text{Cm}$ , $^{243,244}\text{Cm}$ , gross alpha
	Lund University	Radioecology, environmental trace, emergency preparedness	$^{14}\text{C}$ , $^{59}\text{Ni}$ , $^{63}\text{Ni}$ , $^{89,90}\text{Sr}$ , $^{99}\text{Tc}$ , $^{238}\text{Pu}$ , $^{239,240}\text{Pu}$ , $^{241}\text{Am}$ , $^{244}\text{Cm}$ , $^{243,244}\text{Cm}$
	Swedish Defense Research Agency	Emergency preparedness, radioecology, nuclear decommissioning	$^{14}\text{C}$ , $^{63}\text{Ni}$ , $^{89,90}\text{Sr}$ , isotopes of U and Pu, $^{237}\text{Np}$ , $^{241}\text{Am}$ , $^{244}\text{Cm}$ , $^{243,244}\text{Cm}$

measure because of their relative long half-lives, large fission yields and high mobility in the environment.

$^{90}\text{Sr}$  is one of the most important fission products in view of radiation protection because of its high fission yield (5.75 % for  $^{235}\text{U}$ ) and intermediate half-life (28.9 years). Many chemical procedures have been reported for determination of  $^{90}\text{Sr}$  in environmental samples, as well as samples from nuclear facilities.  $^{99}\text{Tc}$  ( $t_{1/2} = 0.211$  My) and  $^{129}\text{I}$  ( $t_{1/2} = 15.7$  My) are long-lived fission products with low specific radioactivity (643 MBq/g for  $^{99}\text{Tc}$  and 4.26 MBq/g for  $^{129}\text{I}$ ), consequentially lower radiation risk. While the high mobility in the environmental and long half-lives make them the most important radionuclides in waste repository and therefore key radionuclides in characterization of waste from nuclear decommission. Due to their high solubility in

seawater and long residence time in the ocean, they are excellent oceanographic tracers. Since the concentration of  $^{99}\text{Tc}$  and  $^{129}\text{I}$  in the environment are normally very low, extensive chemical separation has to be implemented to isolate them from a large size sample matrix and interfering radionuclides. Due to the unique sources of  $^{99}\text{Tc}$  and  $^{129}\text{I}$  in Nordic environment (reprocessing plants at La Hague and Sellafield), they were intensively investigated in Nordic environment, and a number of analytical methods for determination of these two radionuclides have been developed by Nordic laboratories [39, 44, 46–48, 57, 58].

For determination of  $^{90}\text{Sr}$ , two approaches are often applied, i.e. direct separation of  $^{90}\text{Y}$ , the daughter radionuclide of  $^{90}\text{Sr}$ , from sample and measuring it, and separation of  $^{90}\text{Sr}$  from sample and measuring  $^{90}\text{Sr}$  or  $^{90}\text{Y}$

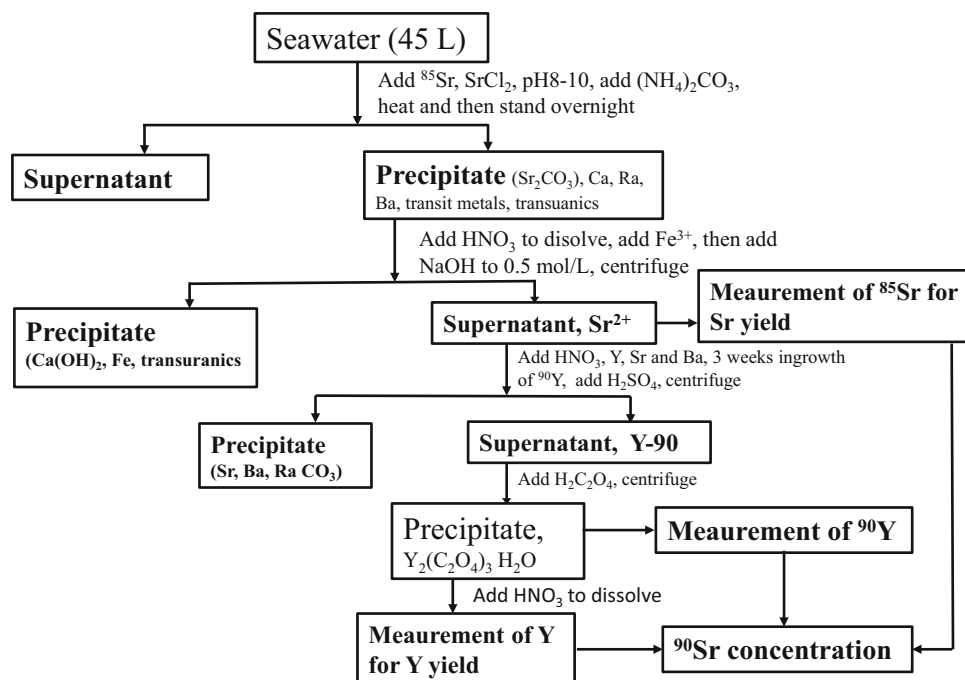
after ingrowth of  $^{90}\text{Y}$  from  $^{90}\text{Sr}$ . The measurement of  $^{90}\text{Y}$  or  $^{90}\text{Sr}/^{90}\text{Y}$  is often carried out using liquid scintillation counter (LSC) or low background gas flow GM counter. An ultra-low level gas flow GM counter (Risø counter GM-25-5A) produced by Technical University of Denmark, is one of major instrument for measurement of low-level beta emitters, such as  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , and  $^{234}\text{Th}$ , especially for environmental samples, which reaches a background of less than 0.2 cpm and counting efficiency of more than 30 % (for  $^{99}\text{Tc}$ ), therefore a detection limit of less than 1.0 mBq. Both  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  are pure beta emitter, which have to be separated from the matrix and all other radionuclides for measurement.

The major challenge in separation of  $^{90}\text{Sr}$  is its separation from calcium, radium,  $^{210}\text{Pb}$ – $^{210}\text{Po}$ , and  $^{133}\text{Ba}$ , because of their similar chemical properties. Vajda and Kim [90] reviewed analytical methods used for separation of  $^{90}\text{Sr}$ . The conventional method for separation of  $^{90}\text{Sr}$  is based on the insolubility of  $\text{Sr}(\text{NO}_3)_2$  in high concentration of  $\text{HNO}_3$  (>70 %), and co-precipitation of Ra, Ba and Pb with  $\text{Ba}_2\text{CrO}_4$  in aqueous solution. However, due to harmfulness and high cost of fuming  $\text{HNO}_3$ , this method is no longer used in many laboratories, and some improved methods based on application of extraction chromatographic method using Sr-Spec resin and prior precipitation of  $\text{Ca}(\text{OH})_2$  in  $\text{NaOH}$  solution are used to replace the conventional method. Figure 2 shows an improved method developed in the Technical University of Denmark for determination of  $^{90}\text{Sr}$  in large size of water samples [44]. The separated  $^{90}\text{Sr}$  can be directly

measured using LSC by measurement of  $^{90}\text{Sr}$  or  $^{90}\text{Sr} + ^{90}\text{Y}$ , meanwhile Cherenkov counting using liquid scintillation counter was also applied by measuring  $^{90}\text{Y}$  in-grown from  $^{90}\text{Sr}$ . However, the further separation of  $^{90}\text{Y}$  after ingrowth of 1–2 weeks from  $^{90}\text{Sr}$  by precipitation of  $\text{Y}_2(\text{C}_2\text{O}_4)_3$  and measurement of  $^{90}\text{Y}$  using ultra-low level gas flow GM counter for improved detection limit are often used for more effective determination of  $^{90}\text{Sr}$  in environmental samples [44].

A Sr-Spec resin has been introduced for separation of strontium from interferences for determination of  $^{90}\text{Sr}$  in waste samples and environmental samples in the recent decades. The major limitation of this resin is its low capacity for strontium and low toleration to high calcium content, which limits its application for analysis of high Ca and Sr samples. Anyway it has become a widely used method for the determination of  $^{90}\text{Sr}$  in waste and environmental samples [90]. Sr spec column has been successfully used to separate Sr and Y for the determination of  $^{89}\text{Sr}$  and  $^{90}\text{Sr}$  in reactor coolant samples, double Sr spec column was confirmed to be useful when the concentration of  $^{89}\text{Sr}$  is much higher than that of  $^{90}\text{Sr}$ . In this case, the freshly separated  $^{89,90}\text{Sr}$  was first measured using Cherenkov counting for  $^{89}\text{Sr}$ , and after a few days ingrowth of  $^{90}\text{Y}$  from  $^{90}\text{Sr}$ , the solution was then loaded to the second Sr Spec column and  $^{90}\text{Y}$  in the effluent was collected and measured for determination of  $^{90}\text{Sr}$  [91]. To avoid possible interference of actinides for determination of  $^{90}\text{Sr}$ , a TRU column is applied in the front of Sr column in a stack model, after loading the sample solution to the columns,

**Fig. 2** Diagram of an analytical procedure for the determination of  $^{90}\text{Sr}$  in large volume of seawater sample (reproduced from Chen et al. [45])



the two columns are disconnected, and Sr adsorbed on the Sr column is eluted for measurement of  $^{90}\text{Sr}$  [92].

For direct separation and measuring  $^{90}\text{Y}$ , solvent extraction (e.g. bis-2-ethylhexyl-phosphoric acid, HDEHP) has been proposed to directly separate yttrium from the decomposed samples, the separated  $^{90}\text{Y}$  is then directly measured by LSC for determination of  $^{90}\text{Sr}$  [93]. A direct separation of  $^{90}\text{Y}$  from large volume of seawater has also been reported by using co-precipitation of  $\text{Fe}(\text{OH})_3$ – $\text{Y}(\text{OH})_3$  and  $\text{LaF}_3$ – $\text{YF}_3$  for preconcentration from the sample matrix, and DGA column for purification of  $^{90}\text{Y}$  from other radionuclides and interfering matrix elements [94].

Table 3 summarizes the methods used in Nordic laboratories for  $^{90}\text{Sr}$  determination. Gamma emitting radionuclides,  $^{85}\text{Sr}$ , is often used for monitoring chemical yields of Sr in the separation procedure when it does not affect the measurement of  $^{90}\text{Sr}$ . While stable Sr and Y (as carrier) have to be applied for measurement of chemical yields of  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  when separated  $^{90}\text{Sr}$  is measured using LSC. The stable Sr and Y can be measured using ICP-OES for monitoring chemical yield of Sr and Y in the separation procedure.

Preconcentration and separation of  $^{99}\text{Tc}$  from sample matrix is mainly based on its high affinity to anion exchange resin in its high oxidation state as  $\text{TcO}_4^-$  in neutral solution, and insolubility of  $\text{Tc}^{4+}$  as  $\text{TcO}_2$ . Large volume of seawater (up to 200 L) can be directly loaded to an anion exchange chromatographic column, the strong adsorbed  $^{99}\text{Tc}$  on the resin is eluted using concentrated  $\text{HNO}_3$  (8–10 mol/L). By reduction of Tc to  $\text{Tc}^{4+}$  following by co-precipitation with  $\text{Fe}(\text{OH})_2$ ,  $^{99}\text{Tc}$  can be also separated from most of matrix elements. The most critical issue in the separation of Tc from samples is volatility of Tc at high temperature, wet ashing (acid digestion) is therefore often used to decompose biological samples and to leach Tc from the soil samples. In this case,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  have been used to decompose biological sample for  $^{99}\text{Tc}$  determination [39, 42, 95]. However, recent investigations

have shown that  $^{99}\text{Tc}$  is relative stable during ashing and evaporation if temperature is well controlled and suitable acids are used [57, 58], e.g. ashing of seaweed at 700 °C and soil/sediment at 550 °C do not cause significant loss of Tc. In HCl medium, Tc is not stable and most of  $^{99}\text{Tc}$  is lost when the solution is evaporated to dryness at temperature higher than 150 °C. While, Tc is relative stable during evaporation in  $\text{HNO}_3$ , neutral and alkaline media [57]. Separation of Tc from Ru and Mo is the major challenge in the determination of  $^{99}\text{Tc}$ , because of the interference of  $^{103,106}\text{Ru}$  and  $^{99}\text{Mo}$  in the radiometric measurement of  $^{99}\text{Tc}$ , and isobaric interference of  $^1\text{H}^{98}\text{Mo}$  and  $^{99}\text{Ru}$  in the mass spectrometric measurement of  $^{99}\text{Tc}$ . Because of the similar behaviors of  $\text{TcO}_4^-$  with  $\text{MoO}_4^{2-}$  and  $\text{RuO}_4^-$  on strong basic anion exchange resin, the decontamination factors of Mo and Ru by anion exchange chromatography are not sufficiently higher for the determination of  $^{99}\text{Tc}$  in environmental samples. Removal of Ru by converting it to volatile species of  $\text{RuO}_4$  was proposed [42]. To improve the decontamination factor for Mo, extraction chromatographic resin TEVA was proposed [63] for further purification after the separation of Tc from the sample matrix using anion exchange chromatography or  $\text{Fe}(\text{OH})_2 + \text{TcO}_2$  coprecipitation. A separation method based on TEVA extraction chromatography and formation of neutral complex of Ru with  $\text{H}_2\text{O}_2$  has been proposed for separation of Tc from interfering radionuclides, especially Ru and Mo [58].

The most often-used measurement methods for  $^{99}\text{Tc}$  are ultra-low level GM counter and ICP-MS, a detection limit of 1.5 mBq for  $^{99}\text{Tc}$  has been reported using ICP-MS with a concentric nebulizer [57, 58], which is comparable with that by ultra-low level GM counter. A detection limit of 0.2–0.3 mBq was reported when highly efficiency sample introduction system such as ultrasonic nebulizer and electrothermal vaporization system was used [63]. Although LSC has also been used for measurement of  $^{99}\text{Tc}$ , but the detection limit is normally higher than 20 mBq due to higher background level.

**Table 3** Analytical methods for the determination of  $^{90}\text{Sr}$  used in Nordic laboratories

No.	Separation of Sr	Separation of Y	Measurement	Reference
1	$\text{Sr}(\text{NO}_3)_2$ precipitation in concentrated $\text{HNO}_3$ , $\text{Ba}_2\text{CrO}_4$ precipitation to remove Ra, Pb and Ba	$\text{Y}_2(\text{C}_2\text{O}_4)_3$ precipitation	LSC or low level GM counter	[156]
2	No	$\text{Y}_2(\text{C}_2\text{O}_4)_3$ precipitation followed by HDEHP solvent traction	LSC	[93]
3	$\text{SrCO}_3$ precipitation followed by Sr Spec extraction chromatography		LSC	[91]
4	$\text{SrCO}_3$ precipitation, $\text{Ca}(\text{OH})_2$ precipitation to remove Ca, and $\text{SrSO}_4$ to remove Sr, Ra and Ba	$\text{Y}_2(\text{C}_2\text{O}_4)_3$ precipitation	Low level GM counter	[44]

Separation of  $^{129}\text{I}$  is mainly based on the volatility of iodine, the solvent extraction of  $\text{I}_2$  in non-polar solvent such as  $\text{CHCl}_3$  or  $\text{CCl}_4$ , as well as high affinity of iodide to anion exchange resin. For solid samples such as soil, sediment, vegetation, the sample is normally directly combusted in a tube furnace under oxygen flow at 800–850 °C. In this case, iodine can be completely released from the sample as gas form, which is then absorbed in a trap solution of NaOH (or amine solution) [96, 97]. The separated iodine in the trap solution can be further purified by solvent extraction. For aqueous samples such as reactor water, rain, river/lake water, seawater and ground water, iodine is first converted to iodide by addition of reductive reagent such as  $\text{NaHSO}_3$  in acidic media (pH 1–2), iodide in the water is then oxidized to  $\text{I}_2$  using  $\text{NaNO}_2$  and extracted to  $\text{CHCl}_3$ , which is then back extracted using a diluted  $\text{NaHSO}_3$  solution [30, 46, 96]. It should be mentioned that this method is only used for determination of total inorganic  $^{129}\text{I}$ , because organic  $^{129}\text{I}$  could not be extracted into  $\text{CCl}_4$  or  $\text{CHCl}_3$ . For determination of total iodine, a procedure by decomposition of organic substance to convert organic iodine to inorganic forms has to be implemented before solvent extraction.

As a beta emitter with gamma ray emission,  $^{129}\text{I}$  can be measured by LSC and gamma spectrometry. However, due to the low specific radioactivity of  $^{129}\text{I}$ , these two techniques can be only used for analysis of high-level samples such as reactor water and nuclear waste. For environmental samples, neutron activation analysis (NAA) and accelerator mass spectrometry (AMS) have to be used, and for samples with a  $^{129}\text{I}/^{127}\text{I}$  ratio lower than  $1 \times 10^{-10}$ , AMS is the only technique for its measurement. In NAA, the separated iodine is normally prepared as a solid form such as  $\text{MgI}_2$  and sealed in a quartz ampoule for neutron irradiation in a nuclear reactor, where  $^{129}\text{I}$  is activated to short lived gamma emitting  $^{130}\text{I}$  (12 h), and measured using gamma spectrometry after a purification, normally by solvent extraction and precipitation as  $\text{PdI}_2$  [46, 97]. For the AMS measurement, the separated iodide is precipitated as  $\text{AgI}$ , which is mixed with conductive metal such as niobium or silver powder and pressed into a cathode holder for AMS measurement [98]. The detection limit of AMS for  $^{129}\text{I}$  can reach to  $10^5$  atoms (or 1 nBq).

### Major activation products ( $^3\text{H}$ , $^{14}\text{C}$ , $^{36}\text{Cl}$ , $^{41}\text{Ca}$ , $^{55}\text{Fe}$ , $^{63}\text{Ni}$ )

Numerous radionuclides are produced in nuclear reactors by neutron activation of stable isotopes of elements in construction materials as well as fuel and circulation water, most of them are short-lived. Among these,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{36}\text{Cl}$ ,  $^{41}\text{Ca}$ ,  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$  are the most important pure beta emitters, and often required to be measured for monitoring purpose

in the nuclear reactors and decommissioning of nuclear facilities.

$^3\text{H}$  and  $^{14}\text{C}$  are two most important pure beta-emitting radionuclides in the nuclear facilities, not only in the water and solid samples, but also in air sample. Actually,  $^{14}\text{C}$  released from the nuclear power plants is the major contribution in view of the radiation dose in the surrounding environment [99]. Therefore  $^{14}\text{C}$  and  $^3\text{H}$  in the air, reactor water and discharged water are often monitored in the nuclear power plants. In addition, due to the large inventory of  $^{14}\text{C}$  and  $^3\text{H}$  in nuclear waste in the nuclear power plants such as exchange resin and in nuclear decommissioning, they are also the most important radionuclides to be measured in decommissioning of nuclear facilities. In Nordic nuclear power plants and research reactors, tritium and  $^{14}\text{C}$  in air are collected using two types of systems. In one system, the air is first passed through a cooled condenser to collect THO, the dried air is then passed through a CarboSorb/NaOH solution to collect  $^{14}\text{CO}_2$ . Another system is pumping the air through a furnace with Pt catalyst where all tritium is convert to THO and  $^{14}\text{C}$  is convert to  $\text{CO}_2$ , following a molecular sieve to trap the HTO and  $\text{CO}_2$ . The collected THO and  $\text{CO}_2$  in the molecular sieves are then released by heating. The released THO is collected using a condenser as condensed water, and  $\text{CO}_2$  is collected using CarboSorb trap solution. The separated tritiated water (THO) and  $^{14}\text{CO}_2$  in CarboSorb are mixed with scintillation cocktail solution to measure  $^3\text{H}$  and  $^{14}\text{C}$  using LSC, respectively.

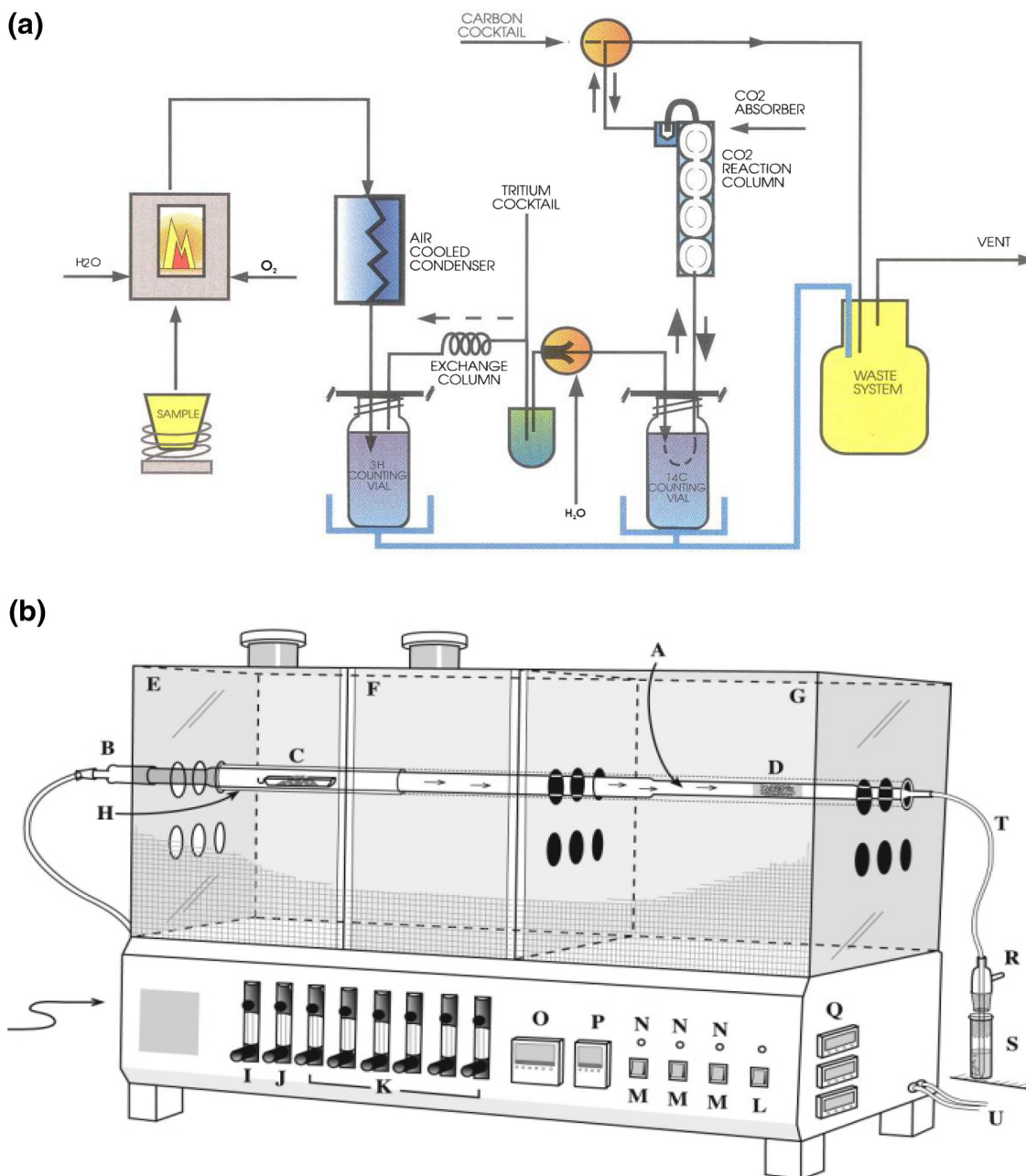
For the determination of  $^3\text{H}$  and  $^{14}\text{C}$  in solid samples such as exchange resin, concrete, graphite, metals, sediment and vegetation, oxidizing combustion method is often used. In this technique, the samples are combusted at high temperature (850–1000 °C) under  $\text{O}_2$  flow and with Pt or Cu catalyst. Tritium in the samples regardless of its species is converted to water vapor, which is released from the sample and collected by a condenser or water/diluted acid trapping. Meanwhile,  $^{14}\text{C}$  in both inorganic and organic forms is converted to  $\text{CO}_2$ , which is released from the sample and trapped in an alkaline solution such as CarboSorb or NaOH. The separated  $^3\text{H}$  in water and  $^{14}\text{C}$  in trap solution are measured by LSC after mixing with scintillation cocktails, respectively. Pt or Cu catalyst is used to convert any CO to  $\text{CO}_2$ , because CO cannot be effectively trapped in alkaline solution. Two combustion systems have been used in Nordic laboratories: Pyrolysis based tube furnace (Raddec International, Southampton, UK) [100] and Sample Oxidizer (PerkinElmer, USA) [75]. Sampler Oxidizer can rapidly separate  $^3\text{H}$  and  $^{14}\text{C}$  from solid samples in 2–3 min/sample compared to tube furnace of about 4 h for each batch (4–6 samples). However, the tube furnace system can treat a large size sample up to 20 g for concrete, soil and metal and 5 g for biological samples,



compared to only less than 1 g concrete, soil and metal, and 0.5 g biological samples in Sample Oxidizer system. Figure 3 shows principal diagram of two systems. Besides these samples, Sample Oxidizer has also been used to analyze oil, bitumen and plastic samples. The results showed that both inorganic and organic forms of  $^3\text{H}$  and  $^{14}\text{C}$  could be quantitatively separated from samples using these two systems.

Due to high mobility and long half-life (301 ky),  $^{36}\text{Cl}$  is one of important radionuclides in the waste repository and decommissioning. Meanwhile, naturally occurring  $^{36}\text{Cl}$  as

a good tracer is widely used in hydrological and geological investigation. In this case,  $^{36}\text{Cl}$  concentration is too low to be measured by any radiometric method, and AMS has to be used. In the AMS measurement,  $^{36}\text{Cl}$  in  $\text{AgCl}$  form is pressed in cathode target holder for measurement. As an isobaric interference, stable  $^{36}\text{S}$ , which also form negative ion in the ion source of AMS, is the major interference in AMS measurement of  $^{36}\text{Cl}$ , and has to be removed by chemical separation and instrument setup in AMS [101]. The chemical separation of  $^{36}\text{Cl}$  is mainly based on  $\text{AgCl}$  precipitation, the purification of  $^{36}\text{Cl}$  can be carried out by



**Fig. 3** Schematic diagram of combustion system for separating tritium,  $^{14}\text{C}$  and  $^{129}\text{I}$  from solid samples. **a** Sample Oxidizer and **b** tube furnace

dissolution of AgCl in ammonium and re-precipitation by acidification. For the measurement of pure beta emitting  $^{36}\text{Cl}$  in waste samples, LSC is often used. In this case, direct measurement of AgCl or solution of AgCl in ammonium cause a high quench effect because of the solid particles of AgCl and high alkaline media of ammonium. A new procedure was reported to improve the purification of  $^{36}\text{Cl}$  and the quench effect by separation of Cl using an anion exchange chromatography [102]. The dissolved AgCl in ammonium is loaded to a strong basic anion exchange column (e.g. Bio Rad 1-X4) which was converted to  $\text{OH}^-$  form and conditioned with ammonium,  $\text{Ag}^+$  cation does not adsorbed on the anion exchange column and is removed, the  $\text{Cl}^-$  retained on the column is eluted with diluted  $\text{NH}_4\text{NO}_3$  solution (0.2 mol/L), which is evaporated to less than 2 ml for measurement using LSC after mixed with scintillation cocktail. By this way, the decontamination factors for most of interfering radionuclides are higher than  $10^5$ , and the counting efficiency of  $^{36}\text{Cl}$  by LSC is higher than 90 %. Various types of samples from the nuclear facilities, such as concrete, graphite, steel, lead, aluminum, swipe and water have been successfully analyzed for  $^{36}\text{Cl}$  [102]. Due to the high volatility of chlorine, sample cannot be ashed at high temperature, and acid dissolution/digestion and alkali fusion have to be used to decompose samples. For graphite, a mixture of  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$  (volume ratio of 15:4:1) has been proposed to completely decompose the sample and transfer  $^{36}\text{Cl}$  in the sample to solution, meanwhile do not introduce too much stable chlorine to the sample solution. For analysis of stainless steel, the normal acid dissolution method introduce a large amount of chlorine by using HCl, which increases the Cl (salt) content in the final separated  $^{36}\text{Cl}$  solution for LSC measurement, therefore worsening the detection limit of  $^{36}\text{Cl}$ . A procedure has been reported to use a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  (volume ratio of 10:1) to dissolve steel sample. In this case, no stable Cl is introduced by chemical reagents in the sample dissolution, therefore a large size sample can be analyzed, consequently improved the detection limit of  $^{36}\text{Cl}$  to 14 mBq [102].

$^{41}\text{Ca}$  is an important radionuclide in the concrete shield in nuclear reactor because of its high production by neutron activation of highly content stable  $^{40}\text{Ca}$  in the concrete. Chemical separation of  $^{41}\text{Ca}$  mainly focus on its separation from all other radionuclides, especially radioisotopes of strontium ( $^{89}\text{Sr}$  and  $^{90}\text{Sr}$ ), barium ( $^{133}\text{Ba}$ ) and radium ( $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ), which have similar chemical properties as calcium. These interfering radionuclides can be separated by  $\text{BaCrO}_4$  precipitation for removal of  $^{133}\text{Ba}$  and Ra, Sr-spec. column for removal of  $^{89,90}\text{Sr}$ , and  $\text{Fe}(\text{OH})_3$  precipitation for removal of all transit metals and actinides [103]. A simple and effective procedure for

separation of  $^{41}\text{Ca}$  from concrete samples has been reported, which is based on solubility of Ca in solution with  $\text{pH} < 10$  to separate Ca from most of transit metals and transuranic, and formation of insoluble  $\text{Ca}(\text{OH})_2$  in NaOH solution of  $> 0.5$  mol/L to separate Ca from Sr, Ba and Ra which are soluble in NaOH solution even at a concentration of 2 mol/L [78]. Alkaline fusion is often used to decompose geological samples, while experimental results have shown that acid leaching using *aqua regia* [78] or 8 mol/L  $\text{HNO}_3$  and HCl [104] can leach most of Ca ( $> 95\%$ ) from concrete, this method is more convenient and rapid compared to alkali fusion. After addition of some metals, the leachate solution is neutralized to  $\text{pH} 9$ , the formed metal hydroxides precipitate containing most of interfering radionuclides such as radioactive Eu, Co, Fe, Ni, Pu and Am is removed, Ca in the supernatant is then precipitated as  $\text{CaCO}_3$  by addition of  $\text{Na}_2\text{CO}_3$ . Meanwhile, Sr, Ba and Ra are also precipitated and separated from the solution. In this step, water soluble radionuclides such as radioactive cesium ( $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ ),  $^3\text{H}$ ,  $^{40}\text{K}$ ,  $^{36}\text{Cl}$ ,  $^{99}\text{Tc}$ , and  $^{129}\text{I}$  are also removed. The carbonate precipitate is then dissolved in HCl, and some stable metals are added, and the solution is neutralized to  $\text{pH} 9$  to further separate radioactive metal.  $^{41}\text{Ca}$  in the solution is precipitated by addition of NaOH to a concentration of 0.5 mol/L. The formed  $\text{Ca}(\text{OH})_2$  precipitation is dissolved with HCl, and transit metal hydroxides precipitation followed by  $\text{Ca}(\text{OH})_2$  precipitation process is repeated two times. The final dissolved  $\text{Ca}(\text{OH})_2$  in HCl is mixed with scintillation cocktail for LSC measurement. By this way, the decontamination factors for all interfering radionuclides including  $^{90}\text{Sr}$  and  $^{133}\text{Ba}$  are higher than  $10^5$ , and a detection limit of 15 mBq for  $^{41}\text{Ca}$  can be obtained [78]. Another procedure based on anion exchange chromatography and  $\text{CaCO}_3$  precipitation has also been proposed for determination of radioactive calcium in concrete. In this procedure, radioactive metals and anions are removed from Ca by formation of anions in strong  $\text{HNO}_3$  or HCl and adsorption in anion exchange column, while Ca does not form anion with either  $\text{Cl}^-$  or  $\text{NO}_3^-$  remains in the effluent, which is precipitated as  $\text{CaCO}_3$  and separated from other interfering radionuclides. The  $\text{CaCO}_3$  is finally dissolved in HCl for LSC measurement. This method was successfully applied to determine short-lived  $^{45}\text{Ca}$  in concrete, but did not consider separating Ca from radioactive strontium, barium and radium, and not demonstrated to be useful for determination of  $^{41}\text{Ca}$  in concrete [104].

$^{55}\text{Fe}$  and  $^{63}\text{Ni}$  are two important radionuclides both in decommissioning of nuclear facilities and monitoring different processes and discharges of nuclear facilities, because of their high production yields in nuclear reactors.  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  are neutron activation products of stable Fe

and Ni, which are major elements in construction materials of a nuclear reactor.  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  can also enter the coolant water and discharge water of the facility.

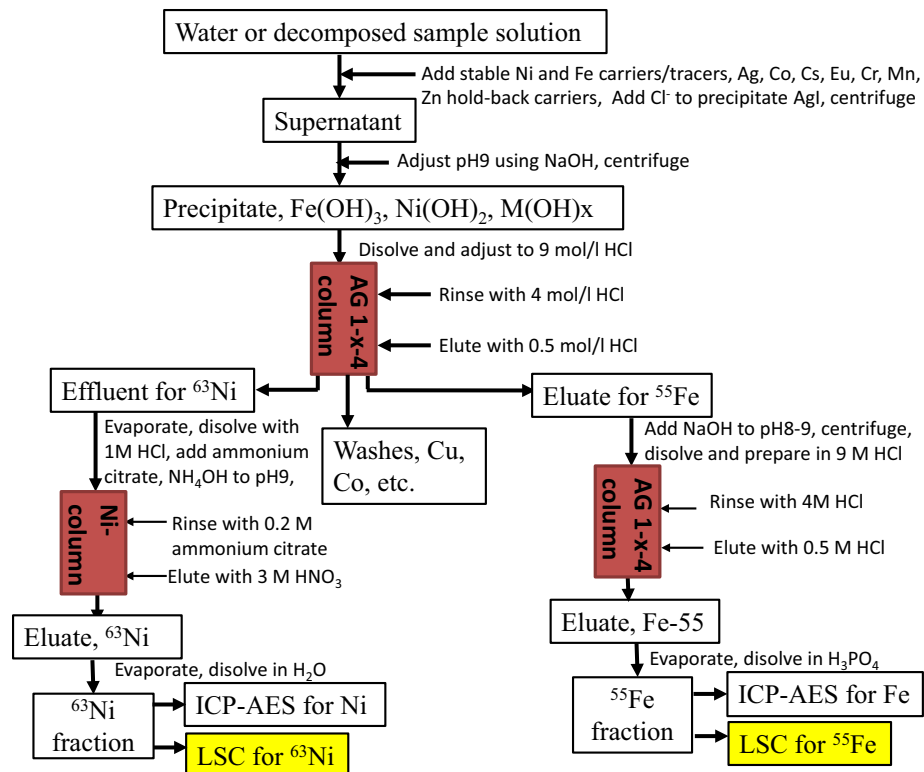
Different analytical methods have been proposed and applied for the determination of  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  in waste and environmental samples. A method for determination of  $^{63}\text{Ni}$  in environmental samples such as vegetation, sediment and algae samples has been reported in the 1990s [79, 80]. This method is based on the formation of a complex of Ni with dimethylglyoxime (DMG) and the adsorption of most of the interfering radioactive metals on an anion exchange resin in concentrated HCl media. The decomposed sample is first neutralized with  $\text{NH}_3$  to remove most of the transit metals as hydroxides, while Ni, as a complex with  $\text{NH}_3$  remains in the solution, which is then extracted to chloroform as a DMG complex after addition of citrate and DGM to the solution. The extracted DMG–Ni complex is back extracted using 1.5 mol/L HCl, which is conditioned in 9 mol/L HCl and loaded on a strong basic anion exchange column, most of the interfering radioactive metals such as Co, Mn and Zn are absorbed on the column, while  $\text{Ni}^{2+}$  passes through the column and is collected in the effluent. The separated  $\text{Ni}^{2+}$  is electroplated on disc for measurement using gas flow GM counter or silicon detector [80].

An improved procedure has been reported for the determination of  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  in graphite, concrete, metals, sediment, and waters [76]. This method is based on precipitation of hydroxides of Ni and Fe, anion exchange chromatography for separation of Ni and Fe from other metals such as Co, Mn, Zn and Eu, and then extraction chromatography separation using Ni resin (Triskem International, France) to obtain purified Ni (Fig. 4). In this procedure, both  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  are separated as hydroxide by neutralizing solution using NaOH instead of  $\text{NH}_3$ , because part of Ni (10–30 %) can be also precipitated with  $\text{Fe}(\text{OH})_3$  by wrapping Ni into the  $\text{Fe}(\text{OH})_3$  precipitate when using  $\text{NH}_3$  to neutralize the solution. In this step, most of water soluble radionuclides such as  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{134,137}\text{Cs}$ ,  $^{89,90}\text{Sr}$  are removed. Anion exchange chromatography is used to separate  $\text{Ni}^{2+}$  from  $\text{Fe}^{3+}$  and to remove other radioisotopes of transit metals. This is based on the fact that  $\text{Ni}^{2+}$  does not form a complex anion with  $\text{Cl}^-$  in a HCl medium, while  $\text{Fe}^{3+}$  can form a strong  $\text{FeCl}_4^-$  complex, which is retained on the anion exchange column. Other radioactive metals, such as  $^{58,60}\text{Co}$ ,  $^{65}\text{Zn}$ ,  $^{54}\text{Mn}$ ,  $^{110\text{m}}\text{Ag}$ ,  $^{99}\text{Mo}$  and  $^{103,106}\text{Ru}$  are also adsorbed on the column, and they can be sequentially removed from the column using different solutions, for example  $^{58,60}\text{Co}$  can be removed using 4 mol/L HCl, and  $\text{Fe}^{3+}$  can be eluted from the column using 0.5 mol/L HCl, while  $^{99}\text{Mo}$ ,  $^{103,106}\text{Ru}$ ,  $^{65}\text{Zn}$ ,  $^{54}\text{Mn}$  still remain on the column. With this process,  $^{55}\text{Fe}$  can be separated from most of the interfering radionuclides.

The effluent from the anion exchange column containing  $^{63}\text{Ni}$  also contains other radionuclides such as  $^{152,154}\text{Eu}$ ,  $^{144}\text{Ce}$ , and  $^{51}\text{Cr}$  as they do not form anion complexes with HCl either. Also, other remaining radionuclides such as  $^{90}\text{Sr}$  and  $^{133}\text{Ba}$  stay in the effluent and therefore it has to be purified. An extraction chromatography using Ni resin, on which DMG function group is immobilized on the inert resin matrix, can significantly improve the separation efficiency. Besides  $\text{Ni}^{2+}$ , other transit metals, such as  $\text{Co}^{2+}$  and  $\text{Fe}^{3+}$  can also form complexes with DMG, but have a different affinity to the column, the extraction chromatography step can therefore significantly improve decontamination factors to the interfering radionuclides. The measured decontamination factors for interfering radionuclides using this procedure are higher than  $10^5$ , resulting in detection limits of 18 and 14 mBq for  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$ , respectively [76]. For the samples containing short-lived activation radionuclides, e.g. reactor water and spent exchange resins from nuclear power plants,  $^{110\text{m}}\text{Ag}$  might be a potential interference which may not be sufficiently removed. A  $\text{AgCl}$  precipitation step is needed to obtain a better detection limit. For the determination of  $^{55}\text{Fe}$  in a sample that contains high level of radioactive cobalt (e.g.  $^{58}\text{Co}$ ,  $^{60}\text{Co}$ ) compared to  $^{63}\text{Ni}$  and  $^{55}\text{Fe}$ , the single anion exchange chromatographic separation might not be sufficient, a repeated separation step using anion exchange chromatography might be needed to obtain a high decontamination factor for radioactive cobalt (e.g.  $>10^6$ ).

Solid samples such as soil, sediment, biological samples, graphite, steel, aluminum, lead and concrete have to be decomposed to transfer iron and nickel to the solution before chemical separation. For soil and sediment samples, an acid leaching can be applied because  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  in the environmental sample is mainly released from nuclear facilities, which adsorbed on the surface of the soil and sediment samples and can be quantitatively leached out using acid (or *aqua regia*). The biological samples such as vegetation and animal tissues can be first ashed at 450–500 °C, and then dissolved in  $\text{HNO}_3$  or *aqua regia*. High temperature ( $>600$  °C) ashing should be avoided to prevent from formation of refractory compound of Fe and Ni. For bioshield concrete from nuclear reactor, alkali fusion might be the best choice because some iron and nickel might present in the minerals which is difficult to be leached out using acid. While the experiment shows that acid leaching using *aqua regia* can leach out more than 90 % of Fe and Ni from the bioshield concrete including heavy concrete containing high amount of  $\text{BaSO}_4$ , indicating acid leaching might be applied in the case of high analytical uncertainty is accepted. Graphite samples can be first ashed at 800 °C, and Fe and Ni in the residue are then leached using acid for further separation. Ashing at higher temperature, e.g.  $>1000$  °C might cause loss of Fe and Ni

**Fig. 4** Analytical procedure for the determination of  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  in nuclear waste using precipitation, anion exchange chromatography and extraction chromatography



during ashing by formation of some refractory compounds. Metal samples such as steel, lead and aluminum can be easily dissolved using acid or a combination of acids.

Another method based on only extraction chromatography for separation of  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$  from reactor water samples has also been proposed [63]. In this procedure, the evaporated reactor water is first dissolved in 8 mol/L  $\text{HNO}_3$ , and the solution is loaded to a 2 mL-TRU column (Triskem International, France).  $\text{Fe}^{3+}$  and transuranics are adsorbed on the column, while  $\text{Ni}^{2+}$  and other radionuclides pass through the column and are collected in the effluent. The  $\text{Fe}^{3+}$  on the TRU column is then eluted using 2.0 mol/L  $\text{HNO}_3$  for measurement of  $^{55}\text{Fe}$ . The effluent containing  $\text{Ni}^{2+}$  is conditioned with citrate and adjust to pH 8 using  $\text{NH}_3$ , this solution is loaded to a Ni column, and finally eluted with 2 mol/L  $\text{HNO}_3$ . A repeat separation of Ni using another Ni column is confirmed to be necessary to obtain a better decontamination factor for radioactive cobalt for LSC measurement of  $^{63}\text{Ni}$ . This procedure has been used in Nordic nuclear power plants for determination of  $^{63}\text{Ni}$  in reactor coolant water. It should be mentioned that for samples containing high levels of radioactive cobalt, e.g. reactor processing water, radioactive cobalt might not be sufficiently removed from  $^{63}\text{Ni}$ , a correction by measuring the content of  $^{60}\text{Co}$  and  $^{58}\text{Co}$  in the final separated solution using gamma spectrometry has to be implemented [63, 105].

$^{55}\text{Fe}$  decays by electron capture, its measurement by LSC is implemented by counting its low energy Auger electrons (<6 keV), therefore its counting efficiency is very sensitive to the quench level of the measurement solution. While  $\text{Fe}^{3+}$  solution (yellow/brown) has the highest color quench, causing a serious quench effect and much lower counting efficiency (<10 %) when iron content is higher than 5 mg. A method was proposed to dissolve the separated iron into  $\text{H}_3\text{PO}_4$  solution to form a colorless complex of Fe with  $\text{PO}_4^{3-}$ , which significantly improved the counting efficiency of LSC for  $^{55}\text{Fe}$  [76]. Table 4 summarizes the methods used in the Nordic laboratories for the determination of  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$  and  $^{90}\text{Sr}$ .

### Actinides (isotopes of Th, U, Np, Pu, Am and Cm)

Actinides especially the transuranic elements are important in nuclear facilities and environmental monitoring, environmental radioactivity, repository of nuclear waste and decommissioning. This is attributed to a few reasons: (1) most of isotopes of actinides are alpha emitters which are highly radiological toxic; (2) most of these radionuclides are long-lived; (3) some of them are highly mobile and easy to migrate in certain chemical species. However, the concentrations of these radionuclides (except uranium and thorium) are normally very low, therefore an extensive



**Table 4** The currently used radioanalytical methods for the determination of  $^3\text{H}$ ,  $^{14}\text{C}$ ,  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$  and  $^{90}\text{Sr}$  in Nordic labs

Nuclide	Sample type	Method	Laboratory
$^3\text{H}$	Water	Distillation/ion exchange/no treatment	All labs
	Soil sample (concrete, graphite, soil)	Combustion using Packard Oxidizer Combustion using tube furnace	DTU Nutech, STUK Studsvik
	Air	$^3\text{H}$ collector (as tritium water)	Oskarshamn, Ringhals, Forsmark, Loviisa and Olkiluoto NPPs, Studsvik
$^{14}\text{C}$	Water	Evaporation follow by combustion	DTU Nutech
	Soil sample (concrete, graphite, soil metals)	Combustion using Packard Oxidizer Combustion using tube furnace	DTU Nutech, STUK Studsvik
	Air	$^{14}\text{C}$ collector (as $\text{CO}_2$ ) $^{14}\text{C}$ collector (NaOH)	Loviisa NPP Oskarshamn, Ringhals, Forsmark NPP
$^{63}\text{Ni}$	Water	TRU-Ni resin Precipitation-ion exchange-Ni resin	Forsmark, Oskarshamn, Ringhals, Loviisa NPP, Studsvik DTU Nutech, STUK,
	Concrete, graphite, metals	Precipitation-ion exchange-Ni resin	DTU Nutech
$^{55}\text{Fe}$	Water	TRU chromatography Precipitation-anion exchange chromatography	Oskarshamn DTU Nutech,
	Concrete, graphite, metals	Acid digestion/leaching, hydroxide precipitation, anion exchange chromatography	DTU Nutech
$^{90}\text{Sr}$	Water	Carbonate precipitation, $\text{Ca}(\text{OH})_2$ precipitation, Sr (Ra, Ba, Pb) precipitation, $\text{Y}_2(\text{CO}_3)_3$ precipitation for $^{90}\text{Y}$	DTU Nutech
		Oxalate precipitation, chromate precipitation to remove Pb, carbonate precipitation of Sr, extraction chromatography using Sr resin, LSC measurement	STUK
		Cation exchange chromatography + extraction chromatography using Sr resin	Oskarshamn, Ringhals NPP
	Environmental and biological samples, concrete, graphite, metals	Direct solvent extraction of Y Ashing, acid digestion (HCl, or $\text{HNO}_3 + \text{HCl}$ ), separation using the same procedure as for water sample	Forsmark NPP DTU Nutech, STUK

DTU Nutech: Technical University of Denmark, Center for Nuclear Technologies; STUK: Radiation and Nuclear Safety Authority; Studsvik: Studsvik Nuclear AB

chemical separation is required to isolate them from matrix and interferences.

Some review articles on the separation of transuranics have well presented the methods used for separation of each transuranic or sequential separation of them for the measurement of isotopes of these elements [90, 106–110]. The early separation methods are mainly based on solvent extraction using organic compounds as extraction reagent such as TBP (tributyl phosphate), di(2-ethylhexyl) orthophosphoric acid (HDEHP), and TIOA (tri-isooctylamine)/xylene [35, 43, 89, 111]. While, chromatographic techniques, especially extraction chromatography, are often used to obtain a better separation regarding to the decontamination of interferences, meanwhile it also creates less toxic waste. Anion exchange chromatography has been used to separate U, Pu, Np, Am and Cm from waste

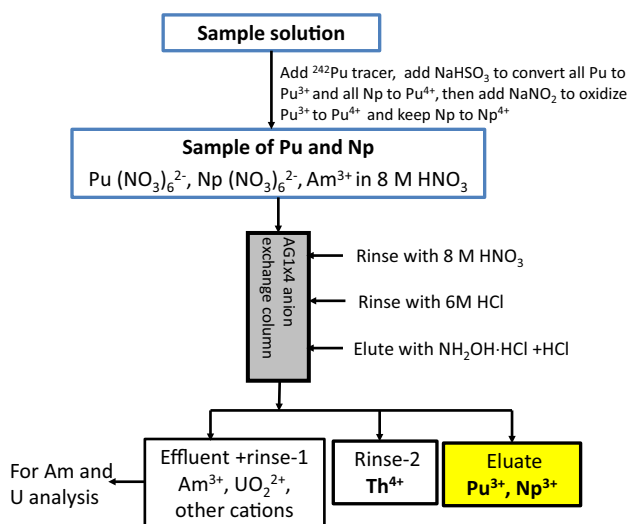
and environmental samples, which is mainly based on formation anion complex of these elements with  $\text{Cl}^-$  or  $\text{NO}_3^-$  in high concentration of HCl or  $\text{HNO}_3$ . For examples,  $\text{UO}_2^{2+}$ ,  $\text{Pu}^{4+}$  and  $\text{Np}^{4+}$  form anion complex in high concentration of  $\text{HNO}_3$  (>6 mol/L) as  $\text{UO}_2\text{Cl}_4^{2-}$ ,  $\text{PuCl}_6^{2-}$ ,  $\text{NpCl}_6^{2-}$  which are retained on anion exchange resin and separated from most of cations and interfering radionuclides [89, 106].

It should be mentioned that the chemical properties of different species of actinides are different. For example,  $\text{PuO}_2^+$ ,  $\text{NpO}_2^+$  and  $\text{PuO}_2^{2+}$  could not form stable anion in  $\text{HNO}_3$  solution, therefore Pu and Np need to be adjusted to tetra-valence species ( $\text{Pu}^{4+}$  and  $\text{Np}^{4+}$ ) before separation using anion exchange chromatography. Meanwhile  $\text{Pu}^{3+}$  and  $\text{Np}^{3+}$  could not form anions in both HCl and  $\text{HNO}_3$  solution, and this feature is often used to eluate Pu and Np

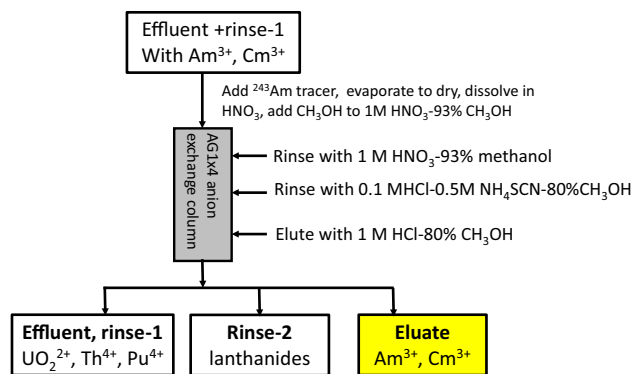
from the column using a diluted HCl solution containing reductive reagent such as  $\text{NH}_2\text{OH}\cdot\text{HCl}$  or  $\text{NH}_4\text{I}$ .

$\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  do not form anions in aqueous solution in HCl and  $\text{HNO}_3$  media, therefore could not be retained on the anion exchange column in aqueous medium. However,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  can form anions in non-aqueous solution such as 93 %  $\text{CH}_3\text{OH}$ –1 mol/l  $\text{HNO}_3$ , therefore anion exchange chromatography is also used for separation of Am and Cm, but in non-aqueous medium. Among transuranic elements,  $\text{Pu}^{4+}$  and  $\text{Np}^{4+}$  are similar in chemical properties and behaviors on chromatographic column, and  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  are chemically similar. Therefore they are often separated in the same solution to be measured by alpha spectrometry or mass spectrometry. Figure 5 shows a procedure for separation of Pu and Np, and Fig. 6 shows separation procedure of Am and Cm using anion exchange chromatography. It should be mentioned that these procedures are normally combined with co-precipitation for pre-concentration of target radionuclides [43].

Due to high selectivity, solvent extraction has been widely applied in the radiochemical separation, but the single extraction normally could not reach a high decontamination of interfering radionuclides. Meanwhile the application of solvent creates more organic waste. Extraction chromatography was introduced in the radiochemical analysis, which combines the advantages of high selectivity of solvent extraction and high separation efficiency of chromatography by immobilizing extraction reagents on solid support material. In the past two decades, this technique has been widely applied in radiochemical analysis for separation of various radionuclides, and it gradually replaced many solvent extraction methods in many radiochemistry laboratories. Sr Spec resin, Ni resin,



**Fig. 5** Separation of Pu and Np using anion exchange chromatography



**Fig. 6** Separation of Am and Cm using anion exchange chromatography

TEVA (for  $^{99}\text{Tc}$  separation) and TRU resin (for Fe) mentioned in the previous sections are extraction chromatographic resin.

TEVA (tetra valence actinides) resin has been widely used for separation of Pu and Np. This resin has similar properties as strong basic anion exchange resin, but a better decontamination to uranium, which does not retained on the resin in  $\text{HNO}_3$  medium [112]. For the separation of Am and Cm, DGA resin is often used [113–115], because it has a very high affinity to  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  in high concentration  $\text{HNO}_3$  and HCl compared to all other extraction chromatographic resin. However, many actinides such as  $\text{Pu}^{4+}$ ,  $\text{Np}^{4+}$ ,  $\text{Th}^{4+}$ ,  $\text{UO}_2^{2+}$  also have high affinity to DAG in high concentration of  $\text{HNO}_3$  and HCl, therefore have to be removed before DGA chromatographic separation. A single TRU column has been used to separate actinides sequentially, this is based on the high affinity of  $\text{Am}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Np}^{4+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  in  $\text{HNO}_3$  medium,  $\text{Am}^{3+}$  is first eluted using 4 M HCl, followed by eluting Pu using 4 M  $\text{HCl}$ –0.01 M  $\text{TiCl}_3$  by on-column reduction of  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$  which has a low affinity to the TRU resin, Th is then eluted using 1.5 M HCl.  $\text{UO}_2^{2+}$  and  $\text{Np}^{4+}$  retained on the TRU column are finally eluted using 0.1 m  $\text{HCl}$ –0.1 HF-solution [116]. This procedure might be suitable for analysis of nuclear waste samples which contain high level actinides. For environmental samples which contain low level actinides, an extensive separation of target radionuclides from matrix and interferences is necessary.

Because of high affinities of extraction chromatographic resin to the target radionuclides, the column size is normally much smaller than that of ion exchange chromatographic column, the often used column is just 2-mL (0.7 cm in diameter and 5 cm in height for standard Triskem/Eichrom column) or even smaller. For determination of multi actinides, more extraction chromatographic columns can be applied. In this case, these columns can be sequentially stacked, the samples solution is loaded to the first column, from which the effluent is directly loaded to

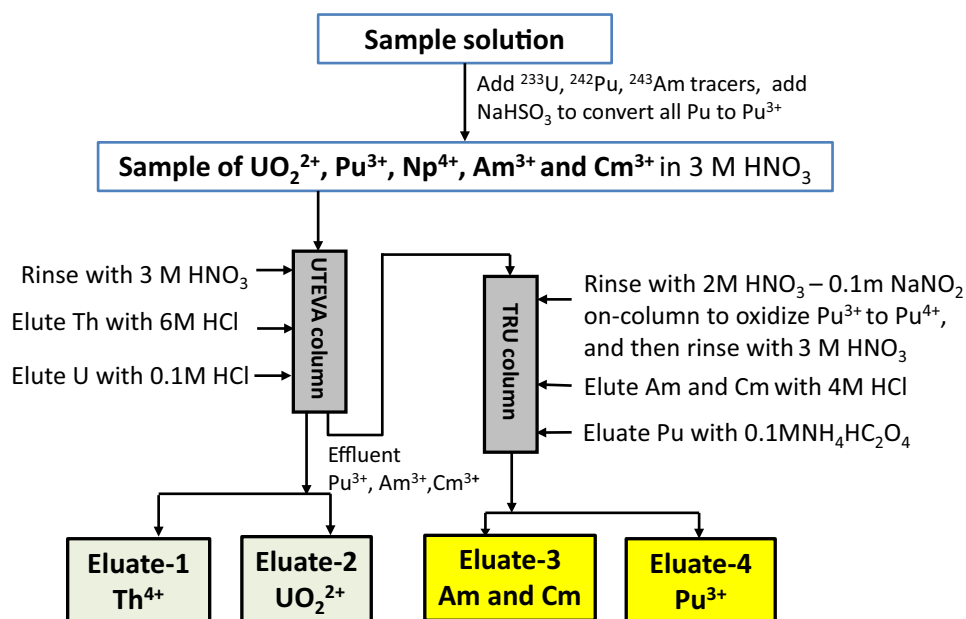
the following columns. Afterwards, the stacked columns are disconnected, and each column is rinsed respectively to remove the interfering elements/radionuclides, and finally the target radionuclides adsorbed on each column are eluted respectively for measurement of each (group) radionuclides. Figure 7 shows a combined procedure by using both UTEVA and TRU columns, Th, U, Pu, Am + Cm can be sequentially separated for measurement of their radioisotopes [71]. A modified procedure by using three columns of TEVA, UTEVA and TRU has been used for determination of isotopes of U, Pu, Np, Am, Cm. The sample prepared in 3 M HNO<sub>3</sub> solution is loaded to the stacked columns, Pu<sup>4+</sup> and Np<sup>4+</sup> are retained on the first TEVA column, UO<sub>2</sub><sup>2+</sup> is adsorbed on the second UTEVA column and Am<sup>3+</sup> (Cm<sup>3+</sup>) is trapped on the last TRU column [64]. In this case, a better purification of Pu fraction can be obtained, which is useful for determination of low-level Pu samples. Similar procedures are also used for determination of radioisotopes of U, Pu Am and Cm in water samples in the Nordic nuclear power plants.

The concentrations of transuranic elements are normally very low in environmental samples, a large size samples, e.g. 100–200 L seawater, are required for determination of Pu, Np and Am. Pre-concentration is normally needed to enrich transuranic elements from the samples. Co-precipitation of transuranic elements with Fe(OH)<sub>3</sub> is the most often used method for large volume of water samples, which also used to separate transuranic elements from dissolved/leached solution from soil or sediment samples to remove most of matrix elements. For the solid samples, such as soil and sediment, both acid leaching using *aqua regia* and concentrated HNO<sub>3</sub> and

completely decomposition method like fusion are used. For the samples without hot particles, acid leaching method is generally sufficient to extract transuranic elements from the sample, because these anthropogenic elements in the environment is deposited and adsorbed on the surface of the samples grain, which can be leached out using acid. If transuranic elements exist in refractory form, e.g. in the hot particles, total dissolution using mixed acids (HNO<sub>3</sub> + HF) or fusion using lithium borate [117], NaOH [115, 118] are the often used methods. For the determination of natural isotopes of Th and U, a completed decomposition is always required, because they are associated with the components of soil and sediment including minerals, which could not be leached out by acids. While for the determination of anthropogenic isotopes of uranium, e.g. <sup>236</sup>U, from the weapons testing or reprocessing discharges, acid leaching might be used because it is often adsorbed on the surface of sample grains. For the analysis of environmental soil and sediment, the sample is first ashed to decompose the organic matters in order to easily transfer the actinides into solution in the following acid digestion or fusion process. The temperature of ashing is confirmed very important to avoid transform transuranic elements to refractory form, a ashing temperature of 450 °C was recommended for this purpose [119].

In the determination of actinides, chemical yields of the target radionuclides always need to be measured to correct the loss of these radionuclides during chemical separation. Isotopes that are suitable to be measured with the target isotopes, easily available, and not exist in most of samples are used. The most often used yield tracers are <sup>233</sup>U for

**Fig. 7** Separation of U, Pu and Am using extraction chromatography



uranium isotopes,  $^{242}\text{Pu}$  for Pu and Np isotopes, and  $^{243}\text{Am}$  for isotopes of Am and Cm.

### Recent progress of radioanalytical chemistry for radionuclides

With the development of new separation and detection techniques and the increased requirement for the knowledge and information on the species of radionuclides, a significant development on radiochemical analysis of radionuclides has been achieved in the past decades. This mainly focuses on four aspects: (1) the synthesis and commercialization of various extraction chromatographic resins and application of them in the separation of specific radionuclide or groups of radionuclides; (2) sensitive detection of long-lived radionuclides using mass spectrometric techniques, especially ICP-MS and accelerator mass spectrometry (AMS); (3) speciation analysis of radionuclides in environment and waste samples; (4) development of various approaches for rapid determination of hard to measure radionuclides in order to quick responses in the emergency preparedness and analysis of large numbers of samples for decommissioning of nuclear facilities. They are briefly discussed below, presenting some examples in Nordic laboratories.

### Measurement methods

The radiometric methods including gamma spectrometry, alpha spectrometry, LSC and gas flow counting are still the dominated techniques for the measurement of radionuclides in nuclear samples with relative high concentration, and for short-lived radionuclides (<100 years). With the rapid development of mass spectrometry techniques, especially ICP-MS and AMS, they are becoming popular measurement techniques for long-lived radionuclides, especially in low-level environmental samples, e.g.  $^{14}\text{C}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ,  $^{135}\text{Cs}$ ,  $^{232}\text{Th}$ ,  $^{235,236,238}\text{U}$ ,  $^{239,240,241}\text{Pu}$  and  $^{237}\text{Np}$ . Meanwhile mass spectrometry is also being applied for some radionuclides important for decommissioning and repository but not easy to measure using radiometric methods such as  $^{59}\text{Ni}$ ,  $^{79}\text{Se}$ ,  $^{93}\text{Mo}$ ,  $^{93}\text{Zr}$ ,  $^{126}\text{Sn}$ . Besides the long-lived radionuclides, the mass spectrometry has also shown a high potential for measurement of radionuclides with half-life less than 100 years, such as  $^{90}\text{Sr}$ ,  $^{241}\text{Am}$ , and isotopes of Cm. Besides the comparable or better detection limit compared to radiometric method for long-lived radionuclides, mass spectrometry can provide better isotope resolution. In the past decade, increased numbers of AMS systems have been installed and operated, including those in environmental and geological laboratories. Therefore it is becoming an often used technique for

measurement of radionuclides in environmental sciences. The major features of AMS are its high abundance sensitivity and low background, therefore very low detection limit, down to  $10^5$ – $10^6$  atoms, corresponding to nBq– $\mu\text{Bq}$  depending on radionuclides. ICP-MS technique has also been significantly improved in measurement sensitivity, removal of interference by dynamic reaction/collision cell, and increased abundance sensitivity by using tandem quadrupoles for mass separation, therefore better detection limits.

Table 5 compares radiometric and mass spectrometry methods for measurement of major long-lived radionuclides. In general, mass spectrometry methods have a better detection limit for radionuclides with longer half-lives. The major problem on the mass spectrometry measurement is the isobaric interferences, especially from the stable isotopes, as well as polyatomic ions in ICP-MS, e.g.  $^{99}\text{Ru}$  and  $^1\text{H}^{98}\text{Mo}$  to  $^{99}\text{Tc}$ ,  $^{129}\text{Xe}$  and  $^2\text{H}^{127}\text{I}$  to  $^{129}\text{I}$ ,  $^{135}\text{Ba}$  to  $^{135}\text{Cs}$ ,  $^{238}\text{U}$  to  $^{238}\text{Pu}$ ,  $^1\text{H}^{238}\text{U}$  to  $^{239}\text{Pu}$ , etc. Therefore, chemical separation for decontamination of these isobaric interference is critical, which directly influence the detection limit and the analytical accuracy. The detection limits listed in Table 5 are measurement values reported in the literatures. Besides the isobaric interference, abundance sensitivity is another key parameters in mass spectrometry measurement, it refers to the contribution of the peak “tail” of a major isotope (with a certain  $m/z$  value) to an adjacent  $m/z$  value (both higher and lower  $m/z$  sides), e.g. the tailing of  $^{238}\text{U}$  to the measurement of  $^{237}\text{Np}$  and  $^{239}\text{Pu}$ . The super good abundance sensitivity of AMS, down to  $10^{-15}$ – $10^{-16}$ , makes it enable to measure isotope ratios down to  $10^{-13}$ – $10^{-15}$  for many radionuclides, such as  $^{14}\text{C}$  ( $^{14}\text{C}/^{13}\text{C}$ ),  $^{10}\text{Be}$  ( $^{10}\text{Be}/^9\text{Be}$ ),  $^{26}\text{Al}$  ( $^{26}\text{Al}/^{27}\text{Al}$ ),  $^{129}\text{I}$  ( $^{129}\text{I}/^{127}\text{I}$ ) and  $^{236}\text{U}$  ( $^{236}\text{U}/^{238}\text{U}$ ). The abundance sensitivity of ICP-MS is normally in the level of  $10^{-5}$ – $10^{-7}$ , which limits its application for radionuclides with a high concentration of adjacent  $m/z$  stable isotope of the same element, e.g.  $^{135}\text{Cs}$  (because of stable  $^{133}\text{Cs}$ ),  $^{129}\text{I}$  ( $^{127}\text{I}$ ),  $^{236}\text{U}$  ( $^{235}\text{U}$  and  $^{238}\text{U}$ ). The recent development in ICP-MS has significantly improved the abundance sensitivity to  $<10^{-9}$ . By employing tandem quadrupole mass separation, the abundance sensitivity in Agilent 8800 ICP-MS has been improved to  $10^{-14}$  in theory, and a measured value down to  $10^{-9}$  for  $^{135}\text{Cs}/^{133}\text{Cs}$ , which makes it possible to measure  $^{135}\text{Cs}$  in environmental samples with a  $^{135}\text{Cs}/^{133}\text{Cs}$  ratio lower than  $10^{-7}$  [120].

Besides the long-lived radionuclides mentioned above, measurement of other radionuclides including those with half-lives less than 100 years using ICP-MS has been investigated, e.g.  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{226}\text{Ra}$ ,  $^{93}\text{Mo}$ ,  $^{93}\text{Zr}$  and  $^{79}\text{Se}$ . The major challenge on ICP-MS measurement of  $^{90}\text{Sr}$  is the isobaric interference from  $^{90}\text{Zr}$  which has a natural abundance of 51 %, chemical removal of Zr and elimination of Zr by instrument setup in the introduction system



**Table 5** Comparison of radiometric methods and mass spectrometry methods for the measurement of long-lived radionuclides

Nuclide	Half-life	Detection limit		
		Radiometric <sup>a</sup> (mBq)	AMS (mBq)	ICP-MS <sup>b</sup> (mBq)
<sup>14</sup> C	5730 years	17	10 <sup>-4</sup>	–
<sup>99</sup> Tc	211 ky	5	–	1.5
<sup>129</sup> I	15.7 mBq	17	10 <sup>-6</sup>	0.01
<sup>135</sup> Cs	2.3 My	–	–	1 <sup>d</sup>
<sup>232</sup> Th	14,050 My	0.1	–	2 × 10 <sup>-3</sup>
<sup>235</sup> U	703.8 My	0.1	–	1 × 10 <sup>-3</sup>
<sup>236</sup> U	23.4 My	0.1	10 <sup>-7</sup>	–
<sup>238</sup> U	4468 My	0.1	–	2 × 10 <sup>-3</sup>
<sup>237</sup> Np	2.144 My	0.1	3 × 10 <sup>-4</sup>	2 × 10 <sup>-4</sup>
<sup>239</sup> Pu	24,110 years	0.1 <sup>c</sup>	0.003	0.017
<sup>240</sup> Pu	6563 years	0.1 <sup>c</sup>	0.010	0.063

<sup>a</sup> Alpha spectrometry for alpha emitters (<sup>232</sup>Th, <sup>235</sup>,<sup>236</sup>,<sup>238</sup>U, <sup>239</sup>,<sup>240</sup>Pu and <sup>237</sup>Np), LSC for <sup>14</sup>C and <sup>129</sup>I, and low-level gas flow counter for <sup>99</sup>Tc

<sup>b</sup> Assuming 3 mL solution is used for measurement

<sup>c</sup> Energy resolution of alpha spectrometry is not sufficient to measure alpha peaks of <sup>239</sup>Pu and <sup>240</sup>Pu, respectively, normally total activity of <sup>239+240</sup>Pu is given by this technique

<sup>d</sup> Achieved using new ICP-3Q-MS [120]

(e.g. ETV) is the major factors influencing the detection limit of <sup>90</sup>Sr. The tailing of stable <sup>88</sup>Sr in the ICP-MS measurement of <sup>90</sup>Sr is another critical issue which requires a good abundance sensitivity of instrument. The detection limit of ICP-MS for <sup>90</sup>Sr is in the level of 0.1–1 Bq, which is 1–2 orders of magnitude higher than radiometric method [121]. As a gamma emitter, <sup>137</sup>Cs is often measured by gamma spectrometry. However, in the ICP-MS measurement of <sup>135</sup>Cs, <sup>137</sup>Cs can be simultaneously measured, providing useful <sup>135</sup>Cs/<sup>137</sup>Cs information [120]. However, due to its 30 years half-life and isobaric interference of <sup>137</sup>Ba, the reported detection limit of high abundance sensitive 3Q ICP-MS for <sup>137</sup>Cs is only 0.1 Bq, which is higher than gamma spectrometry. <sup>226</sup>Ra (1599 years), an alpha emitter, is generally measured by alpha spectrometry or LSC by counting itself and its decay daughter radionuclides (<sup>222</sup>Rn, <sup>218</sup>Po and <sup>214</sup>Po). The major interference in ICP-MS for <sup>226</sup>Ra is polyatomic ions such as <sup>88</sup>Sr<sup>138</sup>Ba, <sup>208</sup>Pb<sup>18</sup>O, <sup>146</sup>Nd<sup>40</sup>Ar<sub>2</sub>, and several combinations of molybdenum isotopes with xenon isotopes. The reported detection limit of ICP-MS for <sup>226</sup>Ra is 0.1–0.5 mBq, which is comparable with LSC and alpha spectrometry.

It should be mentioned that besides AMS and ICP-MS, other mass spectrometry techniques including thermal ionization mass spectrometry (TIMS), resonance ionization mass spectrometry (RIMS) and secondary ion mass spectrometry (SIMS) have also been used for measurement of radionuclides, among them TIMS is a very sensitive techniques for measurement of low-level radionuclides and isotope ratios, RIMS has also been used for measurement

of low-level radionuclides, which can overcome the isobaric interference. However, these techniques are less applied for routine analysis because of less accessibility.

### Radiochemical separation techniques

The major progress in the radiochemical separation for determination of radionuclides in the recent years is the significantly increased application of extraction chromatography to replace solvent extraction in the separation of radionuclides, especially for purification and decontamination from interferences, even replaced some ion exchange chromatography method for rapid separation. Extraction chromatography has been proposed in 1970s [122], but not well used in determination of radionuclides until 1990s, when a series of extraction chromatographic resins have being synthesized, characterized and become commercial available. In early times, each laboratory has to synthesize their individual extraction chromatographic resin for specific application, therefore restrict the application of this technique. Although some laboratories still synthesize some specific extraction chromatographic resins, but most of laboratories all over the world often use the commercial resins provided by Eichrom Technologies LLC (IL, USA) and Triskem International (Bruz, France). Table 6 summarizes the major commercial extraction chromatographic resins and their major applications. In the past years, great efforts have also been dedicated to develop procedures for simultaneous determination of multi-radionuclides. This approach can not

**Table 6** Summary of extraction chromatographic resins and their principal features for separation of radionuclides

Resin	Function group	Main features	Applications
DGA	<i>N,N,N',N'</i> -tetra- <i>n</i> -Octyldiglycolamide (Normal) or <i>N,N,N',N'</i> -tetrakis-2-éthylhexyldiglycolamide (Branched)	High affinity to Am <sup>3+</sup> and Cm <sup>3+</sup> at high concentration of HNO <sub>3</sub> and HCl High affinity to Ac against Ra, for <sup>228</sup> Ra/ <sup>228</sup> Ac separation High affinity to Y <sup>3+</sup> against Sr <sup>2+</sup> in HNO <sub>3</sub> , for <sup>90</sup> Y/ <sup>90</sup> Sr separation	Actinide, lanthanides, Y, Ra <sup>90</sup> Y, <sup>226,228</sup> Ra)
Ln	Di(2-ethylhexyl) orthophosphoric acid (HDEHP)	High and varied affinity to different lanthanides with HNO <sub>3</sub> concentration for separate different Ln elements High affinity to actinides compared to transit metals and alkaline earth metals, and Ac/Ra(Ba,Sr) separation	Lanthanides, Ra ( <sup>228,226</sup> Ra), <sup>147</sup> Pm, <sup>151</sup> Sm
Nickel	Dimethylglyoxime (DMG)	Form a stable complex with Ni <sup>2+</sup> High adsorption to Ni <sup>2+</sup> against other metals, used for <sup>59,63</sup> Ni determination. Ni is eluted with DMG, not reusable	Ni ( <sup>59</sup> , <sup>63</sup> Ni)
Sr spec.	4,4'(5')-di- <i>t</i> -Butylcyclohexano 18-crown-6 (crown ether) in 1-octanol	High affinity to Sr <sup>2+</sup> at high concentration of HNO <sub>3</sub> Higher affinity to Sr against Ba, Ra and Ca for Sr separation Higher affinity to Pb <sup>2+</sup> compared to Sr <sup>2+</sup> for Pb <sup>2+</sup> separation	Sr, Pb ( <sup>89,90</sup> Sr, <sup>210</sup> Pb)
Pb	4,4'(5')-di- <i>t</i> -Butylcyclohexano 18-crown-6 (crown ether)	The same crown ether extractant as the Sr Resin, but at a lower concentration and with a longer chain alcohol for a diluent to facilitate the stripping of Pb from the resin Higher affinity to Pb <sup>2+</sup> compared to Sr <sup>2+</sup> and Ba <sup>2+</sup> , for <sup>210</sup> Pb/ <sup>89,90</sup> Sr(Ra) separation	Pb ( <sup>210</sup> Pb)
TEVA <sup>®</sup>	Aliphatic quaternary amine	Similar properties to strong base anion exchange resins, strong affinity to TcO <sub>4</sub> <sup>-</sup> , and complex anions of Np and Pu with HNO <sub>3</sub> and HCl High adsorption of complex anions of Am(Cm) with SCN <sup>-</sup> , for Am(Cm)/Ln separation	Tc ( <sup>99m,99</sup> Tc), Np, Pu, Am
UTEVA	Diamyl amylphosphonate (DAAP)	DAAP forms nitrate complexes with Th <sup>4+</sup> , UO <sub>2</sub> <sup>2+</sup> , Pu <sup>4+</sup> , Np <sup>4+</sup> , the affinity increases with increasing HNO <sub>3</sub> and HCl concentration, but not Pu <sup>3+</sup> , Am <sup>3+</sup> , Cm <sup>3+</sup> , used to separate U and Th from Pu, Am, Cm Low affinity to actinides at low concentration of HCl and HNO <sub>3</sub>	Th, U, Np, Pu
TRU	Octylphenyl- <i>N,N</i> -di-isobutyl carbamoylphosphine oxide (CMPO) dissolved in tri- <i>n</i> -butyl phosphate (TBP)	CMPO forms complex with actinides, TRU has very high affinity to actinides in HNO <sub>3</sub> and high concentration of HCl, also a relative high affinity to Am <sup>3+</sup> and Cm <sup>3+</sup> in HNO <sub>3</sub> but not in HCl, use for separate actinides from sample matrix TRU has also a high affinity to Fe <sup>3+</sup> , but not other transit elements, use to separation of Fe for <sup>55</sup> Fe determination	Fe ( <sup>55</sup> Fe), Th, Pa, U, Np, Pu, Am, Cm
Cl	Ag <sup>+</sup> (immobilized on resin)	The resin has a high uptake of Ag <sup>+</sup> , Pd <sup>2+</sup> , Au <sup>3+</sup> , but not the metals. Adsorption of Cl <sup>-</sup> and I <sup>-</sup> based on formation of AgI and AgCl on the resin, for separation of Cl <sup>-</sup> and I <sup>-</sup> SCN <sup>-</sup> can replace Cl <sup>-</sup> on the resin but not I <sup>-</sup> , while S <sup>2-</sup> can replace I <sup>-</sup> on the resin, for separation of Cl <sup>-</sup> from I <sup>-</sup> for determination of <sup>36</sup> Cl and <sup>129</sup> I	Cl, I ( <sup>36</sup> Cl, <sup>131,129</sup> I)
Cs	Ammonium molybdophosphate (AMP) for AMP-PAN resin Potassium nickel ferro cyanate (KNiFC) for KNiFC-PAN resin	Strong selective adsorption of Cs <sup>+</sup> on AMP and KNiFC, directly separate radioactive cesium from water or diluted acidic and alkali solution	Cs ( <sup>134,137</sup> Cs)

only remarkably reduce the entire analytical time, but also requires less amount of samples for analysis of all radionuclides, which will be useful for analysis of samples which are difficult to collect or high cost to collect large amount of samples. This issue will be discussed in later section.

### Speciation analysis of radionuclides

Environmental behavior, dispersion, migration, transfer, bioavailability and environmental impact of radionuclides very much depend on their chemical species. Speciation analysis of radionuclides in environmental, waste and

biological samples and their application is one of the hot topics in the recent years. Speciation analysis for radionuclides can be carried out by two types of methods, i.e. directly physical (instrumental) and indirectly chemical (separation) approaches. The physical method is based on direct measurement of the species (valences state or binding structure) of radioactive elements using specific instrumental approaches including synchrotron based spectroscopy such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES), which has been used for analysis of hot particles (high radioactivity in small size particles, micrometer to millimeter in diameter), and highly contaminated solid samples. This type of method can measure the species of radioactive elements without change of them or significantly destroying the sample during analysis. However, the detection limits of these techniques are not sufficient low to be able to measure radioactive elements in normal environmental level. In addition, these techniques can only provide the information of radioactive elements (such as thorium, uranium, and plutonium), not isotopes of each element. For example, micro-XANES can measure the oxidation states of U in depleted uranium particles by tuning the monochromatic X-ray beam over U  $L_{III}$  absorption edge (17.163 keV) [123]. This technique has also been used for speciation analysis of plutonium and uranium in hot particles from nuclear weapons accidents such as those in Thule, Greenland and Palomare, Spain. It was observed that hot particles consist of an oxides mixture of uranium ( $UO_2$  and  $U_3O_8$ ) and Pu as  $Pu^{3+}$ ,  $Pu^{4+}$ ,  $PuO_2^{2+}$ , but not metal plutonium and uranium [124]. A similar work for speciation analysis of hot particles from a nuclear weapons accident at Thule, Greenland using XANES has showed that in some particles, dominant species of plutonium is  $PuO_2^{2+}$ , while uranium exists in both (IV) and (VI) oxidation states [125]. Using synchrotron EXAFS/XANES, not only the oxidation station but also binding structure of actinides in particles and colloid can be obtained [126]. For the liquid sample, electrospray mass spectrometry has been used to measure ions states of radioactive elements as well as their polymers and complex with ligands, e.g.  $Pu^{4+}$ ,  $Pu(OH)^{3+}$ ,  $Pu(OH)_2^{2+}$ ,  $Pu(OH)_3^+$ ,  $Pu(OH)_5^-$  etc. However, the detection limit of this technique is normally in  $10^{-8}$ – $10^{-7}$  mol/L, therefore it is hard to measure the species of radionuclides in environmental level. Laser spectroscopy techniques, such as time resolved laser fluorescence spectroscopy (TRLFS), laser photoacoustic spectroscopy (LPAS), have also been used for direct speciation analysis of radionuclides in liquid samples. TRLFS can be also used for analysis of solid samples. The detection limit of these techniques can reach to  $10^{-10}$  mol/L, therefore, still not low enough to analyze radionuclides in environmental level, but can provide information of the species and

behavior of radionuclides in the environmental conditions, which is important and useful for the depository of nuclear waste.

Most of speciation analysis of environmental radionuclides is based on pre-separation of each species of elements, followed by further purification and sensitive measurement using both radiometric and mass spectrometric techniques. For water/aqueous samples, element in individual oxidation states ions, as well as those associated with organic substance and as colloids with different size/molecular can be separated using different techniques. For those existing as colloid, ultra-filtration technique can be used to separate them in different sizes/molecules [127–129]. Organic associated species of radionuclides can be separated using chromatographic techniques including size exclusive chromatography (SEC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE). While for simple ions, solvent extraction, selective co-precipitation and ion chromatography were often used [46, 130–132].

Based on the higher affinity of iodide on strong basic anion exchange resin compared to iodate and many other anions, iodide can be easily separated from iodate and matrix using anion exchange chromatography (e.g. AG1-X4 anion exchange resin in  $NO_3^-$  form). Iodate passes through the column to the effluent; the adsorbed iodide is then eluted using high concentration of nitrate after remove of  $Cl^-$  and  $Br^-$  by rinsing with diluted nitrate. After further purification and target preparation,  $^{129}I$  in both iodide and iodate in water samples can be measured using AMS or NAA [29, 46]. Considering relative high fraction of soluble organic iodine in coastal seawater, lake, river and rain water, the procedure can be modified to include determination of total organic iodine. In this case, water sample can be treated with NaOH or  $K_2S_2O_8$  to decompose organic iodine and convert it to inorganic species [133, 134]. Afterward the total iodine in the decomposed samples is separated and purified for measurement of total  $^{129}I$ ; the organic  $^{129}I$  concentration can be then obtained by subtraction of iodide and iodate from the total  $^{129}I$ . This procedure has been used for speciation analysis of  $^{129}I$  in seawater [27, 29, 46, 135], lake and rain water [30, 134, 136] and water leachate of aerosol sample [59, 137]. Based on selective co-precipitation of AgI with  $Ag_2SO_3$ , a method was proposed for speciation analysis of  $^{129}I$  in seawater samples [132]. With addition of only 100 mg/L  $Ag^+$  and 0.3 mmol/L of  $Na_2SO_3$  and control pH 4.2–5.5, iodide can be selectively precipitated as AgI– $Ag_2SO_3$ –AgCl from seawater without addition of iodine carrier, while iodate remains in the solution. After removal of the  $Ag_2SO_3$  by acid washing of the precipitate and excessive amount of AgCl using diluted ammonium solution, the prepared AgI–AgCl can be directly used for AMS

measurement of  $^{129}\text{I}$ . The total inorganic iodine can be obtained by firstly reduce iodate to iodide using  $\text{NaHSO}_3$ , co-precipitate entire inorganic iodine as  $\text{AgI-Ag}_2\text{SO}_3\text{-AgCl}$ , and finally measure total inorganic  $^{129}\text{I}$  in the  $\text{AgI-AgCl}$  precipitate after washing to remove  $\text{Ag}_2\text{SO}_3$  and excessive  $\text{AgCl}$ . This procedure is specifically suitable for speciation analysis, at least pre-separation for speciation analysis of  $^{129}\text{I}$  in seawater on board in scientific vessel because of simple chemical separation. This co-precipitation method for speciation analysis of  $^{129}\text{I}$  in seawater has been successfully applied for analysis of seawater samples collected in south Atlantic and Antarctic seawater, including deep seawater samples, where the concentration of  $^{129}\text{I}$  is very low and carrier free method have to be used to get rid of contamination from iodine carrier and chemical reagents [134].

Based on different physical or physiochemical properties, such as surface adsorption and volatility, speciation analysis of radionuclides can be implemented. In water or urine samples, besides tritiated water (THO) and carbonate, tritium and  $^{14}\text{C}$  exist also as organic bound species. A procedure has been proposed for speciation analysis of tritium and  $^{14}\text{C}$  in water and urine using active charcoal adsorption followed by combustion. Organic bound tritium is first adsorbed by active charcoal, the remaining tritium water (THO) is then distilled for direct measurement of  $^3\text{H}$  in water form (THO) by liquid scintillation counting (LSC). Organic bound tritium adsorbed on active charcoal is combusted at high temperature under  $\text{O}_2$  flow to convert organic tritium into water form (THO), which is condensed and collected for measurement of tritium using LSC [138]. A similar procedure was also used for separation of organic  $^{14}\text{C}$  from inorganic  $^{14}\text{C}$  [138, 139]. In this case, organic bound  $^{14}\text{C}$  is also adsorbed in active charcoal, which is converted to  $\text{CO}_2$  during combustion of active charcoal at high temperature. The released  $^{14}\text{CO}_2$  is trapped in an alkali solution, such as  $\text{NaOH}$  or ammine solution (CarboSorb, PerkinElmer) for LSC measurement. The inorganic  $^{14}\text{C}$ , mainly in carbonate form, remaining in the water, can be separated by precipitate of  $\text{CaCO}_3$  by addition of excessive amount of calcium (e.g.  $\text{CaCl}_2$ ), or by distillation to obtain the carbonate in residue. The carbonate residue or  $\text{CaCO}_3$  precipitate is then combusted at high temperature.  $^{14}\text{C}$  released as  $^{14}\text{CO}_2$  trapped in alkali solution is used for  $^{14}\text{C}$  measurement.

In bioshield concrete in nuclear reactor, tritium might presents as strong bound species which was produced inside the crystal of minerals in the concrete during exposure to neutrons radiation. Meanwhile tritium water (THO) released from the reactor, especially in the reactors which using heavy water as coolant, might also binds to concrete in THO form. Based on volatility of different

species of tritium, they can be separated by heating/combustion at different temperature. Tritium water (THO) associated to concrete can be liberated at  $100\text{ }^\circ\text{C}$ . While strongly bound tritium which produced by neutron activation of concrete cannot be released at temperature  $<300\text{ }^\circ\text{C}$ , and have to be combusted at  $>900\text{ }^\circ\text{C}$  [100]. In the Danish research reactor DR-3, due to leakage of heavy water from the reactor tank, bioshield concrete was contaminated by heavy water with high THO content, meanwhile tritium was also produced in the shield concrete during reactor operation. A concrete core has been sampled under cooling using nitrogen gas from liquid nitrogen container, in order to investigate the distribution of tritium species. The sampled concrete core was immediately cooled and stored at  $-20\text{ }^\circ\text{C}$  until analysis. Before analysis, the concrete core was cooled by immersing the concrete in a plastic bag into liquid nitrogen, and then sliced to about 1 cm slice, which was then immediately crashed to powder ( $<0.5\text{ mm}$ ), and transferred to a round bottom flask. The concrete powder in the flask was quickly connected to a heating and condensing system. The flask was heated using a heating mantle at  $200 \pm 20\text{ }^\circ\text{C}$  for 2 h. The released tritium water (THO) was condensed in the condenser tube and receiver by cooling using nitrogen from liquid nitrogen container, which was transferred into a vial by rinsing the condenser tube and receiver using tritium free water for tritium measurement. The remained concrete powder was further analyzed using Sample Oxidizer for strongly bound tritium by combustion at  $>1000\text{ }^\circ\text{C}$  [75]. Table 7 shows the distribution of tritiated water and strongly bound tritium in the concrete core taken from Danish research reactor DR-3. 2–3 orders of magnitude higher tritiated water compared to the strongly bound tritium was observed in these concrete samples, indicating a significant contamination of bioshield concrete by the leaked heavy water. The tritium water concentrations vary by 3 orders of magnitude, showing an inhomogeneous contamination in the bioshield concrete. The concentrations of strongly bound tritium is also significantly different ranging from 6 to 1600 Bq/g, this might due to the different distance of the sampling site to the reactor core, which results in a different exposure to neutron flux.

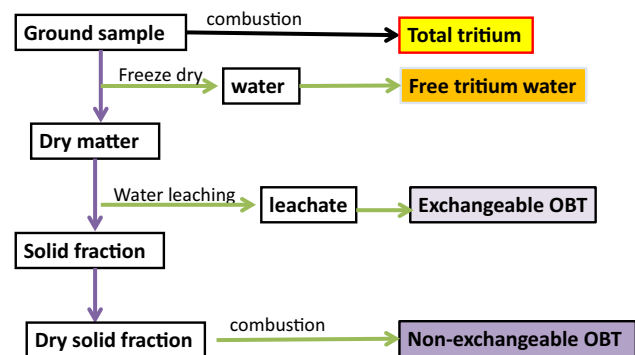
Tritium species in biological samples including food are also an interesting issue, which related to the estimation of radiation exposure dose through food consumption. Meanwhile it is also a key issue in the investigation of the transfer pathway of tritium from soil and air to vegetation. Tritium species in sediment has also being an interesting issue in investigation of its source and retention [140]. Speciation analysis of tritium in biological samples and sediment mainly focus on tritiated water, water exchangeable and non-exchangeable organic tritium. Tritiated water in fresh biological and sediment samples can



**Table 7** Species of tritium in bioshield concrete cores from Danish reactor DR-3

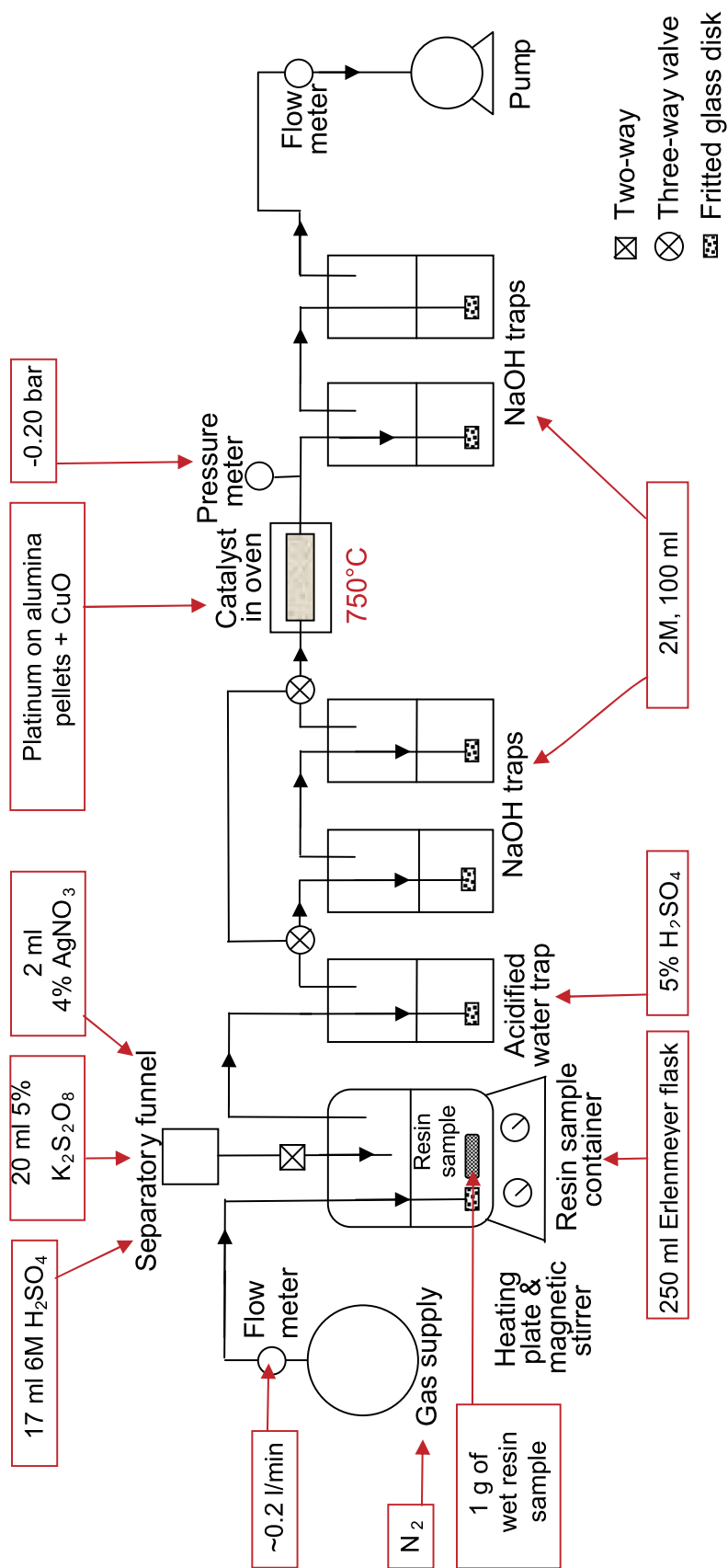
Sample ID	Tritium water (THO) (Bq/g)	Strongly bound tritium (Bq/g)	Ratio of strongly bound tritium to THO (%)
V4A	$(1.03 \pm 0.15) \times 10^4$	$27.4 \pm 3.9$	0.27
V5A	$(5.70 \pm 0.86) \times 10^4$	$143 \pm 25$	0.25
V6A	$(5.83 \pm 0.88) \times 10^2$	$26.7 \pm 8.2$	4.58
V7A	$(1.76 \pm 0.26) \times 10^2$	$7.65 \pm 1.04$	4.35
V4P	$(6.67 \pm 1.00) \times 10^2$	$7.25 \pm 1.71$	1.09
V5G	$(6.25 \pm 0.94) \times 10^3$	$8.09 \pm 3.34$	0.13
V6 J	$(1.22 \pm 0.18) \times 10^3$	$8.77 \pm 1.78$	0.72
V7 K	$(1.20 \pm 0.18) \times 10^3$	$6.25 \pm 1.92$	0.47
V4T	$(1.92 \pm 0.29) \times 10^4$	$819 \pm 90$	4.27
V6P	$(2.63 \pm 0.39) \times 10^3$	$13.9 \pm 2.5$	0.52
V5P	$(1.34 \pm 0.20) \times 10^5$	$208 \pm 41$	0.16
V7T	$(4.71 \pm 0.70) \times 10^4$	$46.7 \pm 7.0$	0.10
V4 W	$(3.29 \pm 0.49) \times 10^4$	$47.5 \pm 1.9$	0.14
V5U	$(2.91 \pm 0.44) \times 10^5$	$1610 \pm 280$	0.55
V6S	$(7.55 \pm 0.11) \times 10^3$	$34.2 \pm 5.6$	0.45

be separated by freeze drying or distillation, water exchangeable tritium is separated from the dried samples by leaching using tritium-free water [141]. The non-exchangeable organic tritium remained in the leached samples is finally separated using combustion method using Sample Oxidizer or tube furnace (Fig. 3). A schematic diagram of speciation analysis of tritium in biological materials is shown in Fig. 8. The tritiated water can be also extracted by water leaching using tritium-free water, based on quick exchange of tritium water in the biological samples and sediment with leaching water. Experiment has shown that tritiated water adsorbed in silica gel, concrete and brick can be quickly leached out by water [77, 142, 143]. However, the water exchangeable organic tritium will be also extracted, therefore obtained a combined fraction of water exchangeable tritium [140].



**Fig. 8** Diagram of a procedure for speciation analysis of tritium in vegetation and tissues

In ion exchange resin and nuclear reactor processing water,  $^{14}\text{C}$  exists in both inorganic (mainly carbonate) and organic forms (i.e. organic compounds). A sequentially extraction/digestion method has been proposed to separate inorganic and organic  $^{14}\text{C}$  in ion exchange resin and processing water from nuclear reactor [86, 87]. Figure 9 shows a schematic procedure for separation of inorganic and organic  $^{14}\text{C}$  in spent ion exchange resin. The ion exchange resin or water evaporator is first acidified using  $\text{H}_2\text{SO}_4$  and gas purged with nitrogen, inorganic  $^{14}\text{C}$  (mainly carbonate) is converted to  $\text{CO}_2$  which is purged out from the sample and trapped in an alkali solution (NaOH or CarboSorb). The organic associated  $^{14}\text{C}$  remained in the sample is oxidized using strong oxidizing reagent (5 %  $\text{K}_2\text{S}_2\text{O}_8$ ) and catalyst of  $\text{AgNO}_3$  (4 %) under heating (80–90 °C), organic compounds is decomposed to  $\text{CO}_2$ , CO or other volatile organic compounds which are purged out the solution and pass through a furnace filled with platinum catalyst to convert CO and organic compounds to  $\text{CO}_2$ , which is then trapped in alkaline solution for  $^{14}\text{C}$  measurement [86, 87]. It should be mentioned that other species of  $^{14}\text{C}$ , e.g. volatile  $^{14}\text{C}$  species in water and exchange resin can be also analyzed. In this case, the water or resin is first purged by nitrogen, the volatile compounds released from resin or water is then trapped using alkaline solution, as well as converted to  $\text{CO}_2$  in the furnace and to be trapped in alkaline solution, which are finally measured by LSC.  $^{14}\text{C}$  in spent ion exchange resin from different types of nuclear power reactors have been analyzed for species of  $^{14}\text{C}$ , it was observed that the concentration of  $^{14}\text{C}$  and ratio of inorganic to organic  $^{14}\text{C}$  vary significantly from reactor



**Fig. 9** Schematic diagram of setup for determination of inorganic and organic <sup>14</sup>C in exchange resin (reproduced from Magnusson et al. [89])

to reactor [85, 87]. This method is now employed for routine analysis of  $^{14}\text{C}$  species in spent ion exchange resin from Swedish nuclear power plants before depository [85].

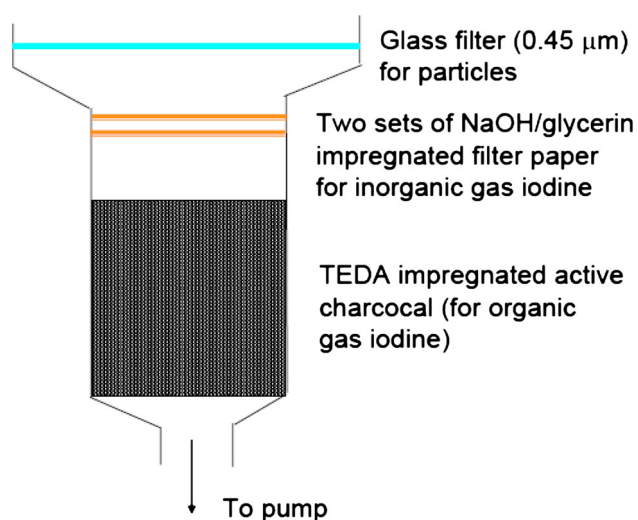
Speciation analysis of radionuclides which are volatile in some species and exist in air has to be carried out in the sampling step to collect different species. Among volatile elements, tritium,  $^{14}\text{C}$ ,  $^{131}\text{I}$ ,  $^{129}\text{I}$  are the most important radionuclides. Other radionuclides such as  $^{134,137}\text{Cs}$ ,  $^{103,106}\text{Ru}$  are also volatile at high temperature during nuclear accident or explosion, but they are particulate active and quickly attached to aerosol particles in the air. Noble gas radionuclides e.g.  $^{41}\text{Ar}$ ,  $^{85}\text{Kr}$ ,  $^{133}\text{Xe}$  and  $^{220,222}\text{Rn}$  are also volatile, but all exist as gaseous form. Therefore the speciation analysis of radionuclides in air is mainly focused on tritium,  $^{14}\text{C}$  and radioactive iodine isotopes.

In air, tritium mainly occurs as hydrogen gas (TH), tritiated water vapor (HTO) and gaseous organic compounds. A sequential separation procedure has been applied for routine monitoring in many laboratories. In this method, filtered air first pass through a column filled with molecular sieve material to trap water vapor, the gaseous HT pass through to the second column filled with platinum catalyst to convert HT to THO, which is trapped in the second column [157]. The remaining gas including gaseous organic compounds pass through a tube furnace filled with platinum catalyst under high temperature up to 500 °C and with oxygen flow to convert tritium in the organic compounds into tritiated water, which is trapped in the following trap solution of diluted acid [144]. All columns are then transported to laboratory to separate the trapped tritiated water in each column by heating followed by condenser for tritium measurement [145]. In general, the HT and organic associated tritium concentration is much lower than that of THO, therefore the monitoring of THO in air is often implemented, especially for nuclear facilities where most of tritium is related to heavy water. In this case, tritiated water in the air can be directly determined by condensing water vapor and LSC measurement.

In air,  $^{14}\text{C}$  mainly exists as  $^{14}\text{CO}_2$  and hydrocarbon ( $^{14}\text{C}_n\text{H}_m$ ), speciation analysis of  $^{14}\text{C}$  in air mainly focus on separation or pre-concentration of two types of gaseous  $^{14}\text{C}$ , which can be carried out by sequential extraction of  $^{14}\text{CO}_2$  and organic gaseous compounds or collecting  $^{14}\text{CO}_2$  and total gaseous  $^{14}\text{C}$  [146]. For low level air samples, a sequential collection of  $^{14}\text{CO}_2$  and  $^{14}\text{C}_n\text{H}_m$  is often implemented by passing through the air to a column and a furnace followed by the second column. The first column is filled with molecular sieve for trapping  $\text{CO}_2$ , the remaining air pass through a tube furnace filled with platinum catalyst to convert organic gaseous compound to  $\text{CO}_2$ , which is then trapped in the second column of molecular sieve. The

two columns are transported to laboratory for further separation of trapped  $\text{CO}_2$  by heating and re-trapping the released  $^{14}\text{CO}_2$  in CarboSorb solution for LSC measurement of  $^{14}\text{C}$  [144]. It has been observed that in the air samples taken from the stack of a pressure light water reactor, major part of gaseous  $^{14}\text{C}$  is organic associated  $^{14}\text{C}$  [146].

Radioactive iodine can exist in many species including gaseous inorganic form ( $\text{I}_2$ , HI, HIO etc.), gaseous organic forms (e.g.  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{CH}_2\text{I}$ , etc.) as well as associated to particles. These species of iodine might be converted from one to others during its dispersion in the air. It has been observed that large fraction of atmospheric  $^{131}\text{I}$ ,  $^{132}\text{I}$  and  $^{133}\text{I}$  originated from Chernobyl accident is in gaseous organic forms, although it might be released from the damaged reactor as inorganic  $\text{I}_2$  or HI forms [147], a high fraction of gaseous  $^{131}\text{I}$  was also observed in the air in the Europe after the Fukushima accident [148], confirming the importance of the gas fraction of radioactive  $^{131}\text{I}$  in air. For monitoring short-lived radioactive iodine ( $^{131}\text{I}$ ,  $^{125}\text{I}$ ,  $^{132}\text{I}$ ,  $^{133}\text{I}$ , etc.) in air, both particles associated and gaseous forms are often collected using filter paper (or membrane) and active charcoal cartridge in a sequential mode. Active charcoal filter paper is not sufficient to trap gaseous iodine, especially organic gaseous iodine because of very short contact time of iodine with active charcoal. Active charcoal cartridge of more than 5 cm thick is often applied for this purpose. For improvement of trapping efficiency for organic gaseous iodine, active charcoal is normally impregnated with amine such as tetrabutylammoniumhydroxide (TBAH) or triethylenediamine (TEDA). A procedure has been proposed for speciation analysis of  $^{129}\text{I}$  in air for particle associated, inorganic gaseous and organic gaseous iodine. A filter paper impregnated with NaOH-glycerin inserted between membrane and active charcoal cartridge for trapping inorganic gaseous iodine (HI,  $\text{I}_2$ , HIO). Figure 10 shows a schematic diagram of air sampling setup for speciation analysis of  $^{129}\text{I}$  in air [149]. Different species of iodine collected on filter or cartridge can be further treated for measurement of iodine isotopes. For  $^{125}\text{I}$ ,  $^{131}\text{I}$ ,  $^{132}\text{I}$  and  $^{133}\text{I}$ , the samples can be directly measured using gamma spectrometry after transferred to a suitable container. While for  $^{129}\text{I}$  and  $^{127}\text{I}$ , a chemical separation is required to separate iodine from the sample matrix and to prepare it into suitable forms for measurement of these two isotopes of iodine. A combustion method using a tube furnace can be used to separate iodine from the filters and active charcoal cartridge, the liberated iodine is trapped in NaOH solution, which can be directly measured using ICP-MS for  $^{127}\text{I}$ .  $^{129}\text{I}$  in the trap solution can be further purified using solvent extraction using  $\text{CHCl}_3$  or  $\text{CCl}_4$  and back extraction using  $\text{NaHSO}_3$ , the purified iodine is precipitated as  $\text{AgI}$  for AMS measurement of  $^{129}\text{I}$



**Fig. 10** Schematic diagram of an air sampler for speciation analysis of radioactive iodine (modified from Hou et al. [149])

[98]. This method has been applied for speciation analysis of  $^{129}\text{I}$  and  $^{127}\text{I}$  in air samples collected in Denmark and Sweden. It was found that organic gaseous  $^{129}\text{I}$  is a major species of  $^{129}\text{I}$  and  $^{127}\text{I}$ , followed by particle associated form, inorganic gaseous  $^{129}\text{I}$  and  $^{127}\text{I}$  is the minor.

For speciation analysis of most anthropogenic radionuclides in environmental solid samples, such as soil and sediment, the direct spectroscopy measurement methods such as TRLFS, EXAFS, XANES are not sensitive enough. The most often used method is sequential extraction combined with chemical separation followed by measurement using sensitive radiometric or mass spectrometric methods. This is based on the association of radionuclides with the components of samples, precisely called fractionation of radionuclides. In this procedure, radionuclides are fractionated as water soluble, exchangeable, carbonate, metal oxides (reducible), organic substance and minerals associated forms by leaching/extraction using different chemicals. Figure 11 shows a typical procedure for fractionation of radionuclides in soil and sediment [150]. Due to the volatility of iodine in acidic condition, the often used procedure is not suitable for fractionation of  $^{129}\text{I}$ , especially for the organic and mineral associated fractions. In general, organic substance is decomposed using  $\text{H}_2\text{O}_2$  in acidic medium ( $\text{HNO}_3$  at pH 2). In this case, the released iodine from the organic substance will be converted to volatile  $\text{I}_2$  and lost during leaching [48]. For this reason,  $\text{NaOH}$  or  $\text{NaOH-NaClO}$  solution is used to replace  $\text{H}_2\text{O}_2\text{-HNO}_3$  to extract organic associated iodine in the modified procedure [139, 151, 152]. For the mineral associated fraction, strong acid such as 7 M  $\text{HNO}_3$  or *aqua regia* is often used. In this case, the released iodine from the associated mineral will be also oxidized to volatile  $\text{I}_2$  and lost during leaching. Therefore, this fraction is separated by combustion at high

temperature using a tube furnace in the modified procedure [51, 139]. The released iodine is trapped in alkali solution for further separation and measurement of  $^{129}\text{I}$ . The results of fractionation analysis can provide information on the mobility and bioavailability of radionuclide, but not directly species information, therefore the result is experiment dependent. It should be mentioned that even using the same procedure, the results might be not well agreed because of difference in the operation condition [139].

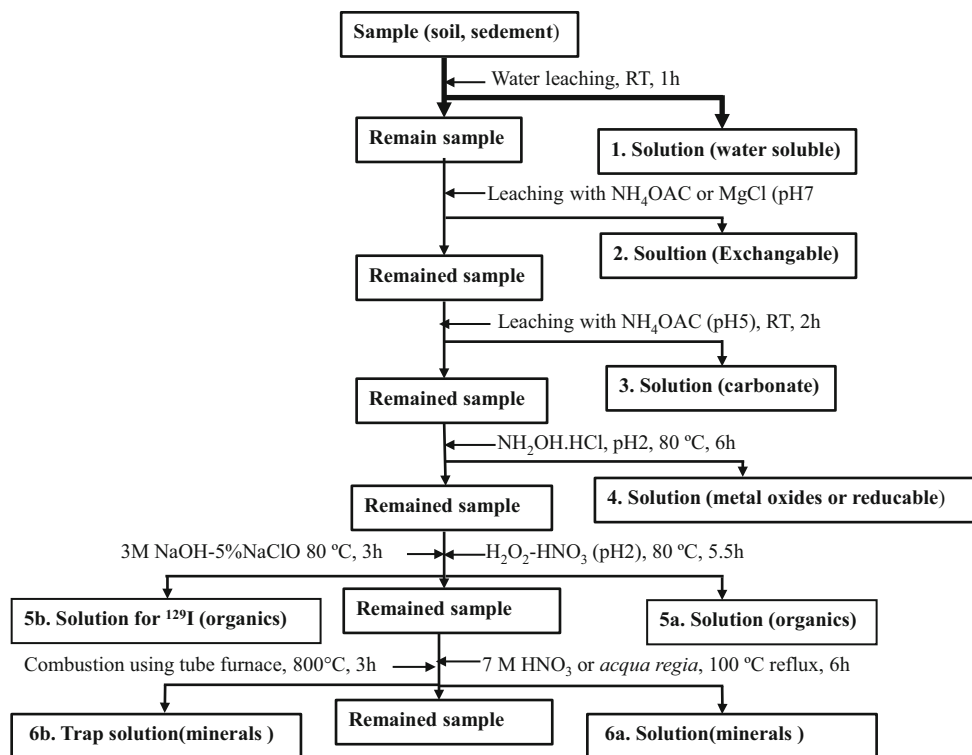
In natural environment, the leaching/extraction is a dynamic process, the results obtained through static leaching/extraction might not reflect the real mobility and bioavailability of radionuclide. A dynamic fractionation system has been proposed for sequential extraction of radionuclides from environmental solid samples using a sequential injection approaches [152, 153]. In this method, the sample is filled in a column, the leaching reagents are sequentially injected to the column, and the leached solution is collected for determination of radionuclides. This is similar/close to the natural process, which can also reduce the re-adsorption of the liberated radionuclides to the sample components again [152]. Figure 12 shows a schematic diagram of a dynamic extraction system for fractionation of radionuclides from environmental solid samples using a sequential extraction approach.

### Simultaneous and rapid determination of multi-radionuclides

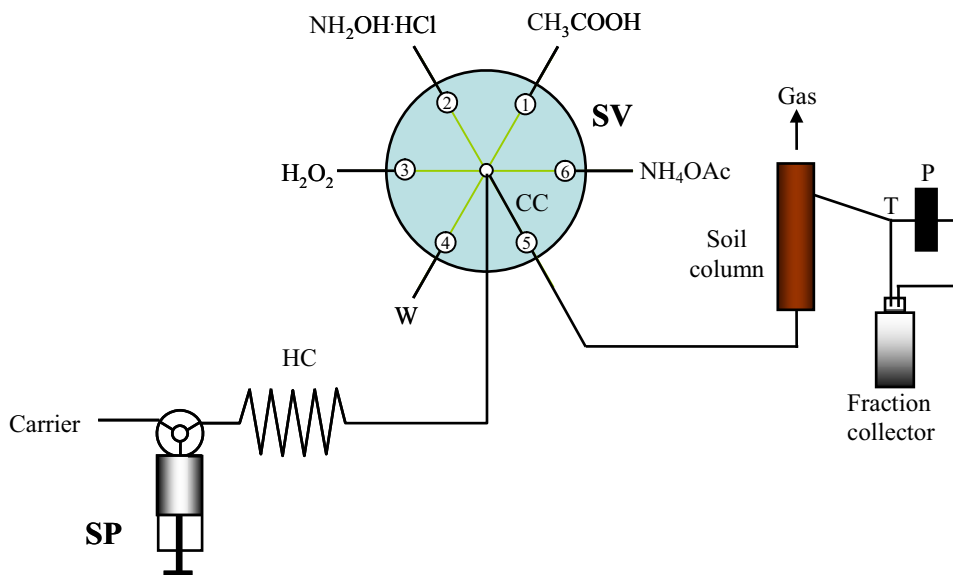
Nuclear emergency preparedness requires rapid determination of radionuclides in large number of biological and environmental samples. Except for the gamma radionuclides, the conventional analytical methods for radionuclides normally take a few days to weeks for one analysis; it is difficult to match the requirement of the emergency action. In recent years, considerable efforts have been devoted to develop rapid methods for radiochemical analysis. With increased number of nuclear facilities to be decommissioned, it is required to characterize various types of waste samples by determination of all radionuclides. In this case, rapid and simultaneous multi-radionuclides analysis is required to reduce cost and time for analysis of large number of samples. The development of rapid analytical methods mainly focus on rapid chromatographic separation techniques using (1) vacuum box to increase flow rate in chromatographic separation, (2) high pressure liquid chromatographic system and (3) flow injection or sequential inject approaches using peristaltic or syringe pump to increase flow rate and automated operation.

Due to high selectivity and high capacity, extraction chromatography has been widely used for determination of various radionuclides in waste and environmental samples. The particle size of the commercial extraction

**Fig. 11** Schematic procedure for fractionation of radionuclides in solid sample using sequential extraction



**Fig. 12** Schematic diagram of the sequential extraction system for dynamic fractionation of radionuclides from soil and sediment. *SP* syringe pump, *HC* holding coil, *SV* selection valve, *CC* central communication channel, *W* waste, *Carrier* Milli-Q water, *T* three way valve, *P* peristaltic pump



chromatographic resin is normally relative small (<150 μm), it makes the flow rate very slow, causing a long chromatographic separation time. Vacuum pump, syringe and peristaltic pump are therefore used for improving column separation time.

A device of vacuum box (Fig. 13) for rapid extraction chromatographic separation is commercially available from Eichrom Technologies and Triskem International. In

the experiment, the chromatographic column is airtight inserted on the box, where the outlet of the column is inside the box, but the inlet of the column, where the sample solution and chemical solution are loaded, is on the top of the box. By creating a negative pressure in the box using vacuum pump, the flow rate of the column separation can be considerably improved and controlled by adjusting the vacuum level in the box. One or more sequentially stacked





**Fig. 13** Vacuum box device for rapid chromatographic separation (provided by Eichrom Ltd. and Triskem International)

columns can be attached to the vacuum box. When sample solution is loaded to the column, the vacuum pump is turned on to produce a negative pressure in the vacuum box, which drives the sample solution rapidly pass through the column. The effluent and rinsing solution are collected in a tube inside the vacuum box. After changing to a new receiver tube inside the vacuum box, the target radionuclide adsorbed on the column is eluted under vacuum. The collected eluate is used for measurement of the target radionuclide. This device is simple and easy to operate, meanwhile up to 24 samples can be treated simultaneously, and separation process can be therefore significantly shortened. This method has been widely used in many radioanalytical laboratories. However, this system has to be operated manually, and relative high labor intensity is still needed. It is also not convenient for analysis of high radioactive samples due to the radiation exposure to the operators. High pressure liquid chromatographic (HPLC) system has been proposed to implement automated separation. But the inflexibility of this system, difficulties in preparation of chromatographic column using specific resin, small capacity, and single column installation makes this approach less attractive for rapid determination of radionuclides.

Flow/sequential injection approach has been proposed for rapid and automated separation of radionuclides using both extraction chromatographic resin and ion exchange chromatography resin. In the flow injection system, solution is loaded to the column using a peristaltic pump (Fig. 14), which can work for more columns, and more samples to be analyzed simultaneously. The major drawback of this approach is that the amount of solution (sample solution, rinsing and eluting solution) cannot be precisely

controlled, and the tubes used in peristaltic pump need to be replaced often. In sequential injection system, solution is loaded using a syringe pump (Fig. 15), and the volume of the solution loaded to the column can be precisely controlled. More columns can be connected in series for multi-radionuclides separation, and columns loaded the sample are then operated one by one because all columns share one syringe pump for loading solution [49, 50]. The major advantage of this approach is that it is controlled by computer, so it can be automated for operation, therefore suitable for analysis of high radioactive level samples in a hot cell.

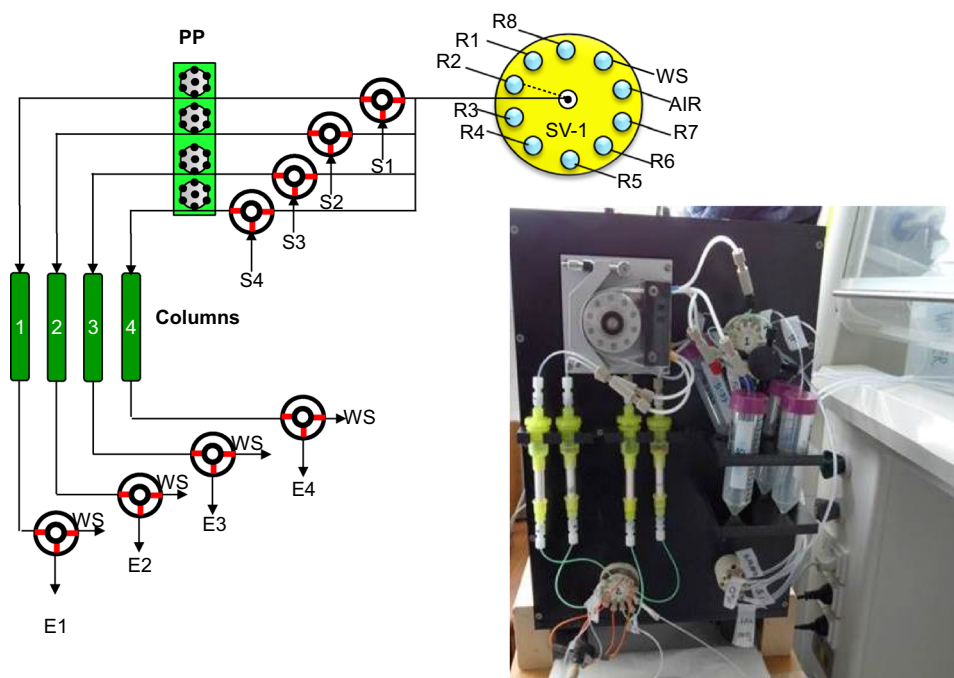
Besides rapid chromatographic separation, simple and rapid sample pre-treatment techniques are also important to shorten the total analytical time. For solid samples, rapid fusion technique and microwave assistant digestion techniques have been proposed to rapidly decompose samples. These techniques are normally work fine for small sample size (<1 g), therefore suitable for analysis of high radioactive level emergency samples and nuclear waste samples from nuclear facilities. For large size water samples, co-precipitation has been used, which is more effective compared to directly chromatographic separation and evaporation followed by column separation [58].

In characterization of nuclear waste and nuclear emergency analysis, determination of multi-radionuclides instead of single one is often required. In this case, a combined procedure is applied, and group radionuclides are separated. Some separation procedure for group elements have been proposed, which is mainly based on the physical–chemical properties of elements and the requirement of analysis, e.g. (1)  $^3\text{H}$  and  $^{14}\text{C}$ ; (2)  $^{36}\text{Cl}$  and  $^{129}\text{I}$ ; (3)  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$ , (4)  $^{90}\text{Sr}$ ,  $^{41}\text{Ca}$ , Ra; (5) actinides (U, Pu, Np, Am and Cm).

#### *Tritium and $^{14}\text{C}$*

As mentioned above,  $^3\text{H}$  and  $^{14}\text{C}$  in air are often sampled simultaneously and collected in different stages. Air is pumped through a system, tritiated water vapor is first adsorbed in a molecular sieve, and  $\text{CO}_2$  remained in the gas is absorbed in the second molecular sieve. The flow gas then passes through a tube filled with platinum and heated in a furnace with oxygen gas flow, TH and organic tritium are converted to THO and trapped in the third molecular sieve column, while  $^{14}\text{C}$  in the CO and organic compounds is converted  $\text{CO}_2$  which is trapped in the fourth molecular column. Four columns are then heated to release the THO in the column and condensed it as water to be measured by LSC, and to release  $\text{CO}_2$  from the columns which is then trapped in CarboSorb solution for LSC measurement of  $^{14}\text{C}$  [144]. For solid samples including concrete, water evaporates, soil, sediment, filter, vegetation and resin, a combustion method using Sample Oxidizer (or pyrolysis

**Fig. 14** A setup of a flow injection system for automation of chromatographic separation



device) has been proposed for simultaneous determination of  $^{14}\text{C}$  and  $^3\text{H}$  [75]. The sample is mixed with tritium and  $^{14}\text{C}$  free cellulose powder, and combusted at more than  $1000\text{ }^\circ\text{C}$  with oxygen flow through the combustion flask, all tritium is converted to THO vapor, which is condensed to liquid water and collected in a vial, while all  $^{14}\text{C}$  is converted to  $\text{CO}_2$  and trapped in CarboSorb solution. The separated fractions of tritium and  $^{14}\text{C}$  are measured using LSC after mixed with scintillation cocktail (Fig. 7).

### $^{36}\text{Cl}$ and $^{129}\text{I}$

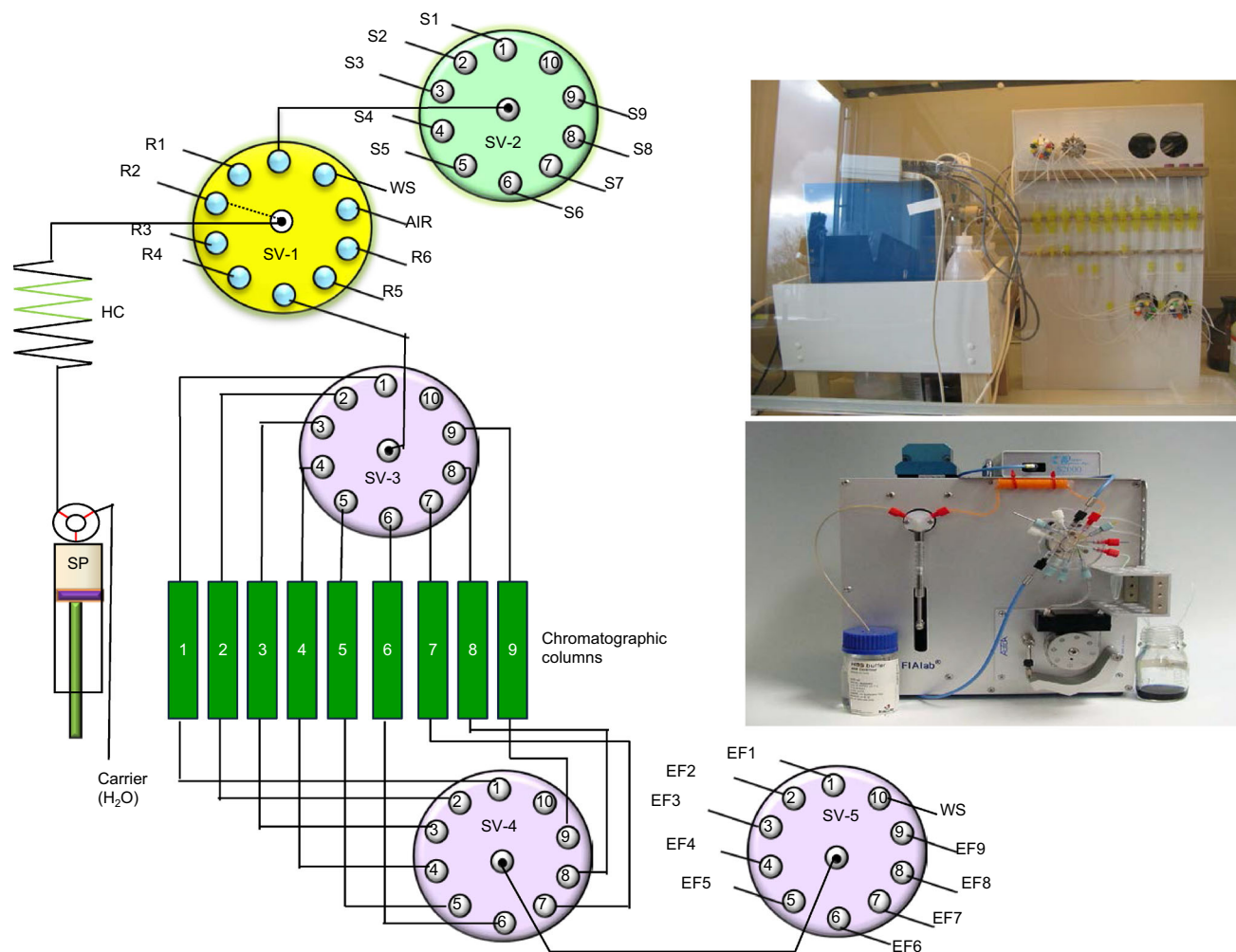
Both  $^{36}\text{Cl}$  and  $^{129}\text{I}$  are long-lived beta emitting halogen isotopes, they are important radionuclides in view of waste depository due to their high mobility in the environment, meanwhile they are also useful environmental tracer for investigation of environmental process. For solid samples, acid digestion, alkali fusion or combustion can be used to release iodine and chlorine and trapping them into alkali solution. For separation of  $^{36}\text{Cl}$  and  $^{129}\text{I}$  from water, leachate or alkaline trap solution, a combined procedure of solvent extraction followed by  $\text{AgI}$  precipitation and anion exchange chromatography (Fig. 16) has been proposed to separate  $^{129}\text{I}$  and  $^{36}\text{Cl}$  from sample matrix and purified from other interferences [102].

A extraction chromatographic method using  $\text{Cl}$  resin (Triskem international, France) has also been proposed for separation of  $^{129}\text{I}$  and  $^{36}\text{Cl}$  from solution.  $\text{Cl}$  resin is prepared by loading  $\text{Ag}^+$  on a resin material which has a high affinity to  $\text{Ag}^+$  and  $\text{Pd}^{2+}$ . The sample solution in  $\text{H}_2\text{SO}_4$

medium is loaded to the  $\text{Cl}$  column, chloride ( $\text{Cl}^-$ ) and iodide ( $\text{I}^-$ ) are adsorbed on the column by forming  $\text{AgCl}$  and  $\text{AgI}$  on-column. Chloride is then eluted using  $0.1\text{ M}$   $\text{KSCN}$  solution, after rinsing with  $1\%$   $\text{NaOH}$ , iodide on the column is eluted using  $0.35\text{ M}$   $\text{Na}_2\text{S}$  solution [154]. Before loading the sample solution, iodine and chlorine have to be reduced to iodide and chloride. This can be implemented using  $\text{NaHSO}_3$  in acidic medium. It should be mentioned that this method might be not suitable for analysis of environmental samples with low level  $^{129}\text{I}$  and  $^{36}\text{Cl}$  because of lower capacity and decontamination factor for many interferences especially isobars, which need a big sample and more sensitive AMS measurement.

### $^{55}\text{Fe}$ , $^{63}\text{Ni}$ , $^{59}\text{Ni}$

$^{55}\text{Fe}$ ,  $^{63}\text{Ni}$  and  $^{59}\text{Ni}$  are major neutron activation products in nuclear reactor. They are often required to be measured in processing water, exchange resin and decommissioning waste. Figure 3 shows a combined procedure for simultaneous determination of  $^{55}\text{Fe}$  and  $^{63}\text{Ni}$ . The separated  $^{63}\text{Ni}$  in  $\text{HNO}_3$  medium is carefully evaporated to about  $0.2$  and transferred to vial for LSC measurement. Evaporation to dryness of  $\text{Ni}$  fraction will cause a significant loss of  $\text{Ni}$  because of volatility of  $\text{Ni}(\text{NO}_3)_2$ .  $^{59}\text{Ni}$  is a long-lived radioisotope of nickel and decays by emitting beta particles. Because the radioactivity of  $^{63}\text{Ni}$  is in the samples is normally about 100 times higher, measurement of  $^{59}\text{Ni}$  using LSC is impossible because of high interference of  $^{63}\text{Ni}$ .  $^{59}\text{Ni}$  is therefore measured by counting its X-rays



**Fig. 15** A setup of sequential injection system for automation of chromatographic separation. *S1–S9* Samples, *W1* 8 mol/L HNO<sub>3</sub>, *W2* 6 mol/L HNO<sub>3</sub>, *W3* 4 mol/L HNO<sub>3</sub>, *W4* 2 mol/L HNO<sub>3</sub>, *W5* 1 mol/L

HNO<sub>3</sub>, *W6* 9 mol/L HCl, *E1* 0.5 mol/L HCl, *C1–C9* anion exchange columns, *EF1–EF9* eluate fractions, *SV1–SV5* multi-position selection valves

after electroplate the separated Ni on a disk. A high sensitive measurement of <sup>59</sup>Ni using AMS has also been reported [83, 84]. In this case, the isobaric interference of stable isotope of cobalt (<sup>59</sup>Co) is a key issue effecting the detection of <sup>59</sup>Ni.

#### <sup>90</sup>Sr and <sup>41</sup>Ca

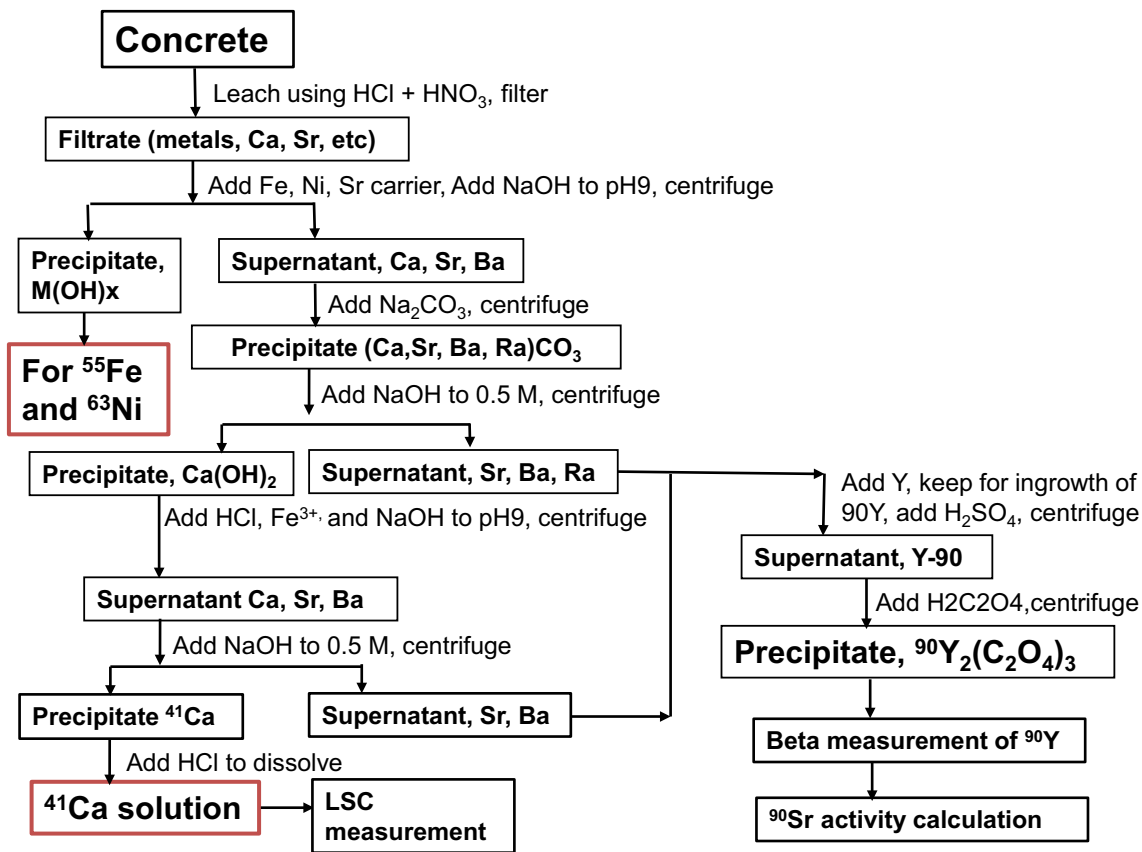
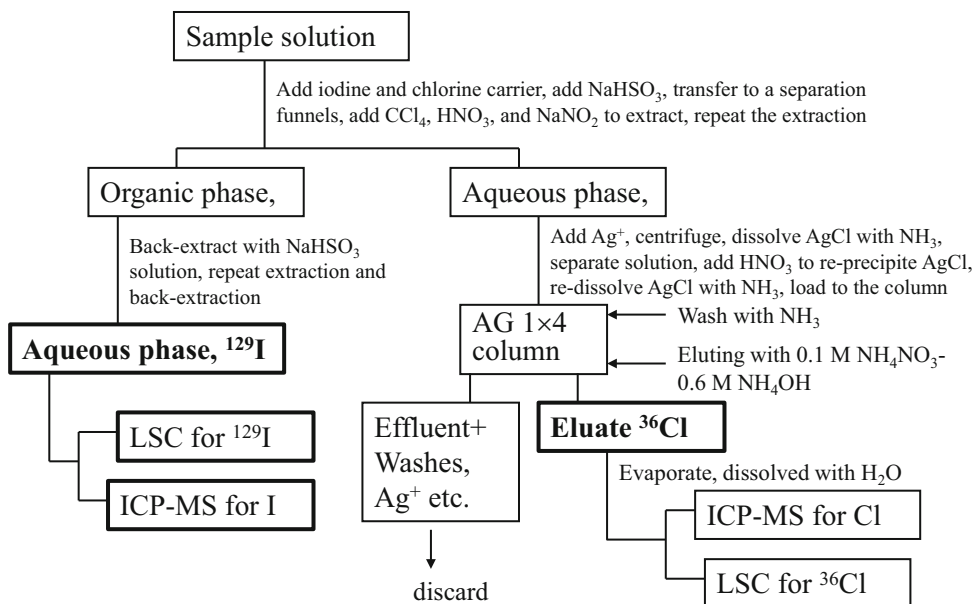
A procedure based on precipitation of Ca(OH)<sub>2</sub> in NaOH solution (>0.5 M) and remaining Sr, Ba and Ra in the solution has been proposed for determination of <sup>90</sup>Sr and <sup>41</sup>Ca [78]. Repeat Ca(OH)<sub>2</sub> precipitation can improve the separation of <sup>41</sup>Ca from radioactive Sr, Ba and Ra. <sup>90</sup>Sr in the supernatant is then kept for days to weeks for ingrowth of <sup>90</sup>Y, which is separated from radioactive Sr, Ba and Ra by sulfate precipitation. <sup>90</sup>Y remained in the supernatant is finally precipitated as Y<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub> for beta measurement. Figure 17 shows the combined procedure for the

simultaneous determination of <sup>41</sup>Ca and <sup>90</sup>Sr in concrete. Using this procedure combined with the procedure for <sup>55</sup>Fe and <sup>63</sup>Ni as shown in Fig. 3, all these radionuclides can be determined simultaneously.

#### Actinides

The most important radionuclides of actinides include <sup>234,235,236,238</sup>U, <sup>238,239,240,241</sup>Pu, <sup>242,233,234</sup>Cm, <sup>237</sup>Np and <sup>241</sup>Am. Among them, <sup>241</sup>Pu is a pure beta emitter, needs to be measured by beta counting or indirectly measured through its decay daughter of <sup>241</sup>Am by alpha spectrometry. It can be also measured by mass spectrometry together with other Pu isotopes. <sup>241</sup>Am emits measurable gamma ray during its alpha decay, therefore can be measured using gamma spectrometry when the concentration is sufficiently high, but often measured by alpha spectrometry in low level. All others are pure alpha emitting radionuclides,

**Fig. 16** Schematic diagram of an analytical procedure for the separation of chlorine and iodine for measurement of  $^{36}\text{Cl}$  and  $^{129}\text{I}$



**Fig. 17** Schematic diagram of procedure for simultaneous determination of  $^{41}\text{Ca}$  and  $^{90}\text{Sr}$

therefore measured by alpha spectrometry and mass spectrometry. Among actinides, Pu and Np are chemically similar and can be separated simultaneously under controlled oxidation states. Am and Cm normally exist in

trivalent states and are behaviors similar, therefore separated together for the measurement of their isotopes. A numbers of separation procedure have been reported for sequential separation of these elements for simultaneous



determination of their isotopes. Based on similar chemical properties of Np(IV) and Pu(IV), a procedure has been proposed to separate Pu and Np using anion exchange chromatography (AG 1-X4 resin, AGMP, TEVA, resin). In this procedure, Pu and Np are first reduced to low oxidation state ( $\text{Pu}^{3+}$ ,  $\text{Np}^{4+}$ ) using  $\text{NaHSO}_3$  in HCl medium, then oxidize  $\text{Pu}^{3+}$  to  $\text{Pu}^{4+}$  using  $\text{NaNO}_2$ , and keep Np in  $\text{Np}^{4+}$  in the solution. The sample solution prepared in  $\text{HNO}_3$  medium is loaded to a chromatographic column, rinsing using  $\text{HNO}_3$  to remove remaining matrix elements, U, Am and Cm, followed by rinsing with HCl to remove Th, the adsorbed Np and Pu on the column are eluted using diluted HCl or  $\text{HCl-NH}_2\text{OH-HCl}$  for simultaneously measurement of Pu isotopes and  $^{237}\text{Np}$  (Fig. 4). Because no suitable isotopic tracer of neptunium is commercially available,  $^{242}\text{Pu}$  is proposed as a yield tracer for both Pu and Np in this procedure [45, 50, 53]. The effluent and  $\text{HNO}_3$  rinse can be used for separation of Am and Cm. Because Am and Cm cannot form anion complex with  $\text{HNO}_3$  or HCl in aqueous medium, the separation of Am and Cm from other interference using anion exchange chromatography is implemented in  $\text{CH}_3\text{OH}$  medium as shown in Fig. 5 [43]. In this case, the column is rinsed using  $\text{NH}_4\text{SCN-CH}_3\text{OH}$  solution after loading the sample solution to remove lanthanides. This is important for the sample containing high level lanthanides because of its effect on the efficiency of electrodeposition and alpha counting step. An extraction chromatographic procedure using TEVA resin has also been used for separation of Am and Cm. In this case, sample is prepared in 4 M  $\text{NH}_4\text{SCN-0.1 M}$  formic acid medium to be loaded to TEVA column, after rinsing with 1.5 M  $\text{NH}_4\text{SCN-0.1 M}$  formic acid solution to remove lanthanides, Am and Cm are eluted using 1 M HCl. This is normally combined with the separation of Pu and Np [114]. Due to high affinities of Am and Cm, DGA resin has also been applied for separation of Am and Cm. The sample solution in high concentration of  $\text{HNO}_3$  medium (e.g. 6–8 M  $\text{HNO}_3$ ) is loaded to the DGA column. After rinsing with 0.5 M  $\text{HNO}_3$  to remove uranium and other matrix elements, Am and Cm are eluted using 0.2 M HCl [113, 114]. A combined chromatographic separation procedure using TRU + Ln resins has also been reported [64] for simultaneous determination of Am and Cm isotopes. The sample solution in 3 M  $\text{HNO}_3$  medium is loaded to TRU column, Am and Cm adsorbed on the TRU column is eluted using 0.01 M  $\text{HNO}_3$ , which is directly load to a Ln column, and Am and Cm adsorbed on the LN is then eluted using 0.5 M  $\text{HNO}_3$  for measurement.

A combined procedure has been reported for simultaneous determination of isotopes of U, Pu and Np using two extraction chromatographic columns TEVA and UTEVA resins. This is based on high retention of  $\text{Np}^{4+}$  and  $\text{Pu}^{4+}$  on TEVA resin and high adsorption of  $\text{UO}_2^{2+}$  on

UTEVA resin. TEVA and UTEVA columns are stacked with TEVA column on the top, samples solution in 3 M  $\text{HNO}_3$  in which Pu and Np were adjusted to  $\text{Pu}^{4+}$  and  $\text{Np}^{4+}$  is loaded to the stacked columns,  $\text{Pu}^{4+}$  and  $\text{Np}^{4+}$  are retained on the TEVA column, while  $\text{UO}_2^{2+}$  passes through the TEVA column and is retained on UTEVA column. After loading the sample solution, the two columns are disconnected. The TEVA column is rinsed with 1 M  $\text{HNO}_3$  and 6 M HCl sequentially, Pu and Np on the column are eluted using 0.1 M  $\text{NH}_2\text{OH-HCl-2 M}$  HCl solution. The UTEVA column is rinsed with 3 M  $\text{HNO}_3$ , U is then eluted using 0.025 M HCl [54]. This procedure has been successfully applied for measurement of  $^{236}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$  in seawater samples collected in European waters [155]. A combined procedure by using UTEVA and TRU resins has also been proposed to measure isotopes of Th, U, Pu, Am and Cm. This is based on the high retention of  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  on UTEVA resin but not trivalent actinides including  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ , as well as high adsorption of  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$  in TRU resin in  $\text{HNO}_3$  medium and high retention of  $\text{Pu}^{3+}$  on TRU in HCl medium [71]. This might be useful for determination of plutonium isotopes, but might not be sufficient good for determination of Am and Cm in environmental samples because of interference from lanthanides and other interference.

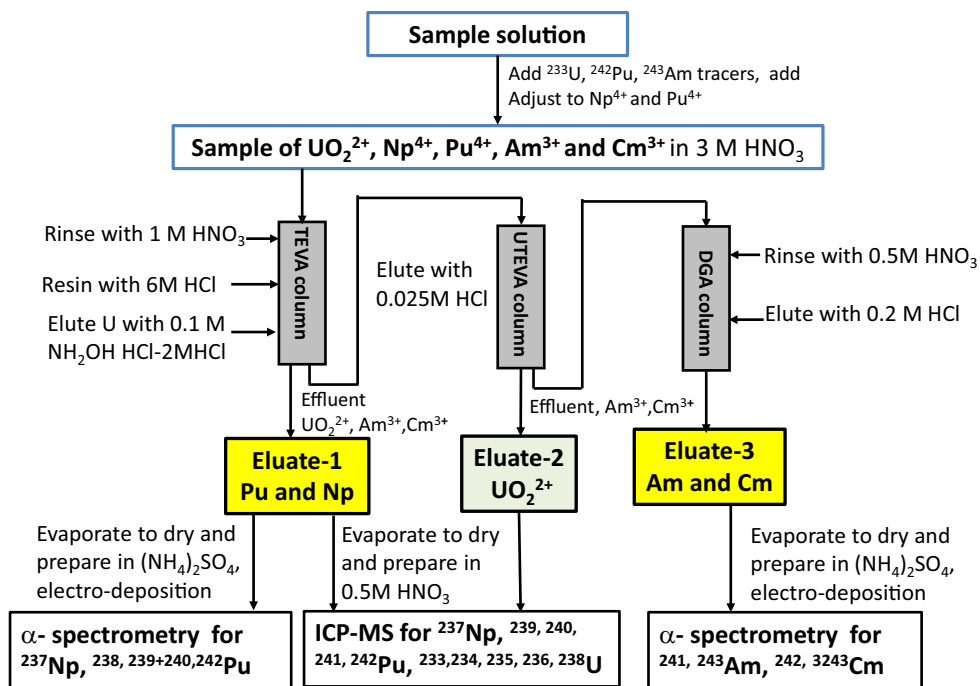
Based on the performance of TEVA, UTEVA and DGA in the separation of Pu/Np, U and Am/Cm, respectively, a combined procedure is proposed to separate Pu, Np, U, Am and Cm for determination the isotopes of these actinides (Fig. 18).

Vacuum box and sequential/flow injection approaches have also been applied for rapid and automated separation of multi-elements in order to reach to an overall rapid radiochemical analysis for multi-radionuclides. A stack of five chromatographic columns (AGMP-UTEVA-DGA-Sr resin-TRU) has been proposed for sequential separation of these elements for the determination of multi-radionuclides ( $^{228,232}\text{Th}$ ,  $^{239,240,242}\text{Pu}$ ,  $^{234,235,236,238}\text{U}$ ,  $^{241}\text{Am}$ ,  $^{242,243,244}\text{Cm}$ ,  $^{147}\text{Pm}$ ,  $^{89,90}\text{Sr}$  and  $^{55}\text{Fe}$ ) [113]. After loading to the columns, these five columns are disconnected, each column is then rinsed and eluted to separate individual element adsorbed on the corresponding column. The separated radionuclides from each column are then prepared for the measurement of each radionuclide using radiometric (LSC, Alpha spectrometry) or mass spectrometry method (ICP-MS or AMS) [113].

A setup of sequential injection approach of two connected chromatographic columns for automatic separation of multi-elements (U, Np, Pu) is shown in Fig. 19 [54]. In this system, TEVA and UTEVA columns are connected and sample solution is loaded to both columns, afterwards each column is individually rinsed and eluted to separate



**Fig. 18** A analytical procedure for a simultaneous determination of isotopes of U, Np, Pu, Am and Cm



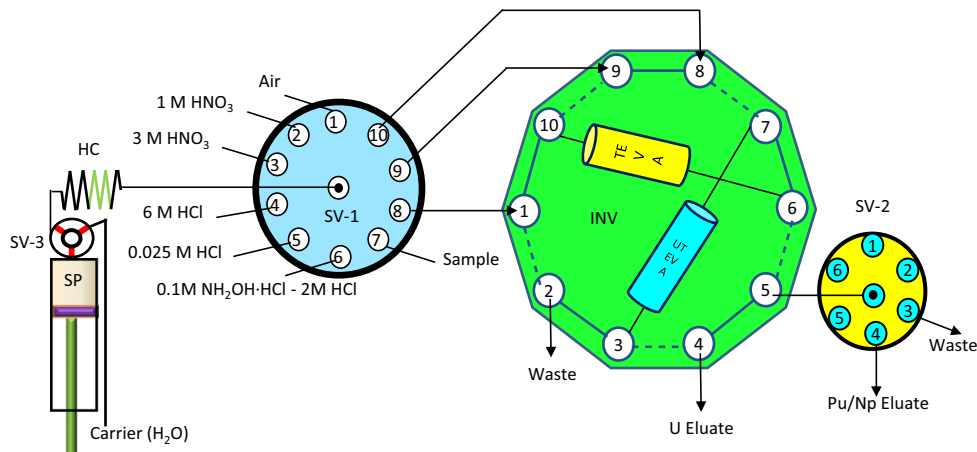
corresponding element. By this approach, multi-radionuclides can be automated determined.

**Summary and Perspectives**

Radiochemical analysis of hard to measure radionuclides is required in radiological monitoring of a nuclear facility, nuclear environmental safety monitoring, radioecology, characterization of nuclear waste for decommissioning of nuclear facilities and repository of nuclear waste. Many radioanalytical methods have been developed in the past decades, they are mainly based on techniques like co-precipitation, solvent extraction and ion exchange chromatography. With the development of new separation

materials and techniques and more sensitive detection techniques occurred in the recent years, as well as increased requirement in emergency analysis and nuclear forensics, radioanalytical methods have been significantly improved in the recent years. The major developments in the radioanalytical methods include: (1) a number of methods have been developed for the determination of radionuclides in decommissioning waste samples, such as  $^{41}\text{Ca}$ ,  $^{36}\text{Cl}$ ,  $^{55}\text{Fe}$ ,  $^{63}\text{Ni}$ ,  $^{59}\text{Ni}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$  and actinides; (2) significantly improved performance of ICP-MS and AMS and their wide application in measurement of radionuclides, especially for  $^{14}\text{C}$ ,  $^{99}\text{Tc}$ ,  $^{135}\text{Cs}$ ,  $^{236}\text{U}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ; (3) remarkable development of extraction chromatographic resins and their commercialization have significantly changed the radiochemical separation

**Fig. 19** Schematic diagram of the sequential injection system for simultaneous determination of U, Th, Pu, Np



procedures; (4) development of techniques and methods for speciation analysis of radionuclides, not only spectroscopic techniques, but also physio-chemical methods to separate different species of radionuclides, has significantly improved our understanding of the behavior of radionuclides in the nuclear facilities and the environment; (5) rapid and automated separation and analytical techniques have attracted high attention, vacuum box and sequential/flow injection approaches are main approaches for this purposes, which considerably shorten the analytical time to meet the requirement of rapid analyses in emergency preparedness. An automated analytical system also reduces or even prevents the radiation exposure of operators and reduces labor costs; (6) a number of procedures and analytical methods have been developed for simultaneous determination of multi-radionuclides based on separating group elements based on their physicochemical properties. These procedures are also combined with the rapid separation approaches, further improving the analytical performance for emergency analyses, as well as analysis of a large number of samples for decommissioning of nuclear facilities.

With continuous development of separation and detection techniques and increased requirement on radioanalysis of radionuclides, it is expected that radiochemical analyses will be further improved in the coming years in the following aspects: (1) New methods for more sensitive and accurate determination of less abundant radionuclides in environmental and waste samples, such as  $^{93}\text{Mo}$ ,  $^{93}\text{Zr}$ ,  $^{94}\text{Nb}$ ,  $^{79}\text{Se}$ ,  $^{126}\text{Sn}$ ,  $^{147}\text{Pm}$ ,  $^{107}\text{Pd}$ ,  $^{135}\text{Cs}$ ,  $^{236}\text{U}$ . Among them,  $^{135}\text{Cs}$  and  $^{236}\text{U}$  are very useful environmental tracers, but have not been well investigated because of the lack of a suitable detection method. AMS technique has demonstrated to be a very suitable method for the measurement of  $^{236}\text{U}$ , but is still limited to a few laboratories and still faces some challenges on environmental/laboratory contamination during chemical separation, preparation and measurement of carrier free microgram uranium target. With the substantial progress in the abundance sensitivity, ICP-MS technique is becoming a promising technique for the measurement of  $^{236}\text{U}$  as it has demonstrated in the measurement of  $^{135}\text{Cs}$ . Other radionuclides are important for the characterization of decommissioning waste of nuclear facilities and repository of nuclear waste, because of the long half-lives of these radionuclides. However, the analytical methods for these radionuclides are not yet well developed. It is expected that more reliable and sensitive analytical methods will be developed for these radionuclides in the near future, by using new separation procedures for the removal of isobaric and spectrometric interferences and applying more sensitive AMS and ICP-MS techniques for their measurement. (2) Further improvement and increased application of AMS and ICP-MS for sensitive measurement of radionuclides. In the past, AMS was mainly

dedicated to measure cosmogenic radionuclides such as  $^{14}\text{C}$ ,  $^{10}\text{Be}$ ,  $^{26}\text{Al}$ ,  $^{60}\text{Fe}$  for dating purpose. In the recent years, an increased applications of AMS have occurred in measurement of  $^{36}\text{Cl}$ ,  $^{129}\text{I}$ ,  $^{236}\text{U}$  for geological and environmental tracer studies, while the measurement of other radionuclides is still very scarce. With the rapid development of AMS techniques and increased installation of AMS systems all over the world, it is expected that AMS will become a more popular detection method for other radionuclides such as  $^{41}\text{Ca}$ ,  $^{59}\text{Ni}$ ,  $^{79}\text{Se}$ ,  $^{126}\text{Sn}$ ,  $^{93}\text{Zr}$ ,  $^{93}\text{Mo}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$  and  $^{242}\text{Cm}$ , which will remarkably enhance its application in environmental process investigations and radiation monitoring, characterization of waste and nuclear forensics. In recent years, ICP-MS technique has been extensively improved in sensitivity, elimination of isobaric and polyatomic ions and abundance sensitivity. With the installation of ICP-MS in most radioanalytical laboratories, ICP-MS is becoming a competitive and often used measurement technique for most radionuclides with half-lives longer than 100 years, such as  $^{99}\text{Tc}$ ,  $^{129}\text{I}$ ,  $^{93}\text{Mo}$ ,  $^{135}\text{Cs}$ ,  $^{226}\text{Ra}$ ,  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ . (3) Fully automated analytical techniques for simultaneous determination of multi-radionuclides. Although many combined procedures have been proposed for the determination of multi-radionuclides, they are still not well developed to achieve simultaneous determination of all radionuclides with different properties, especially when they are required to be determined in the same sample. In addition, most of the present methods are semi-automated methods, i.e. the pre-treatment and pre-concentration of samples is performed separately from automation and rapid chromatographic separation, and the final measurement is also often completed off-line. Further development is still needed to have an entire automated system for simultaneous determination of multi-radionuclides. The major challenge will be the integration of pre-treatment and pre-concentration steps to the automation system, because most of the methods used for this purpose are alkaline fusion, acid dissolution and co-precipitation, which are not simple to automate. This would be very useful for emergency analyses in remote areas without professional personnel for the operation of the analysis.

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