Radioanalysis of ultra-low level radionuclides for environmental tracer studies and decommissioning of nuclear facilities

Hou, Xiaolin

Published in:
Journal of Radioanalytical and Nuclear Chemistry

Link to article, DOI:
[10.1007/s10967-019-06908-9](https://doi.org/10.1007/s10967-019-06908-9)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Hou, X. (2019). Radioanalysis of ultra-low level radionuclides for environmental tracer studies and decommissioning of nuclear facilities. *Journal of Radioanalytical and Nuclear Chemistry*, 322(3), 1217–1245. <https://doi.org/10.1007/s10967-019-06908-9>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

1 **Radioanalysis of ultra-low level radionuclides for**
2 **environmental tracer studies and decommissioning of**
3 **nuclear facilities**

4 Names of the authors: Xiaolin Hou

5 Title: professor

6 Affiliation(s) and address(es) of the author(s): (1) Technical University of Denmark,
7 Center for Nuclear Technologies, Risø Campus, 4000, Roskilde, Denmark; (2) Lanzhou
8 University, School of Nuclear Science and Technology, 730000 Lanzhou, China; (3)
9 Xi'an AMS Center, Institute of Earth Environment, CAS, Xi'an 710061, China; E-mail
10 address of the corresponding author: xiho@dtu.dk

11

Radioanalysis of ultra-low level radionuclides for environmental tracer studies and decommissioning of nuclear facilities

Xiaolin Hou^{1, 2, 3}

¹ *Technical University of Denmark, Center for Nuclear Technologies, Risø Campus,
4000, Roskilde, Denmark*

² *Lanzhou University, School of Nuclear Science and Technology, China*

³ *Xi'an AMS Center, Institute of Earth Environment, CAS, Xi'an 710061, China*

Abstract

Determination of long-lived radionuclides is critical for environmental radioactivity investigation, environmental processes studies and decommissioning of nuclear facilities. This paper summarizes main progress in the radiochemical analysis in our laboratories in the past years for determination of ultra-low level radionuclides in the environment using chemical separation combined with mass spectrometry measurement. The analytical methods for determination of ultra-low level ¹²⁹I and its chemical species in various environmental samples are highlighted. The methods developed in our laboratories for characterization of decommissioning waste, especially the methods for the determination of difficult-to-measure radionuclides using sequential chemical separation and radiometric measurement are also briefly presented. This is also a part of the Hevesy Medal award lecture in the RANC2019 conference.

Keywords

33 Radioanalytical methods for low-level radionuclides; mass spectrometry; speciation
34 analysis; environmental process tracing; decommissioning;

35 **Introduction**

36 Large amounts of anthropogenic radionuclides have been released to the environment by
37 human nuclear activities, meanwhile the industrial activities also significantly increased
38 the level of natural occurred radionuclides in regional environment. The impact of these
39 enhanced level of radionuclides to the environment and ecosystem has become a highly
40 concerned topic. Meanwhile, radionuclides entered into the environment also provide
41 good tracers for the investigation of environmental processes because of their unique
42 source terms. For these purposes, the accurate determination of these radionuclides in
43 various environmental media is needed. Because the concentrations of these
44 radionuclides in the environment are normally very low, highly sensitive measurement
45 techniques are important. Besides some gamma emitting radionuclides, most of long-
46 lived radionuclides are pure beta and alpha emitters, effective chemical separation of the
47 target radionuclides from the sample matrix and other interfering radionuclides and
48 elimination of the interference for the instrumental measurement are critical for their
49 reliable determination. In the recent years, our laboratory has developed, upgraded and
50 improved a number of analytical methods for the determination of long-lived
51 radionuclides and their chemical species in various environmental samples, e.g. ^{99}Tc , ^{129}I ,
52 ^{135}Cs , ^{210}Po , ^{226}Ra , ^{222}Rn , ^{239}Pu , ^{240}Pu , ^{237}Np and ^{236}U , which have been used for
53 environmental trace studies, such as movement and interaction of water masses in the
54 seas/oceans, dispersion and deposition of radioactive substances and other air pollutions,
55 identification of the sources of radioactive substance and estimation of the contributions
56 of these sources to the corresponding environment, and tracing soil erosion and
57 sedimentation.

58 Since the application of atomic energy from 1940's, large number of nuclear facilities
59 have been established all over the world. Some of them have been closed, and many of
60 them are going to be closed in the coming years due to their life of 40-60 years. [Fig. 1](#)

shows the number of nuclear power reactors closed and to be closed in the world [1]. These closed nuclear facilities have to be well decommissioned to release the sites for other purpose. In all processes of decommissioning, including preparation by background radioactivity investigation of the site, cleanout by removal of spent nuclear fuel, decontamination by removal of contaminant from the surface of the facilities and devices, dismantling by cutting, demolition, waste removal and site clearance, waste depository by classification of the produced waste and site release by measurement of the site, various radionuclides in the relevant materials have to be determined for suitable treatment and final repository of the produced wastes, management of the decommissioning process and evaluation of the decommissioning quality. For these purposes, the analysis of various decommissioning samples for their radiological and chemical characterization is the most important issue. Among them, the determination of various difficult-to-measure radionuclides is the major challenge, because of complicated and unknown composition of sample matrix, significant difference in the radioactive level of radionuclides, instability of some volatile radionuclides, and complicated chemical properties and chemical species of some radionuclides. Since 2000, our laboratory has developed a series of radioanalytical methods for determination of difficult-to-measure radionuclides (e.g. ^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{63}Ni , ^{93}Mo , ^{94}Nb , ^{99}Tc , ^{129}I , ^{135}Cs and actinides) in various decommissioning samples such as concrete, graphite, metals, resin, filters, etc. These methods have been successfully applied in the characterization of decommissioning waste of research and power reactors, hot cells and other nuclear facilities, as well as wastes from the operational power reactors.

83

84 Fig.1 Number of power reactors closed and to be closed for decommissioning [1]

85 This paper aims to summarize the radioanalytical methods developed in our laboratories
 86 in the past years for analysis of environmental samples and decommissioning waste. Both
 87 chemical separation of various radionuclides from matrix and interferences and their
 88 measurement techniques are presented.

89 Major sources of radionuclides in the environment

90 Since 1940's, large amount of anthropogenic radionuclides have been released to the
 91 environment by human nuclear activities, mainly from atmospheric nuclear weapons test
 92 before 1980, spent nuclear fuel reprocessing plants, nuclear accidents, and small amount
 93 from operation of nuclear facilities and medical application of radionuclides in the
 94 hospitals. United Nations Scientific Committee on Effects of Atomic Radiation
 95 (UNSCEAR) has reported a comprehensive dataset on the radionuclides released from

nuclear activities to the environment until 1998 [2]. Up to 2013, 2055 nuclear weapons tests were conducted all over the world. Among them, 520 tests were conducted in the atmosphere in 1945-1980. Large amount of radionuclides were released during the weapons testing. Some of them were injected to the stratosphere and dispersed in large scale and deposited all over the world, especially for those of high yield tests. Meanwhile, some radionuclides were released to the troposphere and deposited regionally.

Up to now, two large nuclear accidents happened in April 1986 in Chernobyl NPP and in March 2011 in Fukushima Daiichi NPP (FDNPP) have released large amount of radionuclides to the atmosphere, causing a relative high radioactive deposition in the Europe during Chernobyl accident and in Japan during the Fukushima accident. FDNPP has also discharged some fraction of liquid radioactive substance to the sea, caused significantly increased radioactivity in the seawater off Fukushima [3]. In addition, some relative small scale accidents were also occurred and released some radionuclides to the environment. The accident of a graphite reactor fire at Windscale (UK) in 1957 had released 1×10^{15} Bq of ^{131}I , 9.4×10^{13} Bq of ^{90}Sr to the atmosphere. An explosion in a plutonium production plant in Kyshtym (USSR) in 1957 released 2×10^{15} Bq of ^{90}Sr and 3×10^{13} Bq of ^{137}Cs . Accidents of aircrafts carried nuclear weapons happened in Palomares (Spain) in 1966 and in Thule (Greenland) in 1967 have released some amount of plutonium and americium to the environment. A satellite (SNAP-9A) with ^{238}Pu as fuel fell down and burned over Indian Ocean in 1964 and released 6.3×10^{14} Bq of ^{238}Pu to the atmosphere, and another satellite fueled with a nuclear reactor fell down and burned over Canada in 1978 and released 2×10^{14} Bq of ^{131}I , 3×10^{12} Bq of ^{90}Sr and ^{137}Cs to the atmosphere.

Many spent fuel reprocessing plants have been in operation in USA, Russia, Japan, Germany, France, India and China for separation of uranium and plutonium from the used fuel, some radionuclides have been released to the atmosphere and to the seas during their operation. Among them, the reprocessing plants at Sellafield (UK) and La Hague (France) are the major ones which reprocessed large amount of nuclear fuel from production and power reactors, meanwhile discharged large amount of radioactive

substance to the seas and atmosphere [4, 5]. Compared with the above three sources, the amount of radionuclides discharged to the environment from the operation of nuclear reactors, isotope production and medical application in the hospital is minor (UNSCEAR 2000). Table 1 presents the amount of major long-lived radionuclides released to the environment from the nuclear weapons tests, reprocessing plants (Sellafield and La Hague) and nuclear accidents in Chernobyl and Fukushima. It can be seen that the major contribution of the anthropogenic radionuclides in the environment (excluding those remained in the spent nuclear fuel and stored as nuclear waste) is the atmospheric nuclear weapons tests, they caused a deposition of anthropogenic radionuclides all over the world. Fig. 2 shows temporal variation of the measured ^{137}Cs and ^{90}Sr concentrations in aerosol samples collected at Risø, Denmark from 1950's to the present. The highest levels of ^{137}Cs and ^{90}Sr in the aerosol were observed in early 1960's when large numbers of atmospheric nuclear weapons tests were conducted in 1961-1962 by USA and USRR. Declined levels of ^{137}Cs and ^{90}Sr with some small peaks were observed afterwards because some atmospheric nuclear weapons tests were conducted by UK, France and China, which completely ceased in 1980. This caused a continuously decreased level of ^{90}Sr in the aerosol. Two peaks of ^{137}Cs levels were clearly observed in 1986 and 2011, which were attributed to the releases from Chernobyl and Fukushima accidents, respectively.

Table 1. Amount of the major long-lived radionuclides released to the environment from major human nuclear activities

Nuclide	Released activity, 10^{15} Bq			
	Nuclear weapons tests	Reprocessing	Chernobyl accident	Fukushima accident
^{137}Cs	1280	17.45	85	15
^{90}Sr	850	3.39	10	0.9
^{144}Cs	1.04×10^6	0.51	116	

^{106}Ru	4.25×10^5	7.47	73	
^{131}I	2.3×10^7		1760	160
^{239}Pu	7.8	0.16	0.03	
$^{129}\text{I}, \times 10^{12} \text{ Bq}$	0.412	38.6	0.010	0.0086
$^{99}\text{Tc}, \times 10^{12} \text{ Bq}$	140	1872	0.75	< 0.5

148

149 Although most of anthropogenic radionuclides in the environment were released from the
150 atmospheric nuclear weapons tests, some radionuclides such as ^{129}I and ^{99}Tc in the
151 environment were dominantly originated from the discharges of nuclear fuel reprocessing
152 plants at La Hague and Sellafield. Most of ^{129}I (>85%) and ^{99}Tc (>99%) originated from
153 the two reprocessing plants were discharged to the seas (Irish Sea and English Channel,
154 respectively). Fig. 3 shows the temporal variation of the amount of ^{129}I and ^{99}Tc
155 discharged to the seas from the two reprocessing plants [4, 5, 6]. Among them, Sellafield
156 reprocessing plant is the major source of ^{99}Tc , while ^{129}I was mainly discharged from La
157 Hague reprocessing plants. The unique source terms and specific feature of discharge
158 profiles of the two reprocessing plants combined with the high water solubility and
159 conservative feature of iodine and technetium in the ocean make the reprocessing derived
160 ^{129}I and ^{99}Tc very good oceanographic tracers for investigation of water mass movement
161 and interaction. Besides the marine discharges, about 800 kg of ^{129}I was also released to
162 the atmosphere from these reprocessing plants. Meanwhile ^{129}I discharged to the seas
163 might be also re-emitted to the atmosphere. Gaseous iodine (e.g. alkyl iodide) has a
164 relative long residence time in the atmosphere [6], the reprocessing derived ^{129}I in the
165 atmosphere can be also used to trace the atmospheric dispersion and deposition of
166 radioactive iodine and other air pollutions.

167

Fig. 2 Temporal variation of the concentration of aerosol associated ^{137}Cs and ^{90}Sr in air collected at Risø, Denmark in 1957-2015

Fig. 3 Marine discharges of ^{129}I and ^{99}Tc from two European nuclear fuel reprocessing plants at Sellafield (UK) and La Hague (France)

Determination of ultra-low level radionuclides in the environment

For the environmental radioactivity and radioecology investigation and environmental tracer studies using radionuclides, sensitive and reliable analytical methods are critical. The major gamma emitting radionuclides (e.g. ^{134}Cs , ^{137}Cs , ^{131}I , ^{210}Pb , ^{241}Am , etc.) can be directly measured using gamma spectrometry after some pre-treatment. However, many long-lived radionuclides important for tracing environmental processes are pure beta or alpha emitters and present in low or ultra-low concentration in the environment, they have to be chemically separated from a large size of samples and all interfering isotopes before measurement using radiometric or mass spectrometric methods. A series of chemical separation procedures and sensitive methods for the measurement of the major radionuclides in the environment were developed in our laboratory, which are briefly presented in this paper. The chemical species of radionuclides is critical for their behaviors in the environment and therefore important for estimation of their impact and application of them for tracing environmental processes. A number of chemical speciation methods have been developed in our laboratory. Here, the major methods for speciation analysis of iodine isotopes in water, air, aerosol, soil and sediment samples are briefly presented.

Chemical separation of radionuclides from environmental samples

Various methods can be used for separation of radionuclides from the samples depending on the sample type and properties of the target radionuclides. Besides conventional precipitation, solvent extraction, ion exchange chromatography, extraction chromatography becomes a more often used method in the recent years. The solid samples have to be first decomposed to release the target radionuclides to solution before separation, and a pre-concentration such co-precipitation or exchange chromatography is often applied for pre-concentration of target radionuclide from large size of water samples. While, radionuclides in air have to be collected by selective adsorption or filtration, and then treated as liquid or solid sample. A few chemical separation procedures for determination of radioisotopes of cesium and strontium, ^{99}Tc , isotopes of plutonium neptunium and uranium developed in our laboratory are presented below.

Separation of cesium from water samples for the determination of ^{134}Cs , ^{135}Cs , ^{137}Cs .

Selective adsorption is the most often applied method for separation of cesium from big-size water sample up to 1000 liters. Powder of ammonium molybdophosphate (AMP) and potassium cupriferricyanide ($\text{K}_2\text{CuFe}(\text{CN})_6$, KCuFC) are the most often applied adsorbents for this purpose [7, 8]. AMP was used to separate cesium from water (seawater or fresh water) in acidic medium, the sample is often acidified to pH2 on-site during sample collection using HCl. AMP powder is directly added to the sample solution (stable cesium or ^{134}Cs is added as chemical yield tracer) and mixed by stirring for 1-2 hours. After settling for a few hours (or overnight), the AMP powder is separated by discarding the supernatant, and collecting the sludge AMP on a filter paper. ^{134}Cs and ^{137}Cs adsorbed on the AMP powder are then measured using an HPGe gamma detector. The chemical yield is measured by determining stable cesium in the sample solution before and after separation, or ^{134}Cs in the separated sample by gamma spectrometry and compared with the spiked amount (if no ^{134}Cs is present in the samples). A high recovery of more than 95% can be often obtained. ^{135}Cs as a long-lived (2.3×10^6 years) pure beta emitter is also adsorbed on the AMP, for its determination, a further separation from interferences such as ^{135}Ba for ICP-MS measurement has to be implemented. For some water samples, a pre-filtration through a filter is necessary for removal of any suspending substance/colloids in the water sample, to obtain water soluble radiocesium concentration and a better chemical yield.

For more than 100 liters water samples, the AMP method is not suitable for operation, especially on board of a scientific vessel. In this case, a cartridge impregnated with potassium cupriferricyanide ($\text{K}_2\text{CuFe}(\text{CN})_6$) or other transition metal ferrocyanides (such as $\text{Cu}_2\text{Fe}(\text{CN})_6$, $\text{KTiFe}(\text{CN})_6$, etc.) can be used [9]. This type of material also has a very high selectivity and capacity for adsorption of cesium (K_d of 10^5) in neutral or slight acidic media. For preparation of potassium cupriferricyanide cartridge, a polypropylene cartridge is first impregnated to cupric sulfate solution, then to a solution of potassium hexacyanoferrate (II), $\text{K}_2\text{CuFe}(\text{CN})_6$ precipitate is formed on the cartridge, which can be mounted to the cartridge holder (Fig. 4) after dried. Seawater sample can be directly pumped through two sequentially connected cartridges after past through a pre-filtration

cartridge for removal of suspended substance. The chemical recovery can be monitored using stable cesium or ^{134}Cs spiked to the sample before separation, a recovery of more than 80% is often obtained for two sequential cartridges. Radiocesium on the cartridge can be measured using gamma spectrometry after dried and ashed at low temperature ($< 450\text{ }^{\circ}\text{C}$).

AMP and KCuFC were also prepared as resin material and commercialized by Triskem International Company for chromatographic separation of cesium (AMP-PAN and KNiFC-PAN). With these resins, a further separation of radiocesium from other radionuclides of similar properties (e.g. Rb, Ba) can be implemented for improving the detection limit of radiocesium. Fig. 4 shows an analytical procedure for determination of radiocesium in water samples in our laboratory.

Separation of strontium for determination of radiostrontium (^{89}Sr and ^{90}Sr).

Radiostrontium is one of the most important radionuclides in the environment, because of the high fission yield of ^{235}U and ^{239}Pu and consequently high releases from human nuclear activities. Both ^{89}Sr and ^{90}Sr are pure beta emitters, a complete separation of strontium from sample matrix and all other radionuclides are needed for its measurement. The traditional separation techniques for strontium from environmental samples and interfering radionuclides mainly rely on the specific feature of strontium including low solubility $\text{Sr}(\text{NO}_3)_2$ in high concentration of HNO_3 solution ($>70\%$), and low solubility of SrCrO_4 compared to chromate of Ba and Ra, and precipitation of strontium rhodizonate precipitation. Although these methods were successfully applied for determination of radiostrontium in environmental samples for many decades, it is very tedious and time consuming, and application of fuming nitric acid and chromate is also harmful and expensive.

Fig. 4 Analytical procedure for determination of radiocesium (¹³⁴Cs, ¹³⁵Cs, ¹³⁷Cs) in water samples

A number of methods have been developed to simplify the separation procedure and to improve the detection limit. In our laboratory, an analytical procedure without application of harmful fuming nitric acid and chromate was developed for analysis of large-size water samples (seawater and fresh water) for determination of ⁸⁹Sr and ⁹⁰Sr. Strontium was first separated from large volume of water (up to 100 liter) by precipitation of strontium as SrCO₃ after addition of stable strontium as carrier, and then carbonate (e.g. (NH₄)₂CO₃). Calcium in the sample in a high concentration was also precipitated as CaCO₃ in this step. A precipitation of hydroxide step was therefore followed to remove calcium based on lower solubility of Ca(OH)₂ in a relative high concentration of NaOH solution (0.2-0.5 mol/l) compared to Sr(OH)₂. ⁸⁵Sr (a gamma emitter) can be used as chemical yield tracer in this step. For removal of the interferences of radioisotopes of Ra, the separated strontium solution was settled for 2-3 weeks for the ingrowth of its decay daughter ⁹⁰Y after addition of stable yttrium. Sulfuric acid was then added to the sample

solution, and the formed sulphate precipitate of SrSO_4 , RaSO_4 and BaSO_4 were removed by filtration, and ^{90}Y remaining in the solution was then separated by precipitation of $\text{Y}_2(\text{C}_2\text{O}_4)_3$ by addition of $\text{H}_2\text{C}_2\text{O}_4$ under a slightly acidic condition. The chemical yield of yttrium can be measured using yttrium spiked to the samples solution by gravimetry or ICP-OES. ^{90}Y in the precipitation was measured using an ultra-low background GM counter (Risø multi-counter), and ^{90}Sr concentration can be calculated according to the ingrowth time and chemical yields. The overall chemical yield (including Sr and Y) is normally higher than 85% [10]. Fig. 5 shows the analytical procedure of this method for determination of ^{90}Sr in large volume of water samples. It should be mentioned that for the analysis of fresh water samples, some amount of calcium needs to be added to improve the chemical recovery of strontium in the first step. This procedure has been successfully applied in our laboratory for routine analysis of environmental samples for more than 15 years, and demonstrated to be robust and accurate method for determination of ultra-low level ^{90}Sr in large-size samples with high strontium content.

The method presented above is still time consuming and applicable only for ^{90}Sr , especially because of long waiting time for ingrowth of ^{90}Y . Another method was also developed for rapid determination of both ^{89}Sr and ^{90}Sr by using extraction chromatographic separation. In this method, strontium in the sample leachate (from solid samples, such as soil, sediment, and ash of vegetable and tissues) or small size of water samples (< 2 liters) was first separated from sample matrix by precipitation of SrC_2O_4 at pH2 after addition of small amount of stable strontium carrier. A $\text{Sr}(\text{NO}_3)_2$ precipitation is followed to separate strontium from most of interfering radionuclides (e.g. radium and barium isotopes) by addition of small amount of fuming nitric acid (<10 ml). The separated $\text{Sr}(\text{NO}_3)_2$ was dissolved in water and prepared in 8 mol/l HNO_3 solution, which was then loaded to a Sr-resin column (2-4 ml depending on the sample size and estimated Sr content). After rinsing with 8 mol/l HNO_3 , strontium on the column was eluted using 0.01 mol/l HNO_3 , which was directly used for measurement of ^{89}Sr and ^{90}Y using liquid scintillation counter by counting Cherenkov radiation of ^{89}Sr immediately after separation, and then re-counting after 1-3 weeks for the Cherenkov radiation of $^{90}\text{Y}+^{89}\text{Sr}$, to obtain both ^{89}Sr and ^{90}Sr concentrations. ^{90}Sr can be also measured by LSC with addition of scintillation cocktail after the Cherenkov counting for ^{89}Sr . In this case, no

waiting time for ingrowth of ^{90}Y is needed and the results can be obtained in a short time (<1 day, including the chemical separation and measurement). The chemical yield of strontium in all procedure was measured by determination of stable strontium before and after separation using ICP-OES.

Fig. 5 Analytical procedure of ^{90}Sr in large volume of water samples

Fig. 6 shows the analytical procedure of this method. This method is relatively simple and rapid, but not suitable for the analysis of large-size of samples (e.g. seawater). The main reason is the relative low capacity of Sr-resin. For a 2 ml column, normally 2 mg of stable strontium can be separated, high amount of stable strontium in the sample requires a large column and large amount of resin, which will increase the expenses of the analysis and prolong the analytical time.

Fig. 6 Analytical procedure for determination of ^{89}Sr and ^{90}Sr .

Separation of technetium for determination of ^{99}Tc . Technetium is a radioactive element without any stable isotope. ^{99}Tc is a long-lived (2.1×10^5 years) radionuclide and the major isotope of technetium occurred in the environment. Due to its high fission yield (6.1% for ^{235}U) and high mobility in the environment, it is one of the most important radionuclides in the environmental radioactivity investigation and waste repository [11]. Technetium is volatile at relative high temperature, its stability in the separation procedure is critical for its determination. We have investigated the stability of technetium in different sample matrices during ashing and heating [12]. It was found that technetium is not stable in HCl medium during evaporation, while it is relative stable in

HNO₃ medium. Almost all technetium was lost when a technetium solution in 6 mol/l HCl medium was evaporated to dryness even at 100°C. While more than 95% technetium was remained when technetium in a neutral, alkaline solution or HNO₃ solution up to 8 mol/l was evaporated to dryness. Technetium is quite stable in brown seaweed (e.g. fucus) during ashing even at 700 °C for 14 hours. While significant amount of technetium was lost when it is present in soil and ashed at temperature more than 550 °C. It was observed that more than 60% of technetium in soil was lost when ashing at 700°C for 6 hours. It is therefore recommended that the soil sample should be ashed at less than 550 °C for overnight (12-15 hours) to decompose organic substances before chemical separation. Technetium mainly exists in Tc⁴⁺ and TcO₄⁻ forms, Tc⁴⁺ is not stable in solution and easily formed TcO₂ to be associated with particles, while TcO₄⁻ is quite stable in both acidic and alkaline solutions, which is also the most often occurred species of technetium in oxidative media.

Two methods have been used in our laboratory for separation and preconcentration of technetium from large volume of water and leachate of solid samples, anion exchange chromatography and co-precipitation of TcO₂ with Fe(OH)₂ in reductive condition. The affinity of TcO₄⁻ to strong basic anion exchange resin (e.g. Dowex 1 or Bio-Rad AG1, and Eichrom TEVA) is very high compared to other anions in water. Seawater was directly loaded to an anion exchange column (the size of the column is depended on the volume of seawater, for 200 liters of seawater, a column of 50 cm length and 2.5 cm in diameter was used), technetium was firmly adsorbed on the column. After rinsing with water, 1.0 mol/l of NaOH and 1.0 mol/l of HNO₃, TcO₄⁻ adsorbed on the column was finally eluted with 10-14 mol/l HNO₃. Further purification for removal of Ru (for ¹⁰³Ru, ¹⁰⁶Ru for radiometric measurement and ⁹⁹Ru for ICP-MS) was implemented by heating technetium solution after addition 1-2 ml of concentrated H₂SO₄ and small amount of NaClO and K₂S₂O₈. The separated technetium was electrodeposited on a stainless steel disc from a 2 mol/l NaOH solution. ⁹⁹Tc was then measured using a low background GM counter (Risø Multi-counter). The separated ⁹⁹Tc can be also measured by ICP-MS in a small volume of diluted HNO₃ solution (e.g. 2-5 ml of 0.5 mol/l HNO₃) [13, 14].

A separation procedure based on the co-precipitation of TcO_2 with $\text{Fe}(\text{OH})_2$ in reductive condition, combined with extraction chromatographic separation using TEVA column has been developed for determination of ultra-low level ^{99}Tc in seawater [15]. Seawater samples up to 200 liters were first acidified with HCl to pH2, and FeCl_3 and $^{99\text{m}}\text{Tc}$ tracer were added. $\text{K}_2\text{S}_2\text{O}_5$ was then added to reduce Tc to Tc^{4+} and Fe^{3+} to Fe^{2+} . NaOH was added to adjust pH9-10, and the formed $\text{TcO}_2\text{-Fe}(\text{OH})_2$ coprecipitate was then separated by settling down for overnight followed by discarding the supernatant and filtrate the precipitate. The precipitate was then dissolved with HCl and treated with H_2O_2 to convert technetium to TcO_4^- . After removal iron by $\text{Fe}(\text{OH})_3$ precipitation with addition of NaOH to pH8-9, the TcO_4^- in the supernatant was further purified using 2 sequentially connected TEVA columns. The purpose of two TEVA columns was to improve the decontamination factors to Ru and Mo , which cause high interferences for the ICP-MS measurement through $^{99}\text{Ru}^+$ isobar and $^{98}\text{Mo}^1\text{H}^+$ polyatomic ion. Fig. 7 shows the analytical procedure for determination of ultra-low level ^{99}Tc in large volume of seawater samples.

For solid samples, such as soil, sediment and seaweed, they were first ashed at 550 °C or 700 °C (for brown seaweed) to decompose all organic substance. Technetium was then leached from the ashed samples using HCl and H_2O_2 . Technetium in the leachate was then separated by $\text{TcO}_2\text{-Fe}(\text{OH})_2$ co-precipitation after addition of $\text{K}_2\text{S}_2\text{O}_5$ to reduce technetium to Tc^{4+} and adjusted to pH8-9 to form $\text{TcO}_2\text{-Fe}(\text{OH})_2$ precipitate. ^{99}Tc was then further purified using chromatography with TEVA resin and measured using ICP-MS. The short-lived $^{99\text{m}}\text{Tc}$ obtained from $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator was used as chemical yield tracer. Since minor amount of ^{99}Mo and ^{99}Tc is might present in the $^{99\text{m}}\text{Tc}$ eluate from the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator, the generator needs to be pre-eluted 2-5 times to remove accumulated ^{99}Tc from the generator, and the freshly eluted $^{99\text{m}}\text{Tc}$ was further purified by using a Al_2O_3 cartridge filter [16]. $^{99\text{m}}\text{Tc}$ in the final solution was measured using gamma spectrometry and chemical yield is calculated by comparing it to the amount of $^{99\text{m}}\text{Tc}$ spiked to the sample before separation.

Fig. 7 Analytical procedure for determination of ^{99}Tc in large volume of seawater

Separation of plutonium and neptunium for the determination of their isotopes. The concentrations of plutonium and neptunium isotopes are normally very low in environmental samples, separation of plutonium and neptunium from big-size sample is necessary to obtain reliable analytical results. Pre-concentration of plutonium and neptunium from large volume of water (up to 200 liters) is often implemented by coprecipitation with $\text{Fe}(\text{OH})_2$, MnO_2 , or lanthanide fluoride. After removal of the suspended particles and acidification of the water to pH2 using HCl, carrier (e.g. Fe^{2+}) and chemical yield tracer (e.g. ^{242}Pu) were added, followed by addition of reductant (e.g. $\text{K}_2\text{S}_2\text{O}_5$) and stirring to reduce species of plutonium and neptunium to Pu^{3+} and Np^{4+} to ensure a better recovery. Ammonia was then added to adjust pH8-9 for co-precipitate $\text{Pu}(\text{OH})_3$ and $\text{Np}(\text{OH})_4$ with $\text{Fe}(\text{OH})_2$, which were separated by settling down for overnight, discarding

the supernatant and centrifuge. The precipitate was dissolved with HCl, and coprecipitation was repeated by addition of ammonia to pH8-9 to remove excess of Ca and Mg. The precipitate was dissolved again using HCl, and then concentrated HNO₃ or NaNO₂ was added to convert plutonium to Pu⁴⁺ and remain neptunium as Np⁴⁺ for further separation and purification of Pu and Np [14, 17, 18] .

For solid samples, such as soil, sediment, aerosol, food, bones, the samples were first ashed to decompose the organic substances and convert organic associated plutonium and neptunium to inorganic species. Ashing at low temperature (e.g. 450 °C) was recommended to avoid a low recovery of Pu and Np due to the formation of their refractory species at high temperature [19]. Acid leaching (e.g. *aqua regia*) is an often used method to release Pu and Np from the ashed sample to solution, but it might be not suitable for the samples containing refractory species of Pu and Np such as the samples collected from highly contaminated sites of nuclear weapons tests and nuclear accident with hot particles. In this case, a full decomposition by acid dissolution in the presence of HF or fusion are needed. Lithium metaborate fusion was demonstrated a suitable method for decomposition of large size of samples (up to 20 g), the formed cake can be easily dissolved using *aqua regia* [20, 21]. Separation of Pu and Np in the sample solution is often implemented by coprecipitation of hydroxides or fluorides.

The chemical yield of plutonium is often monitored by spiking ²⁴²Pu tracer before separation, which can be measured in the separated samples by either alpha spectrometry or mass spectrometry. However there is no suitable yield tracer for neptunium. A short-live isotopes of neptunium, ²³⁹Np (2.35 days, beta emitter with gamma emission) has been used for yield monitoring by gamma spectrometry measurement. However, its short half- life makes its application not convenient. Because of similar chemical property of Np and Pu, yield tracer of plutonium was suggested also for neptunium [22, 23] and simultaneous separation of both plutonium and neptunium for determination of their isotopes [24, 25].

Solvent extraction, ion exchange and extraction chromatography are the major techniques for the separation of plutonium and neptunium from interferences, among them ion

exchange and extraction chromatography are becoming the most popular technique for their separation in the recent years, which is mainly based on the formation of anion complexes of Pu and Np with NO_3^- and Cl^- and further formation of complexes with the organic function group on the extraction chromatographic resin (e.g. TRU, DGA). The pre-concentrated Pu and Np in HCl solution were first converted to Pu^{4+} and Np^{4+} using NaNO_2 or concentrated HNO_3 , and prepared in 8 mol/l HNO_3 for separation using anion exchange chromatography or in 3 mol/l HNO_3 using TEVA resin for extraction chromatographic separation. The column was rinsed using HNO_3 and HCl solution to remove matrix elements and interferences such as uranium. Pu and Np on the column were finally eluted using diluted HCl or diluted $\text{HCl} - \text{NH}_2\text{OH} \cdot \text{HCl}$ solution. AGMP-1 (Bio-Rad company) was confirmed to be the best anion exchange resin for simultaneous separation of plutonium and neptunium because of their same behaviors in chromatographic separation [24]. TEVA resin was also confirmed to be suitable for the separation of both plutonium and neptunium [25]. Fig. 8 shows an analytical procedure used in our laboratory for determination of plutonium isotopes and ^{237}Np in the environmental samples. For the measurement of ^{239}Pu and ^{237}Np using ICP-MS, the major interference is ^{238}U through tailing to $m/z=237$ and 239, and forming $^{238}\text{U}^1\text{H}^+$ polyatomic ions. The decontamination factor of uranium is a critical feature of the separation procedure, it was noticed that TEVA resin showed a better decontamination factor compared to anion exchange resin. This might be attributed to the relative high uranium content in the anion exchange resin than that in TEVA resin and a larger size anion exchange resin was used compared to TEVA resin (5-10 times larger). A decontamination factor up to 10^7 was reported by using a sequential extraction chromatographic separation using TEVA-UTEVA and DGA resins in the analysis of soil and sediment samples for plutonium isotopes [26].

Fig. 8 Analytical procedure for determination of isotopes of plutonium and ²³⁷Np in environmental samples.

Determination of iodine-129 and its chemical species in environmental samples

Iodine is a volatile and redox sensitive element, anthropogenic ¹²⁹I is a very useful oceanographic and environmental process tracer, determination of the concentration and chemical species of ¹²⁹I and stable iodine are needed for this purpose [6]. In the past years, we have developed a series of methods for determination ultra-trace amount of ¹²⁹I in various environmental samples, meanwhile some methods for speciation analysis of ¹²⁹I in water, air, aerosol, sediment and soil were also developed.

Because of the long half-life (1.57×10⁷ years), beta decay, low intensive and energy of gamma ray and the ultra-low concentration of ¹²⁹I in environmental samples (<10⁻¹² g/g), separation of iodine from large sample is needed before its measurement, even using high sensitive accelerator mass spectrometry (AMS). Based on the volatile feature of iodine, an oxidative combustion method has been developed for separation of iodine from

various solid samples such as soil, sediment, vegetation and aerosol [27, 28]. By employing a modified 4-tubes Pyrolyse system (RADDEC International), four samples can be treated in the same time. In this method, ^{125}I chemical yield tracer was first mixed with sample in a quartz boat, up to 20 sample (soil/sediment) can be analyzed. The sample boat was inserted to a quartz tube in a three zones furnace, the temperature and heating sequence were programmed and precisely controlled. When the temperature of the furnace was increased up to 800 °C, all iodine was released as gaseous iodine, and trapped in a bubbler filled with diluted NaOH solution. The chemical yield in this process was more than 95% depending on sample type. The most critical step is the burning/carbonization in the analysis of samples of large amount of organic matter, such as vegetation, wood, aerosol/filter and high organic sediment. The rapidly increased temperature might cause quick burning of large amount of organic substance and create large amount of CO_2 and other gasses in a short time. As a consequence, un-decomposed materials (carbon particles) will be transported to the bubbler by the flowing gasses ($\text{N}_2 + \text{O}_2$), even a splashing of the trap solution in the bubbler and small explosion of the quartz tube may occur. Slowly increased temperature in the carbonization step of the sample combustion was found to be an effective approach for solving this problem. A 2 °C/min temperature increasing rate in 250-400°C for soil/sediment samples, and 1°C/min rate in 230-300 °C for vegetation/wood samples were confirmed to be suitable [27, 28].

Alkaline fusion was also used for the separation of iodine from solid sample. This is based on the relative high stability of iodine in alkaline media [29]. Besides soil, sediment and vegetation sample, tissue and aerosol samples were also treated by this method [30]. In this method, sample was mixed with NaOH and ashed at 600-650°C, iodine in the fused sample was leached with water for further separation, the recovery of iodine in this method was normally 70-85% depending on the sample type. Due to the un-completed ash/decomposition of vegetation/aerosol including filter, iodine could not be completely leached out from the treated samples, caused a non-quantitative recovery of iodine. For soil and sediment samples, the fused silicate was soluble in water, but became silica gel when the solution was acidified, some iodine might be wrapped in the gel,

caused a low recovery. Therefore, the oxidative combustion was confirmed to be a more effective method for releasing iodine from solid sample matrix.

Solvent extraction using CCl_4 or CHCl_3 is the most often used method for separation of iodine from water samples (including the trap solution and water leachate of the fused sample). The most critical step in this procedure is to adjust all iodine species to I_2 to be extracted to organic phase. For inorganic iodine, iodate can be reduced to I_2 by NH_2OH HCl in acidic media, and iodide can be oxidized to I_2 using NaNO_2 in acidic solution. For simplifying the separation process, all inorganic iodine was first reduced to iodide using sulfite in acidic media, and then oxidized to I_2 using NaNO_2 in acidic media for extraction. The most critical parameter is pH of the media, reduction of iodate and oxidation of iodide need to be implemented at $\text{pH} < 2$, the higher pH might cause slow reaction rate and low recovery of iodine. H_2O_2 has also been used to oxidize iodide to I_2 , but repeated extractions were used to get better recovery, this might be attributed to the low reaction rate of H_2O_2 with iodide.

The major disadvantage of the solvent extraction method is the production of toxic organic waste, a direct precipitation method was developed to separate iodine from water/aqueous samples. In this case, all inorganic iodine was converted to iodide, and excessive amount of AgNO_3 was added to form AgI precipitate, which was separated from sample matrix by centrifuging. Since chloride, bromide, sulfide, sulfite can also form precipitates with Ag^+ , a large amount of precipitate might be formed. Acidification of sample to $\text{pH} < 2$ before addition of Ag^+ and washing the precipitate with HNO_3 and ammonia could remove these precipitates and remained only AgI . The separated AgI could be directly used for AMS measurement of ^{129}I [31]. Fig. 9 shows a schematic diagram of analytical procedure for determination of ^{129}I in environmental samples.

Iodine is also present in organic form in water samples [6], direct solvent extraction and AgI precipitation only separate inorganic iodine (mainly iodide and iodate). For determination of total ^{129}I or organic associated ^{129}I , an oxidative decomposition method was developed using strong oxidant $\text{K}_2\text{S}_2\text{O}_8$ at an increased temperature. It was found that organic iodine in water samples can be converted to inorganic forms by addition of

532 $K_2S_2O_8$ to a concentration of 30 mg/g, adjusting pH 0.5-1 and digesting at about 60 °C for
 533 20 hours [32]. Afterwards all iodine is separated using the method presented above for
 534 determination of total ^{129}I .

536 Fig. 9 Schematic diagram of analytical procedure for determination of ^{129}I in
 537 environmental samples

539 For easy separation of iodine for ^{129}I determination, stable carrier containing very low
 540 level ^{129}I (e.g. iodine from Woodward company with original $^{129}I/^{127}I$ ratio of 2×10^{-14}) is
 541 often added. To avoid the contribution of stable iodine carrier in the determination of
 542 ultra-low level ^{129}I (natural occurred), a carrier free method was developed for the
 543 separation of iodine from samples and preparation of measurement target [31]. In this
 544 method, iodine released from the sample and trapped into a solution was directly
 545 precipitated as AgI-AgCl-Ag₂SO₃ co-precipitate after reduction of all iodine to iodide
 546 and addition of excessive amount of Ag⁺. Addition of sulfite was important in the
 547 separation of carrier free iodide by coprecipitation because of the similar particle size of
 548 AgI and Ag₂SO₃ precipitate [33]. Ag₂SO₃ can be removed by washing the co-precipitate
 549 with HNO₃, and the excessive amount of AgCl was removed by washing with diluted
 550 concentrations of ammonia, and only AgI and small amount of AgCl (in total 2-4 mg)
 551 were remained for preparation of AgI target for measurement of ^{129}I by AMS.

In seawater, iodine is present as iodide, iodate and minor amount of organic iodine depending on the marine environment. While in fresh water samples, organic iodine might accounts for a relative large fraction. In the atmosphere, iodine is present as both gaseous forms and particle associate forms. The specific species of gaseous iodine in the atmosphere are very complicated [34], but can be classified as gaseous inorganic iodine (mainly I_2 , HI, HIO, etc.) and gaseous organic iodine (mainly alkyl iodide). In aerosol, soil and sediment, iodine is mainly associated to different components of the sample, therefore often separated into different fractions such as water soluble, exchangeable, carbonate, oxides, organic and mineral associated forms. While, in biological samples including vegetation and animal tissues, iodine is mainly bound to different organic compounds [6].

We have developed a series of methods for speciation analysis of ^{129}I in different environmental samples. Separation method based on anion exchange chromatography [35], co-precipitation [33], and solvent extraction were developed for separation of iodide and iodate for the speciation analysis of iodine in water samples. The anion exchange chromatographic procedure is based on the high affinity of iodide compared with iodate on strong base anion exchange resin (e.g. Dowex 1 or AG1). Water samples were directly loaded to an anion exchange column filled with Bio-Rad AG1- $\times 4$ resin in NO_3^- form. Iodide was adsorbed on the column, while iodate and organic iodine passed through. Small fraction of iodate remained on the column was removed by rinsing with diluted (0.5 mol/l) KNO_3 , iodide on the column was finally eluted with 2 mol/l KNO_3 . For separation of iodate, the effluent and rinsing solution were combined, acidified to $pH < 2$ using HCl. Iodate in the sample was reduced to iodide by addition of $KHSO_3$ solution and separated using the same procedure as for iodide (Fig. 10). The eluted iodine from the column was further separated from matrix using solvent extraction and prepared as AgI for AMS measurement [35]. A simple co-precipitation method was developed to separate iodide and iodate from seawater for speciation analysis of ^{129}I , which is more suitable for application on board of a ship. This method is based on the selective coprecipitation of AgI with Ag_2SO_3 and AgCl at $pH 4-6$, the $Ag_2S_2O_3$ and excessive amount of AgI could be removed by washing with HNO_3 and ammonium. Addition of

KHSO₃ and controlling pH 4-6 are critical for selective precipitation of iodide, lower pH will cause the reduction of iodate and therefore split over iodate to iodide fraction [33]. This method has been successfully applied for speciation analysis of ¹²⁹I in seawater samples [36, 37], but not suitable for fresh water samples, because of less chloride in the fresh water. A selective solvent extraction method was therefore developed for separation of iodide and iodate from water samples. This method is based on the oxidation of iodide to I₂ by low concentration of NaClO (1%) at pH4-7, followed by solvent extraction of the formed I₂ into organic phase (CHCl₃ or CCl₄). It is well known that NaClO is a strong oxidant, which can oxidize iodide directly to iodate. However, our experiment showed that NaClO of low concentration can only oxidize iodide to I₂ if the pH of solution is higher than 4. The key parameters in this method are the concentration of NaClO and the pH value of the sample solution. The total inorganic iodine (iodide plus iodate) can be obtained by first reducing iodate to iodide at pH<2, and then oxidizing iodide to I₂ by NaNO₂, and extract I₂ to the organic phase. In this method, stable carrier needs to be added before solvent extraction, because the recovery of solvent extraction is related to the concentration of iodide and the other salt. The very low concentration of iodine in fresh water and high salt content in seawater cause a low recovery of iodine in the extraction step if no stable iodine carrier is added.

Fig. 10 Schematic diagram of separation procedure for speciation analysis of ¹²⁹I in water samples using anion exchange chromatography

A three-fraction air iodine collector was developed for separation of particle associate, inorganic gaseous iodine and organic gaseous iodine from air, the collector was connected to an air pump [6]. In this collector, particle associate iodine (aerosol) was first collected on a glass fiber filter of 0.45 μm pore size, followed by two layer cellulous filter impregnated with NaOH for collecting inorganic gaseous iodine (HI , I_2 , HOI , etc.), and the organic gaseous iodine (alkyl iodide) was finally collected by an active carbon cartridge, in which the active charcoal was purified by washing with NaClO and NaOH , and impregnated with triethylenediamine. Iodine collected in the filter or cartridge was then separated by combustion using tube furnace, and prepared as AgI for determination of ^{129}I .

For speciation analysis of ^{129}I in aerosol, a sequential extraction followed by anion exchange chromatographic method was developed in our laboratory. Iodide, iodate, water soluble iodine organic and mineral associated iodine were sequentially separated, each fraction of iodine was then purified and finally prepared as AgI for measurement of ^{129}I using AMS [30]. In this method, aerosol samples cut into small pieces was first leached with deionized water, and the leachate was divided into two parts, one was used for determination of total water soluble ^{129}I by digestion with $\text{K}_2\text{S}_2\text{O}_8$ in acidic condition and heating followed by solvent extraction. Iodide and iodate in another part of water leachate were separated using anion exchange chromatographic method as described above for water samples, and used to determine ^{129}I in iodide and iodate form. The residue filter after water leaching was leached with 0.5 mol/l NaOH at 45°C . The leachate was treated using the same method as that for determination of the total ^{129}I , i.e. digestion with $\text{K}_2\text{S}_2\text{O}_8$ followed by solvent extraction, this fraction of ^{129}I was considered as organic associated ^{129}I . Iodine still remained in the remained residue was separated by oxidative combustion using tube furnace, followed by purification by solvent extraction or direct AgI precipitation for determination of ^{129}I in the mineral fraction of aerosol. The analysis of aerosol collected in Denmark showed that most ^{129}I is present as organic associate iodine, and the water soluble ^{129}I is mainly present as iodide [30].

Speciation analysis of ^{129}I in soil and sediment was performed using sequential extraction (Fig. 11). In consideration of the volatile feature of iodine, the ordinary sequential

fractionation method was modified to avoid the loss of the iodine during the separation [38, 39, 40] .

635

636 Fig. 11 Schematic procedure for speciation analysis of ^{129}I in soil and sediment samples.

637 In this procedure (Fig. 11), the ground sample was leached with 1.0 mol/L NH_4OAc -
 638 NH_3 (pH8) at room temperature to obtain water soluble and exchangeable iodine, the
 639 residue was then leached with 1.0 mol/L NH_4OAc (ammonium acetate) in 25% HOAc
 640 (acetic acid) (v/v) (pH of 5) for 4h at room temperature to obtain carbonate associate
 641 iodine. The residue was further leached with 0.3 mol/L NaOH at 80 °C for 8h to obtain
 642 organic substance associated iodine. The residue was then leached with 0.04 mol/L
 643 $(\text{NH}_2\text{OH})_2\cdot\text{H}_2\text{SO}_4$ in 25% (v/v) HOAc at 80°C for 8 hours, and 0.1 mL 1mol/L NaHSO_3
 644 was added every hour to prevent the loss of iodine by reducing the leached iodine to
 645 iodide form. The remained residue was dried and transferred to a quartz boat for
 646 separation of iodine by combustion using a Pyrolyser furnace to obtain the mineral
 647 associated iodine. The analysis of soil and sediment showed that most of ^{129}I was
 648 associated with organic substances and metal oxides [38-41].

649

650 ***Measurement of ultra-low level radionuclides using mass spectrometry***

651 Depending on the decay model, radionuclides are conventionally measured by
652 radiometric methods through their radioactive decay [42]. Gamma spectrometry using
653 HPGe detector is the often used technique for measurement of gamma emitting
654 radionuclides in environmental samples because of its high resolution and single energy
655 feature of gamma rays. By employing anti-Compton electronic setup to suppress the
656 spectrum background, installing spectrometry instrument in underground laboratory of
657 few hundreds to a few thousands meters depth to shield the cosmic rays causing
658 background radiation, lining the wall of the laboratory with pure copper and instrument
659 with high purity shielding materials to reduce the background radiation from the
660 surrounding environment, and using big germanium crystal detector to increase the
661 detection efficiency, the gamma spectrometry can be used for measurement of ultra-low
662 level gamma radionuclides in the environment. The major advantage of this technique is
663 its direct measurement without chemical separation. Liquid scintillation counting (LSC)
664 is the most often used techniques for measurement of pure beta emitting radionuclides
665 (including those decay by internal conversion) [43], and low background GM counter
666 especially those equipped with anti-coincidence device is also an often used technique for
667 measurement of radionuclides emitting high energy beta particles at low level in the
668 environment. Alpha spectrometry is still the dominant technique for measurement of the
669 alpha emitting radionuclides, especially the relative short lived alpha radionuclides (e.g.
670 ^{210}Po , ^{238}Pu , ^{241}Am , ^{242}Cm , $^{243,244}\text{Cm}$). Before the measurement, beta and alpha emitting
671 radionuclides, the target radionuclides have to be separated from the sample matrix and
672 interfering radionuclides. Inorganic mass spectrometry as an instrument for isotope
673 measurement is becoming an attractive measurement technique of radionuclides.
674 Compared with radiometric measurement techniques, mass spectrometry is used to
675 measure the number of atoms of the target isotope. Based on the decay equation: $A =$
676 $N \cdot \ln(2)/t_{1/2}$ (A is the activity of radionuclide; N is the numbers of atoms and $t_{1/2}$ is the
677 half-life of radionuclide), the mass spectrometry is suitable for the measurement of long-
678 lived radionuclides. Assuming a detection limit of 2 mBq for radiometric techniques and
679 10^6 atoms for mass spectrometry, the mass spectrometry technique will become more

sensitive than radiometric method if the half-life of radionuclide is longer than 10 years. However, the detection limit of a measurement technique depends on many parameters, including the interferences, specific instrument setup and property of the specific radionuclide. A selection of measurement technique has to consider all these factors.

Many mass spectrometry techniques can be used to measure radionuclides, such as inductively coupled plasma mass spectrometry (ICP-MS), accelerator mass spectrometry (AMS), thermal ionization mass spectrometry (TIMS), resonance ionization mass spectrometry (RIMS), secondary ion mass spectrometry (SIMS) and glow discharge mass spectrometry (GDMS) [42]. Among these mass spectrometry techniques, ICP-MS and AMS are the most attractive and popular mass spectrometry techniques for measurement of long-lived radionuclides because of the rapid development/improvement of these two mass spectrometry techniques in the past years. The major challenges in the measurement of radionuclides by mass spectrometry techniques are sensitivity (including ionization, transmission and detection efficiency), spectral interferences (mainly from isobars, molecular/polyatomic ions and matrix), and instrumental limitations (e.g. abundance sensitivity, sample introduction, and possibility of ionization). The most efforts on the development of instrument and measurement methods are dedicated to solve these problems to get accurate and sensitive measurement of the target radionuclides. In the past years, we have developed a number of measurement methods for the determination of ^{99}Tc , ^{135}Cs , isotopes of plutonium and uranium and ^{237}Np using ICP-MS, and ^{129}I using AMS. Some of these methods are briefly presented below.

Measurement of isotopes of plutonium using ICP-MS. The major isotopes of plutonium in the environment are ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Pu . It is almost impossible to measure ^{238}Pu using mass spectrometry (except RIMS) because of isobaric interference of ^{238}U , the difference of the atomic mass of ^{238}U and ^{238}Pu of 5.2×10^{-6} ($\Delta m/m$) is too small to be discriminated by mass spectrometry, even for high resolution instrument. Measurement of plutonium isotopes using mass spectrometry is therefore mainly dedicate to the measurement of ^{239}Pu , ^{240}Pu and ^{241}Pu . The major challenges on the ICP-MS measurement of these isotopes of plutonium are abundance sensitivity of the instrument and the interferences of molecular ions (e.g. $^{238}\text{U}^1\text{H}^+$, $^{238}\text{U}^1\text{H}_2^+$, $^{205}\text{Hg}^{35}\text{Cl}^+$, $^{202}\text{Hg}^{37}\text{Cl}^+$,

²⁰⁰Hg⁴⁰Ar⁺, etc.). Uranium is an abundant element on the earth, the concentration of uranium in the environment is normally more than 6 orders of magnitude higher than that of plutonium, causing ²³⁸U the major interferences in the ICP-MS measurement of ²³⁹Pu and ²⁴⁰Pu. To eliminate the interference of uranium hydrides (²³⁸U¹H⁺, ²³⁸U¹H₂⁺), different dynamic reaction gases were investigated in our lab. It was found that simple collision reaction using He cannot effectively destroy hydrides of uranium, therefore could not remove its interference. By introducing O₂ as reaction gas, UH⁺ and U⁺ were converted to oxides (UO⁺, UHO⁺, UO₂⁺ or UHO₂⁺), meanwhile Pu was also converted to oxides (PuO⁺, PuO₂⁺), the interference of uranium hydrides could not be effectively eliminated in the measurement of ²³⁹Pu and ²⁴⁰Pu. Injection of ammonium into the reaction cell could significantly suppress the signal of UH⁺ by 2 orders of magnitude, while the intensities of Pu⁺ keep constant. Meanwhile, the intensity of U⁺ signal was reduced 3-4 orders of magnitude (Fig. 12). This indicated that ammonium as reaction gas could effectively eliminate the interference of hydrides of uranium to the measurement of ²³⁹Pu and ²⁴⁰Pu. This was attributed that U⁺ and UH⁺ reacted with NH₃ and formed UNH₂⁺, but Pu⁺ does not react with NH₃ [44]. This method could reduce the contribution of ²³⁸U to the ²³⁹Pu to 1×10⁻⁷. CO₂ as reaction gas was also investigated, it was found that CO₂ can effectively react with UH⁺ to form UO⁺ ions, while Pu partly react with CO₂ to form PuO⁺. At optimal condition, this method can reduce the contribution of ²³⁸U to ²³⁹Pu to 1×10⁻⁸, one order of magnitude better than NH₃. It was also observed that injection of He with NH₃ or CO₂ in to reaction/collision cell could significantly improve the measurement sensitivity of plutonium isotopes by a factor of 3. This was attributed to the collision focusing of He through reducing and narrowing the energy distribution of Pu⁺ ion during transmission to the detector from the quadrupole.

By employing two quadrupole mass separators in the Agilent 8800 ICP-MS, the abundance sensitivity (tailing) of the ²³⁸U was significantly improved. It was observed that the contribution of ²³⁸U to m/z=237 was significantly reduced to <10⁻⁹ when two quadrupole mass separators were applied, which is 4 orders of magnitude better compared with the conventional signal quadrupole mass separator instrument. Introducing collision/reaction gases can further improve the abundance sensitivity. The

contribution of ^{238}U to $m/z=237$ was reduced to $<2 \times 10^{-11}$ when $\text{CO}_2\text{-He}$ gasses were injected into the reaction/collision cell. Besides the double separation by two quadrupoles, removal of $^{238}\text{U}^+$ ions by converting U^+ to UO_2^+ or UO_2^+ ions in the reaction cell also reduced its contribution to $m/z=237$ and 239. In addition, collision focusing of $^{238}\text{U}^+$ by helium atoms in the DRC also helps to reduce the tailing contribution to $m/z=237$ and 239. A schematic mechanism of the triple quadrupole ICP-MS with $\text{NH}_3\text{-He}$ as reaction gasses is illustrated in Fig. 13.

Fig. 12 Variation of the signal intensities of $^{238}\text{U}^+$, $^{238}\text{U}^+\text{H}^+$ and $^{239}\text{Pu}^+$ with the flow rate of NH_3 (mixed with 8.8 ml/min He) as reaction gas measured in uranium standard solution (^{238}U) and ^{239}Pu standard solution using ICP-MS/MS

Fig.13 Diagram illustrating the mechanism of triple-quadrupole ICP-MS with $\text{NH}_3\text{-He}$ as reaction gas to eliminate interferences for measurement of ^{239}Pu

Accelerator mass spectrometry for measurement of ^{129}I . AMS can well overcome the isobaric and spectral interferences occurred in ICP-MS measurement of radionuclides, therefore achieve very low background and ultra-low detection limit, it is the most powerful method for the measurement of many long-lived radionuclides such as ^{14}C , ^{10}Be , ^{26}Al , ^{36}Cl , ^{41}Ca , ^{79}Se , ^{129}I , ^{236}U , ^{239}Pu , ^{240}Pu , etc. Fig. 14 illustrates the major features of AMS in the measurement of radionuclides (e.g. ^{129}I).

Fig. 14 Schematic diagram illustrating the mechanism of AMS measurement of radionuclides

In the AMS, negative ions are selected to be injected to the system, most of isobaric interferences can be excluded in this step, because many elements cannot form negative ions in the ion source. The most serious isobaric interference for the measurement of ^{129}I can be completely eliminated in AMS because ^{129}Xe cannot form negative ions. The first mass analyzer at low energy part selects the target m/z (e.g. 129 for ^{129}I , and 127 for ^{127}I)

to be injected to the system. For the measurement of ^{129}I , both $^{127}\text{I}^-$ and $^{129}\text{I}^-$ are sequentially injected to the accelerator through the first mass analyzer, meanwhile other ions are excluded. All ions entered into the accelerator are accelerated through an electric field, and out layer electrons of the ion are then stripped through a film or gas filled in the middle of the accelerator. The formed positive ions are further accelerated in the second part of the accelerator. By this way, all molecular ions (e.g. $^{127}\text{I}^1\text{H}_2$ for ^{129}I measurement) are destroyed and eliminated. Afterwards, the target ions (e.g. $^{129}\text{I}^{3+}$ or $^{127}\text{I}^{3+}$) are selected and entered to the second mass analyzer (high energy part) to further eliminate other interference. By these ways, almost all interferences can be eliminated and a very low background can be achieved. The major isotope ions (e.g. $^{127}\text{I}^{3+}$) are measured by a Faraday cup, and the minor isotope ions (e.g. $^{129}\text{I}^{3+}$) are measured by a more sensitive detector, e.g. ionization chamber. An electrostatic analyzer is normally installed before the detector to further eliminate some interference, e.g. ^{10}B in the measurement of ^{10}Be , which cannot be sufficiently removed in the previous steps.

We have developed a numbers of AMS measurement methods for ^{129}I using a 3MV AMS system in the Xi'an AMS center. An instrumental background of 2×10^{-14} for $^{129}\text{I}/^{127}\text{I}$ atomic ratio was obtained by direct measurement of a target prepared by directly pressed NaI and niobium powder into a copper holder. The procedure blanks were measured to be lower than 1×10^{-13} for $^{129}\text{I}/^{127}\text{I}$ ratio in AgI targets containing 0.2-1.0 mg iodine carrier, which is corresponding to a detection limit of 3×10^6 atoms (3 times of blank count rate).

For the measurement of ^{129}I in surface environmental samples (with $^{129}\text{I}/^{127}\text{I}$ ratio $> 10^{-9}$), 0.5-2.0 mg of stable iodine carrier prepared from a low-background iodine crystal (Woodward Company) was spiked to the sample after separation using combustion, or directly to the water samples. The separated iodine in iodide form was precipitated as AgI by addition of AgNO_3 . After dried at 70-75°C in a 1.5 ml centrifuge tube, the AgI precipitate was ground to fine powder and mixed with niobium powder of 3-5 times by mass, which was then pressed in a copper holder for AMS measurement of ^{129}I . In general, 10 mg of mixture can be pressed into target holder, i.e. maximum 2 mg of AgI can be pressed into the holder. In practice, only small fraction of sample in the target holder was used for measurement due to a relative short analytical time (< 20 min.).

Therefore, for the analysis of low-level samples, it is better to reduce the final mass of samples, to enable more samples were used for measurement. In this case, 0.2 mg iodine carrier was used and the final mass of the precipitate of 0.5-1.0 mg was mixed with 2-3 mg of niobium to be fully pressed into the target holder and used for measurement of ^{129}I .

An AMS method using carrier free iodine target was developed for the determination of ^{129}I in ultra-low level samples. In this method, no stable iodine was spiked to the sample to avoid the ^{129}I background resulted from iodine carrier. Because the concentration of iodine in environmental samples (except seaweed, thyroid, brine, etc.) is normally very low, only small amount of iodine (<0.05 mg) can be separated from the sample, e.g. 20 g soil), which is not sufficient to prepare AgI precipitate, therefore an AgI-AgCl co-precipitation method was developed to prepare the target. The final AgI-AgCl precipitate of 0.5-1 mg was prepared, ground, mixed with 2-5 mg of niobium powder, and pressed into a niobium holder for measurement of ^{129}I using AMS. The main challenge in this method is stabilization, control and precise measurement of the beam current of iodine ions, because of very low current of <100 nA. With this method, samples with $^{129}\text{I}/^{127}\text{I}$ atomic ratio of 2.0×10^{-13} can be measured when 0.05 mg iodine is separated and used for measurement. This method is therefore useful for analysis of ultra-low level ^{129}I samples, e.g. deep soil, seawater, or pre-nuclear samples. For a sample with $^{129}\text{I}/^{127}\text{I}$ ratio of 1×10^{-10} , this method only needs 3 μg iodine for measurement, i.e. a small size sample is needed, which is very useful for the application in which only small sample is available [31].

In the AMS measurement of ^{129}I , the AgI or AgI-AgCl precipitate is often pressed into a copper (or titanium, stainless steel) holder. The aluminum target holder often used for measurement of ^{14}C is not suitable for this type of target. A violent reaction (bubbles) was observed shortly (< 10 minutes) after AgI-AgCl was pressed into an aluminum holder and exposed to air. A similar but weaker reaction was observed for AgI precipitate when it was pressed into an aluminum holder, and liquid bubbles on the surface of the sample were observed. No visible reaction was observed when they were pressed in holders made of copper for both AgI and AgI-AgCl precipitate, even after exposure to air for more than 7 days. This might be attributed to a solid phase reaction: $3\text{AgI} + \text{Al} = 3\text{Ag}$

827 + AlI_3 and $3\text{AgCl} + \text{Al} = 3\text{Ag} + \text{AlCl}_3$, these reactions take place when water vapor and
828 water soluble iodide/chloride are present [45].

829 In the AMS measurement, the target radionuclide is always separated from the sample
830 matrix and purified from other impurity before measurement. This procedure is normally
831 time consuming and not suitable for rapid analysis. We have developed a direct AMS
832 measurement method without chemical separation. The sample was only ground to
833 powder and directly pressed into target holder after mixed with niobium powder. The
834 prepared target was measured for ^{129}I in the 3MV AMS. The analytical results indicate
835 that this method is valid for the measurement of ^{129}I in environmental solid samples (e.g.
836 vegetation, soil, aerosol /dust) in a level of $0.1 \mu\text{Bq/mg } ^{129}\text{I}$ with an analytical uncertainty
837 of less than 20%. For normal environmental sample with low concentration of iodine (< 5
838 $\mu\text{g/g}$), stable iodine carrier pre-mixed with niobium was used, which can significantly
839 improve the stability of the measurement and accuracy of the analytical result [46]. This
840 method is very useful for emergency analysis, the analytical time is only less than 5 min
841 per sample. In consideration of sample preparation, a batch of 40 samples can be
842 analyzed in 5 hours.

843 **Determination of difficult-to-measure radionuclides for** 844 **decommissioning of nuclear facilities and emergency preparedness**

845 Since 2002, our laboratory at DTU Nutech has developed serious analytical methods for
846 the determination of radionuclides of difficult to measure (mainly long-lived beta and
847 alpha emitters and some low-level gamma emitters), including ^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe ,
848 ^{63}Ni , ^{90}Sr , ^{93}Mo , ^{99}Tc , ^{129}I , ^{237}Np , ^{238}U , ^{239}Pu , ^{240}Pu , ^{241}Pu , ^{241}Am and ^{244}Cm . Various
849 types of materials have been analyzed for decommissioning of nuclear facilities,
850 including concrete, graphite, metals, stainless steel, exchange resin, liquid waste
851 concentrate, ordinary water, heavy water, silicate gels, paint, oil, soil/sand,
852 sediment/slurry, etc. The analytical results have been used to characterize these materials
853 and treatment of the produced wastes for the decommissioning of research and power
854 reactors and other nuclear facilities in Denmark, Sweden.

The main challenges in the radiological characterization of decommissioning waste includes instability of some radionuclides (e.g. ^3H , ^{14}C , ^{36}Cl , ^{99}Tc , ^{129}I , etc.) during sampling, storage and chemical separation, complicated and unknown components of sample matrix, difficulties in decomposition and pre-treatment of some samples, high radiation exposure for some samples. Fig.15 shows an overall sequential separation procedure for determination of various radionuclides in different samples. Brief description of analytical methods for individual radionuclide are also presented below.

Fig. 15 Schematic diagram of overall separation procedure of radionuclides for characterization of radioactive waste

Determination of ^3H and ^{14}C .

Tritium and ^{14}C are major radionuclides in both contaminated or neutron activated samples due to their high concentration. For water samples, tritium normally present as tritiated water (HTO), a simple distillation and direct measurement of tritium in the

distilled water using LSC is sufficient. However, for some water, tritium is present both as water and organic tritium. The organic associated tritium can be separated by active charcoal adsorption first, and then tritium is determined in water form. Organic tritium adsorbed on active charcoal can be determined using the same method as for solid samples (see below). ^{14}C might also present as inorganic (mainly carbonate) and organic associated form [47]. The organic ^{14}C can be also adsorbed on active charcoal and analyzed as for solid samples (see below). While inorganic ^{14}C in the sample can be separated by digestion of sample in a closed system (Fig. 16), in which gasses released from the samples are adsorbed in a bubbler filled with alkaline solution (e.g. CarboSorb). Acid (e.g. H_2SO_4) is added to the sample, and N_2 flows to the sample solution, all inorganic carbon is converted to CO_2 and released from sample, which is trapped in bubbler filled with CarboSorb, and ^{14}C in the separated samples was measured by LSC after mixed with scintillation cocktail [48, 49]. A simple method was also applied to measure total ^{14}C in water samples. In this method, water sample was first neutralized to pH7-8, small amount of Na_2CO_3 (0.1 mmol) was spiked to the sample as carrier. The sample was then evaporated to small volume (>0.5 ml), and then transferred to a cellulose pad filled with cellulose powder and analyzed as solid sample (see below).

A combustion method using Sample Oxidizer has been developed for determination of ^3H and ^{14}C in solid samples [49]. Solid samples in powder such as graphite, concrete, active charcoal, soil, sediment, metal pieces (<2 mm), resin, etc. were mixed with cellulose powder in a cellulose pad of about 2.5 ml, which was put into a Sample Oxidizer. In the Sample Oxidizer, the sample was combusted at 1200°C with oxygen flow. All tritium in the samples was converted to H_2O vapor during combustion with oxygen, which was flushed with nitrogen gas through a closed system, and condensed in an air condenser, and the condensed tritiated water was collected in a LSC vial after the combustion. The scintillation cocktail stored in a reservoir was used to flush the tubes and combined to the vials with tritiated water. All ^{14}C in the samples including carbon, carbonate and organic carbon were converted to CO_2 , and flowed through the system with the input N_2/O_2 gasses, and finally absorbed in CarboSorb (an amine solution) filled into a column. The absorbed ^{14}C in the CarboSorb solution was collected in a LSC vial after the combustion,

and the column was washed with a scintillation cocktail which was stored in a reservoir to remove any remaining CarboSorb in the tubes, and the CarboSorb, and scintillation cocktail are then directly collected in the vial and mixed. The separated tritium and ^{14}C in the vials were directly measured using LSC. The whole procedure of combustion takes about 2 minutes. No any suitable radioisotopes for tritium and ^{14}C can be used in this procedure for monitoring the chemical yield of tritium and ^{14}C in the whole procedure. Standard addition methods were used by analysis the same samples with or without spike tritium (both organic tritium and tritiated water) or ^{14}C (both organic and inorganic ^{14}C), the results indicate a quantitative recovery of both tritium and ^{14}C in this method [50].

Determination of ^{36}Cl and ^{129}I

Both iodine and chlorine are volatile elements, and instable during sample treatment and analysis. For water sample, solvent extraction was directly used for the separation of iodine from matrix; the aqueous phase from the extraction was used for separation of ^{36}Cl by AgCl precipitate. While for solid sample, a special attention has to be given to avoid loss of ^{129}I and ^{36}Cl during analysis. An acid digestion method in a closed system was developed to decompose graphite, iron, aluminum, stainless steel and ion exchange resin for the determination of ^{129}I and ^{36}Cl (Fig. 16). In this method, the sample was first put into the flask, yield carriers (stable Cl and I) were added. All apparatus in the system were connected and leakage was checked. Acid or mixed acids were added through the funnel (No. 5) to avoid the loss of the produced gasses. Afterwards, the sample with acid was heated to dissolve the sample and release iodine and chlorine to the solution. Different acid or acid mixture were used depending on the sample types. It was found that mixed acids of $\text{H}_2\text{SO}_4:\text{HNO}_3:\text{HClO}_4 = 15:4:1$ were effective for completely dissolve graphite, 5-8 mol/l of H_2SO_4 was effective for completely dissolve stainless steel and iron without addition of any chlorine, while HNO_3 is sufficient for dissolution of aluminum, lead, copper. For soil and sediment, HNO_3 can be used to leach iodine and chlorine out [51]. Alkaline fusion was also used to release iodine and chlorine from soil, sediment and vegetation samples [29]. For releasing iodine from ion exchange resin, NaOH and NaClO leaching was a simple and sufficient method. In this case, the closed digestion system was not necessary, because iodine was stable in alkaline solution in the present of NaClO .

After the acid digestion of the sample, the iodine was released from the sample solution and remained in the trapping solution and on the condenser walls. The trap solution and washes of the tubes and condenser are combined as iodine trap solution. Solid samples (soil, sediment and vegetation) decomposed by an alkali fusion method were leached with water, and filtered through a filter paper. ^{129}I in the filtrate/trap solution and water samples was then separated by solvent extraction.

Fig. 16 Schematic diagram of acid digestion system for decomposition of graphite, metals, concrete, soil and sediment samples. 1-Heating mantle; 2-three-neck-flask; 3-sample and digestion acids; 4-bubbling tube; 5-separation funnel for adding acids; 6,7-reflux cooler; 8-condenser receiver; 9-washing bottle with diluted acid; 10, 11-absorption bottle with NaOH

Chlorine released from the sample during the acid dissolution/digestion remained in the sample solution, and small fraction on the condenser walls and diluted acid/water trap solution. These solution and washes of the tubes and condenser were combined, ^{36}Cl was then separated by precipitation and ion exchange methods after the separation of iodine using solvent extraction. To the aqueous phase from the solvent extraction of iodine, some more NaNO_2 solution was added to convert all chlorine to chloride. AgNO_3 was then added to precipitate chloride as AgCl , which was then separated by centrifuging.

950 The AgCl precipitate was dissolved with NH_4OH and then Cl^- was re-precipitated as
 951 AgCl by addition of HNO_3 to pH 1-2. The formed AgCl was dissolved in 5 ml NH_4OH
 952 and loaded to an anion exchange column which has been conditioned with NH_4OH
 953 solution. After washing with NH_4OH to remove all Ag^+ , Cl^- adsorbed on the column was
 954 finally eluted with NH_4NO_3 - NH_4OH solution. The eluate was evaporated to dryness and
 955 the residue was dissolved with 2-3 ml water and transferred to a vial for LSC
 956 measurement of ^{36}Cl [51]. Fig. 17 shows a combined analytical procedure for
 957 determination of ^{129}I and ^{36}Cl in decommissioning samples.

958

959 Fig. 17 Schematic diagram of a combined analytical procedure for the determination of
 960 ^{36}Cl and ^{129}I in decommissioning samples

961

962 Determination of ^{99}Tc .

963 In oxidative condition, ^{99}Tc is mainly present as TcO_4^- , therefore can be separated from
 964 matrix by anion exchange chromatography. Based on the high affinity of TcO_4^- on anion

exchange resin, ^{99}Tc was separated from most of interfering radionuclides. ^{99}Tc in water or leachate of sample was first oxidized to TcO_4^- using H_2O_2 , then the solution was neutralized to pH8-9 to separate the transit metals and actinides by hydroxides precipitation. The supernatant was loaded to an anion exchange column (e.g. AG1 $\times$ 4, Cl^- form) after acidified to pH4-5. The column was washed with 1.0 mol/l NaOH, H_2O and 0.5-1.0 mol/l HNO_3 , ^{99}Tc on the column was finally eluted using 10 mol/l HNO_3 . The eluate was evaporated to 0.5-1.0 ml on a hotplate, and then diluted with 20 ml H_2O . The prepared solution was loaded to a 2 ml TEVA extraction chromatographic column, the column is washed with 2 mol/l HNO_3 , ^{99}Tc on the column was finally eluted with 10 mol/l HNO_3 . The eluate was evaporated to 0.5-1.0 ml and diluted to 5 ml with H_2O . Chemical yield was measured by gamma counting of $^{99\text{m}}\text{Tc}$ spiked to the sample before separation, and ^{99}Tc in the separated sample solution was finally measured using ICP-MS [12, 15]. LSC can be also used for measurement of ^{99}Tc . In this case, the eluate can be evaporated to near dryness at $<100^\circ\text{C}$, and transferred to 20 ml vial with 2-3 ml water. After addition of scintillation cocktail, ^{99}Tc can be measured using LSC. However, the detection limit of ICP-MS for ^{99}Tc is generally better than LSC by more than one order of magnitude [42].

Determination of ^{55}Fe and ^{63}Ni .

Based on hydroxides precipitation, anion exchange chromatography, and extraction chromatography using Ni specific resin, we have developed an analytical procedure for determination of both ^{55}Fe and ^{63}Ni [52]. To the water samples or leachates of solid samples, stable iron (4 mg) and nickel (2 mg) and hold-back carriers (Co, Eu, etc.) were spiked, the solution was adjust to pH8-9 by addition of NaOH solution. The formed hydroxides precipitate was separated by centrifuging, and afterward was dissolved in HCl, and the sample solution was adjusted to 9.0 mol/l HCl by addition of concentrated HCl. The prepared sample solution was loaded to an anion exchange column (AG1 $\times$ 4, Cl^- form), the column was rinsed using 30-40 ml of 9.0 mol/l HCl. The effluent and rinse solution were collected for ^{63}Ni determination. The column was rinsed with 5-6 mol/l HCl to remove ^{60}Co , ^{58}Co and other transition metals (e.g. Cu). ^{55}Fe on the column was eluted with 0.5 mol/l HCl. The eluate was evaporated to dryness. For the sample

containing high iron or radioactive cobalt, a further purification step was added. The dried ^{55}Fe fraction was dissolved with 9 mol/l HCl, hold-back carriers (e.g. Co^{2+}) were spiked. The solution was loaded to a new anion exchange column. The column was rinsed with 5-6 mol/l HCl, and ^{55}Fe on the column was finally eluted with 0.5 mol/l HCl. The eluate was evaporated to dryness, and dissolved with 1mol/l H_3PO_4 to obtain a colorless solution (Fig. 18). The second anion exchange chromatographic purification is needed when ^{60}Co and ^{58}Co concentration are high and/or the iron content is high in the sample to get a high decontamination factors for ^{58}Co and ^{60}Co . The iron in the final solution and the original solution was measured by ICP-OES to calculate the chemical yield. In this procedure, ^{55}Fe is normally quantitatively recovered, a chemical yield of more than 98% was often achieved. The remaining solution was used to measure ^{55}Fe by LSC.

Fig. 18 Diagram of analytical procedure for determination of ^{55}Fe and ^{63}Ni

It should be mentioned, application of H_3PO_4 to dissolve $\text{Fe}(\text{OH})_3$ or Fe_2O_3 is important, otherwise a high quench color (yellow/brown) solution is obtained, causing a low LSC counting efficiency of ^{55}Fe . H_3PO_4 can not only dissolve $\text{Fe}(\text{OH})_3$ and Fe_2O_3 , but also form a colorless solution of complex of iron with H_3PO_4 , Fig. 19 shows quench curve of ^{55}Fe in different amount of Fe solution and at different media (FeCl_3 , $\text{Fe}-\text{H}_3\text{PO}_4$ or FeSO_4), a significantly improved quench level and high counting efficiency of ^{55}Fe was achieved by using H_3PO_4 .

Fig. 19 Quench curves of ^{55}Fe in different media against the iron content in the sample.

For the separation of nickel, a specific extraction resin based on dimethylglyoxime (DMG) as function group was used. Nickel can form a stable complex with DMG, Ni^{2+} loaded to the Ni-resin column can be adsorbed on the resin. However, other transition metal ions (e.g. Fe^{3+} , Co^{2+} , Cu^{2+} , etc.) can also form complexes to be adsorbed on the column. Because the complex of other transition metal with DMG are not stable, which can be removed by rinsing. For obtaining a better decontamination factor for some high radioactive radionuclides (e.g. ^{60}Co , ^{58}Co), a further separation of these transition metals is necessary. Therefore, ^{63}Ni was first separated from many other transition metals using anion exchange chromatography, most of ^{60}Co and ^{58}Co ($\text{DF} > 10^3$) can be removed in this step. However, rare earth elements could not form anions in HCl solution and entered the

effluence with Ni. Since rare earth elements could not form complex with DMG, they could be well removed in the Ni-resin extraction chromatographic separation step. The effluent from the anion exchange column was evaporated to dryness, the residue was dissolved using 1.0 mol/l HCl. 1-2 ml of 1 mol/l ammonium citrate (depending on the amount of residue) was added to the solution to complex most of metals. Then ammonia solution was added to the solution to pH 8-9. The prepared sample solution was then loaded to an extraction chromatographic column (Eichrom Ni-column, 2 ml). The column was rinsed with 0.2 mol/l ammonium citrate at pH9 to remove all possible interfering radionuclides. Ni adsorbed on the column (red band) was finally eluted using 3.0 mol/l HNO₃. The eluate was evaporated to 0.1-0.3 ml on a hotplate, and transferred to a vial with 2 ml water. 0.1 ml of the final solution, as well as the original solution, were taken for the determination of Ni using ICP-OES for the chemical yield measurement. It was observed that nickel can be quantitatively recovered in this procedure with a chemical yield of >98%. ⁶³Ni in the remaining solution was measured by LSC [52]. The pre-separation of nickel from iron and cobalt was confirmed very necessary for the samples with high ⁶⁰Co and ⁵⁸Co, because the decontamination factor of Ni-column is not sufficient high to remove all radioactive isotopes of cobalt, which can cause a high interference in the measurement of ⁶³Ni [53].

Determination of ⁴¹Ca and ⁹⁰Sr.

Calcium-41 is a long-lived (1.3×10^5 years) radionuclide decaying by electron capture, without any gamma or beta rays emission. LSC is the most suitable method for its measurement by counting its low-energy Auger electrons. ⁴¹Ca is a neutron activation product, mainly produced in concrete biological shield, which contains high concentration of calcium and is exposed to neutrons. ⁹⁰Sr is one of the important fission products because of its high fission yield, and therefore an important radionuclide in the decommissioning of nuclear facilities. ⁹⁰Sr is a pure beta emitter, and therefore needs to be separated from all other radionuclides before measurement, especially from radioisotopes of alkaline earth metals (e.g. ¹³¹Ba, ²²⁸, ²²⁶Ra). In some heavy concrete used

in nuclear reactors, BaSO₄ was added to obtain a better shield of radiation, the separation of ¹³¹Ba is one of major challenge in the analysis of such type of samples. We have developed a simple precipitation method for separation of calcium from matrix and interfering radionuclides, as well as to separate calcium from strontium [54]. In this method, calcium and strontium were first released from concrete to solution. Both acid leaching and alkaline fusion were investigated, and found acid leaching using *aquia regia* can release almost all calcium and strontium from concrete, and more simple compared to alkaline fusion. Meanwhile, most of BaSO₄ can be removed because of its insolubility in acid solution. Sr²⁺ and Ca²⁺ carriers, Fe³⁺ hold back carrier and ⁸⁵Sr tracer were added to the sample before separation. The leachate was then neutralized to pH8-9, all transit metals (e.g. Fe, Co, Eu, etc.) and actinides were precipitated and removed from calcium and strontium. The supernatant containing calcium and strontium was used for further separation of ⁴¹Ca and ⁹⁰Sr.

Na₂CO₃ solution was added to the supernatant, which was heated to 95 °C and keeping for 1 hour. The formed precipitate of Ca and Sr as carbonate was separated by centrifuge. The precipitate was dissolved with HCl, and 2 mg of Fe³⁺, Co²⁺, and Eu³⁺ were added, and then the NaOH was added to adjust pH to 8-9. The Fe(OH)₃ precipitate was removed by centrifuging, 6 mol/l NaOH was added to the supernatant to 0.5 mol/l NaOH, and the precipitate of Ca(OH)₂ was separated by centrifuging. The supernatant was used for the separation of ⁹⁰Sr. The Ca(OH)₂ precipitate was dissolved with HCl, 2 mg of Fe³⁺. Co²⁺ and Eu³⁺ were added and pH adjusted to 8-9 using NaOH again. The precipitate was removed by centrifuge, and 6 mol/l NaOH was added to the supernatant to 0.5 mol/l of NaOH. Ca(OH)₂ precipitate was then separated by centrifuging. This dissolution and precipitation step were repeated. The final obtained Ca(OH)₂ precipitate was dissolved using HCl. The chemical yield was measured by determination of stable calcium in the final solution and the solution before separation. ⁴¹Ca in the final solution was measured by LSC counting [54]. An overall recovery of more than 85% was obtained, and decontamination factors to all interfering radionuclides were more than 5×10⁴. Fig. 20 shows the analytical procedure for ⁴¹Ca in concrete.

To the supernatant from the first Ca(OH)₂ precipitation step, HCl is added to adjust pH2. The chemical yield of strontium was measured by gamma counting of ⁸⁵Sr in the

1089 solution. After addition of Y^{3+} carrier, the solution was kept 3 weeks for in-growth of
 1090 ^{90}Y . Afterwards, Na_2SO_4 was then added to precipitate Sr as well as Ra, and Ba as
 1091 sulphate. ^{90}Y ingrown from ^{90}Sr and remained in the supernatant was then separated by
 1092 $Y(OH)_3$ precipitation after addition NH_4OH to pH to 8-9 and centrifuging. The
 1093 precipitate was then dissolved using HCl , $H_2C_2O_4$ was added to the solution to precipitate
 1094 yttrium as $Y_2(C_2O_4)_3$, and the chemical yield of ^{90}Y was measured by weighing the dried
 1095 $Y_2(C_2O_4)_3$ precipitate or by ICP-OES after ^{90}Y measurement. ^{90}Y in the precipitate was
 1096 measured by beta counting using a low background GM counter (Risø Multi-counter),
 1097 ^{90}Sr in the samples was calculated from the measured ^{90}Y with correction for chemical
 1098 yield of strontium and yttrium, as well as the in-growth time of ^{90}Y from ^{90}Sr [10].

Fig. 20 Schematic diagram of analytical procedure for ^{41}Ca

Determination of isotopes of plutonium, americium and curium

1104 The major isotopes of plutonium in the environment and decommissioning waste are
1105 ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Pu , they are the important alpha and beta emitters and have to be
1106 determined in the decommissioning of nuclear facilities. Separation of plutonium mainly
1107 relies on the formation of anion complexes of Pu^{4+} with NO_3^- and Cl^- in high
1108 concentration of HNO_3 or HCl , and no such anion is formed for Pu^{3+} , and less anion
1109 complexes of other valence states of plutonium are formed in HCl and HNO_3 . Therefore,
1110 adjustment of valence state of plutonium is critical in the separation of plutonium. For
1111 acidified water sample or acid leachate of samples, ^{242}Pu and ^{243}Am as yield tracers and
1112 Fe^{3+} as carrier were spiked. NaOH was then added to adjust pH 8-9 to separate plutonium
1113 as co-precipitate with $\text{Fe}(\text{OH})_3$. The co-precipitate was dissolved with HCl , and KHSO_3
1114 solution was added to reduce plutonium to Pu^{3+} , then NaOH was added to adjust pH to 8-
1115 9 to precipitate $\text{Pu}(\text{OH})_3$ with $\text{Fe}(\text{OH})_2$. The precipitate was dissolved with concentrated
1116 HCl , and then concentrated HNO_3 was added, Pu^{3+} was oxidized to Pu^{4+} by NO_2^- in the
1117 concentrated HNO_3 . The sample solution was prepared in 8 mol/l HNO_3 medium and
1118 loaded to an anion exchange column (AG1 $\times$ 4, Cl^- form). The column was rinsed with 8
1119 mol/l HNO_3 , the effluent and washes were combined and collected for the determination
1120 of ^{241}Am and $^{242, 244}\text{Cm}$. The column was rinsed with 9 mol/l HCl , and plutonium
1121 adsorbed on the column was finally eluted using 0.05 mol/l $\text{NH}_2\text{OH}\cdot\text{HCl}$ -2M HCl
1122 solution. In this case, Pu^{4+} on the column was reduced to Pu^{3+} , which could not form
1123 anion complex and eluted from the column. The eluate was evaporated to dryness,
1124 concentrated HNO_3 was added and heated to decompose the $\text{NH}_2\text{OH}\cdot\text{HCl}$, and the
1125 solution was evaporated to dryness again. The residue was dissolved with 0.5 mol/l
1126 HNO_3 , one aliquot was used for ICP-MS measurement of ^{239}Pu , ^{240}Pu and ^{241}Pu , another
1127 aliquot was evaporated to dryness again and dissolved with 0.5 mol/l H_2SO_4 for alpha
1128 spectrometry measurement of ^{238}Pu after electrodeposition on a stainless steel disk [14,
1129 55]. With this procedure, a high chemical yield up to 98% could be obtained.
1130 ^{241}Am and $^{243,244}\text{Cm}$ are the major radioisotopes of americium and curium in the
1131 decommissioning waste due to their relative long half-lives and high production in the
1132 nuclear reactors. The chemical properties of americium and curium are similar, and
1133 therefore could be separated together. The energies of alpha particles of ^{243}Cm and ^{244}Cm
1134 are too close to be discriminated in the alpha spectrometry, and therefore were measured

together and reported as $^{243}\text{Cm}+^{244}\text{Cm}$ ($^{243,244}\text{Cm}$). Americium and curium are often presented as Am^{3+} and Cm^{3+} , they cannot form anion complexes with HNO_3 and HCl in aqueous solution due to the small ion radius and strongly bound water molecules, but could form anion complexes in non-aqueous media. To the effluent from the ion exchange separation of Pu, Fe^{3+} was added, and NH_3 was added to pH8-9 to form co-precipitates of Am and Cm hydroxides with $\text{Fe}(\text{OH})_3$. The precipitate was dissolved using concentrated HNO_3 . 30% H_2O_2 was added and the solution stirred for 2 minutes. CH_3OH was added to the solution to prepare the sample in 93% CH_3OH -1.0 mol/l HNO_3 solution. The solution was then loaded to an anion exchange column (AG1 $\times$ 4, Cl^- form). The column was rinsed with 1.0 mol/l HNO_3 -93% CH_3OH and 0.1mol/l HCl -0.5 mol/l NH_4SCN -80% CH_3OH , followed by 1.0 mol/l HNO_3 -93% CH_3OH to remove interfering radionuclides and lanthanides. Am and Cm on the column were finally eluted using 1.5 mol/l HCl -86% CH_3OH solution. The eluate was evaporated to dryness, concentrated HNO_3 was added to the residue and digested for 30 min on a hotplate and then evaporated to dryness. The residue was dissolved with 10 ml of 0.05M H_2SO_4 , and the solution was transferred to an electrodeposition cell to electrodeposit Am and Cm on a stainless steel disk. ^{241}Am and ^{244}Cm on the disc were finally measured by alpha spectrometry. ^{243}Am on the disc was also measured and used as chemical yield tracer for correction of the measured concentration of ^{241}Am and $^{234,244}\text{Cm}$ [14]

A new analytical procedure using extraction chromatography was developed in our lab for separation of plutonium, americium and curium in the nuclear waste samples (Fig. 21). The sample solution was first acidified using HCl , ^{242}Pu and ^{243}Am tracers, Fe^{3+} carriers were spiked, and then NaHSO_3 was added to reduce plutonium to Pu^{3+} . NaOH was added to the sample solution to adjust pH8-9 to co-precipitate Pu^{3+} , Am^{3+} and Cm^{3+} hydroxides with $\text{Fe}(\text{OH})_2$. The precipitate was dissolved with HCl and concentrated HNO_3 was added to oxidize Pu^{3+} to Pu^{4+} . The sample solution was prepared in 4 mol/l HNO_3 medium, and loaded to two sequential connected columns of TEVA and DGA, the columns were then rinsed with 4 mol/l HNO_3 . $\text{Pu}(\text{NO}_3)_2^-$ was adsorbed on TEVA column, while Am^{3+} and Cm^{3+} passed through the TEVA column, and adsorbed on DGA column by forming complex with the functional group of tetra-n-octyldiglycolamide on

the DGA column. Afterwards, the two columns were disconnected, TEVA column was used for separation of plutonium, and DGA column was used for separation Am and Cm. The TEVA column was rinsed with 6 mol/l HCl, and plutonium on the column was then eluted using 0.5 mol/l $\text{NH}_2\text{OH}\cdot\text{HCl}$ –2 mol/l HCl solution. The DGA column was rinsed with 0.2 mol/l HCl, and Am and Cm were eluted using 0.5 M HCl. The separated plutonium and Am+Cm fractions were prepared using the same method described above for the determination of plutonium isotopes using ICP-MS and alpha spectrometry for ^{238}Pu , ^{241}Am , and $^{243,244}\text{Cm}$.

Fig. 21 Schematic diagram of analytical procedure for determination of isotopes of plutonium, americium and curium using extraction chromatography

Determination of other radionuclides.

In our laboratory, the methods for the determination of ^{93}Mo , ^{94}Nb , and ^{135}Cs in the decommissioning wastes were also developed, and the methods for the determination of other radionuclides, such as ^{79}Se , ^{93}Zr , ^{126}Sn , and ^{151}Sm are under development. Although the concentrations of these radionuclides are very low in most of decommissioning waste, but their long half-lives make them also important in view of waste repository.

The separation of ^{93}Mo and ^{94}Nb was implemented using ion exchange chromatography followed by a purification using alumina column. After spiked the yield tracers of stable Mo, Nb and Zr and hold-back carriers, such as stable Co, Ni and Eu, the sample was prepared in 0.02 mol/l HF and loaded to a strong acidic cation exchange chromatographic column. Mo, Zr and Nb present as anions MoO_4^{2-} , ZrF_6^{2-} or NbF_6^- passed through the column, while cations including transition metals, alkali and alkaline earth metals were adsorbed on the column and removed. The effluent from the column was then loaded to a TEVA column, MoO_4^{2-} , ZrF_6^{2-} and NbF_6^- were adsorbed on the column. After rinsing with 0.02 mol/l HF solution, Zr was first eluted using 7 mol/l HCl-0.5 mol/l HF solution, Mo was eluted with 4 mol/l HF solution, and Nb was eluted with 1 mol/l HNO_3 solution. The Nb fraction was directly used for measurement of ^{94}Nb by gamma spectrometry after evaporated to < 5 ml. Zr fraction can be used for determination of ^{93}Zr after a further purification. The Mo fraction was evaporated to dryness and converted to HNO_3 medium by addition of HNO_3 and evaporated to dryness, and the residue was dissolved in 1.0 mol/l HNO_3 solution. The prepared solution was then loaded to an alumina column, after rinsing the column with 1.0 mol/l HNO_3 , 0.1 mol/l HNO_3 , water and 0.01 mol/l ammonia. MoO_4^{2-} adsorbed on the column was finally eluted with 25% ammonium. The eluate was evaporated to dryness and the residue was dissolved in water, which was transferred to a 20 ml vial for LSC measurement of ^{93}Mo . The chemical yield was obtained by measurement of stable Mo and Nb in the separation sample and the spiked sample solution using ICP-OES.

For the determination of ^{135}Cs , the sample solution was prepared in a neutral or slight acidic medium. Ammonium molybdophosphate (AMP) powder was added and mixed with the sample solution, AMP powder adsorbed cesium was separated by filtration. Cesium on the AMP powder was then leached out with 5 mol/l NH_4Cl solution. By this

way, most of radionuclides can be removed because of the specific adsorption of cesium on the AMP powder. The leachate was then loaded to a cation exchange chromatographic column (e.g. Bio-Rad AG 1×-50), Cs^+ was adsorbed on the column. After rinsing with H_2O and 0.1 mol/l HNO_3 , Cs^+ was eluted with 1.0 mol/l HNO_3 . In this step, most of Ba was removed. The eluate was then evaporated to dryness and prepared in 5 ml of 0.5 mol/l HNO_3 for ICP-MS of ^{135}Cs using a triple-quadrupole ICP-MS (Agilent 8800) with N_2O as reaction gas to eliminate the interferences including isobar (e.g. $^{135}\text{Ba}^+$). Meanwhile, ^{137}Cs can be also measured by ICP-MS. In this case, no external chemical yield tracer is needed, ^{137}Cs can be used as an internal yield tracer. ^{137}Cs in the samples was first measured using gamma spectrometry, the concentration of ^{135}Cs was calculated using the measured $^{135}\text{Cs}/^{137}\text{Cs}$ ratio by ICP-MS and the ^{137}Cs concentration in the sample measured by gamma spectrometry. For the sample containing high level radioactivity of other radionuclides (e.g. ^{60}Co), ^{137}Cs can be determined by measurement of the AMP powder adsorbed cesium from the sample, in which ^{60}Co and many other radionuclides were removed.

The methods presented in this work have been successfully used for the characterization of various radioactive wastes from the decommissioning of research reactors in Denmark (DR-1, DR-2 and DR-3) and Australia, nuclear power reactors in Barsebäck, Sweden, and other nuclear facilities such as hot cells in Denmark. Meanwhile they were also used for characterization of radioactive waste from the operation of nuclear power plants (e.g. concentrate, ion exchange resin, etc.) in Finland. [Table 2](#) list the sample amount required for analysis and the minimum detectable activity (MDA) of our methods for the difficult-to measure radionuclides. This is mainly for the clearance samples (less contaminated). For the samples directly exposed to neutrons or highly contaminated ones, e.g. graphite, metals from reactor tank or first circulation system, ion exchange resin for purification of reactor water, small sample (0.05- 0.5 g) is required depending on the radioactive level, while the MDAs for the corresponding radionuclides (in unit of Bq/mBq) are similar as listed in the table.

1238 Table 2 Minimum detectable activity (MDA) for the concerned radionuclides

Sample type	Nuclides	Measurement method	MDA (Bq/g) #
concrete, soil, sediment, vegetation, animal tissues	^3H	LSC	0.1 Bq/g
	^{14}C	LSC	0.05 Bq/g
	^{55}Fe	LSC	0.05 Bq/g
	^{63}Ni	LSC	0.01 Bq/g
	^{36}Cl	LSC	0.01 Bq/g
	^{129}I	LSC/AMS	0.01 Bq/g, 0.1 $\mu\text{Bq/g}$ (AMS)
	^{41}Ca	LSC	0.15 Bq/g
	^{90}Sr	Beta counting	0.01 Bq/g
	^{99}Tc	Beta counter /ICP-MS	0.01 Bq/g
	^{94}Nb	γ -spectrometry	0.5 Bq/g
	^{238}Pu	α -spectrometry	0.1 mBq/g
	^{239}Pu	α -spectrometry /ICP-MS	0.1 mBq/g
	^{240}Pu	α -spectrometry /ICP-MS	0.1 mBq/g
	^{241}Pu	ICP-MS	0.03 Bq/g
	^{241}Am	α -spectrometry	0.1 mBq/g
	^{244}Cm	α -spectrometry	0.1 mBq/g
Water	^3H	LSC	0.05 Bq/ml
	^{14}C	LSC	0.02 Bq/ml
	^{55}Fe	LSC	0.01 Bq/ml
	^{63}Ni	LSC	0.002 Bq/ml
	^{36}Cl	LSC	0.002 Bq/ml
	^{129}I	LSC/AMS	0.002 Bq/ml, 0.1 $\mu\text{Bq/g}$ (AMS)
	^{41}Ca	LSC	0.02 Bq/ml
	^{90}Sr	Beta counting	0.002 Bq/ml
	^{99}Tc	Beta counter /ICP-MS	0.002 Bq/ml
	^{94}Nb	γ -spectrometry	0.1 Bq/ml
	^{238}Pu	α -spectrometry	0.1 mBq/ml
	^{239}Pu	α -spectrometry /ICP-MS	0.1 mBq/ml
	^{240}Pu	α -spectrometry /ICP-MS	0.1 mBq/ml
	^{241}Pu	ICP-MS	0.01 Bq/ml
	^{241}Am	α -spectrometry	0.1 mBq/ml
	^{244}Cm	α -spectrometry	0.1 mBq/ml

1239
 1240 # The value was estimated by using 20 g solid samples (1 g for ^3H and ^{14}C) and 100 ml
 1241 for water samples. * For metal samples exposed to the neutrons or direct contaminated,
 1242 0.1-0.5 g is required depending on the radioactivity level, and the MDAs are
 1243 corresponding to the sample amount. .

Conclusions

This paper presents the progress in the development of Radioanalytical methods for determination of radionuclides in ultra-low level samples in the environment, and analytical methods for the characterization of radioactive waste from decommissioning of nuclear facilities, the main achievements are briefly summarized below.

1) A series of radioanalytical methods have been developed and updated for determination of low-level anthropogenic and naturally occurring radionuclides in various environmental and biological samples for environmental radioactivity investigation, environmental process and oceanographic tracing.

2) A number of highly selective pre-concentration methods using AMP powder adsorption and $\text{K}_2\text{CuFe}(\text{CN})_6$ impregnated cartridge filtration were developed and applied for separation of cesium from 100-1000 liter water for determination of low-level ^{134}Cs and ^{137}Cs using gamma spectrometry. With further purification using ion exchange chromatography combined with triple quadrupole ICP-MS and N_2O as reaction gas, a method was also developed for determination of ^{135}Cs in environmental samples.

3) A simple method was developed for separation of strontium from large volume of environmental water samples (up to 100 L) and more than 20 g soil by precipitation without using highly toxic fuming nitric acid and chromate. By removal of Sr and Ra by sulfate precipitation and separation of yttrium as oxalate, ^{90}Sr was determined by measurement of its decay daughter of ^{90}Y . A rapid method based on extraction chromatography using Sr-resin was also developed for determination of ^{89}Sr and ^{90}Sr in samples of low strontium content, especially decommissioning samples, both ^{89}Sr and ^{90}Sr were determined using Cherenkov counting and LSC.

4) The stability of technetium in separation processes were investigated, a method was developed to separate technetium from large size environmental samples using co-precipitation. Ultra-low level ^{99}Tc in various environmental samples was

- 1272 determined by completely eliminating the isobaric and molecule ions
1273 interferences of Ru and Mo and sensitive measurement using ICP-MS.
- 1274 5) A method based on pre-concentration using co-precipitation and ion exchange
1275 chromatographic separation was developed for simultaneous separation of
1276 plutonium and neptunium from large environmental samples based on the
1277 precisely control of the valence states of two elements. Ultra-low level ^{239}Pu ,
1278 ^{240}Pu , ^{237}Np in environmental samples were determined using ICP-MS.
- 1279 6) A series of analytical methods for determination of ^{129}I in various environmental
1280 samples, such as water, air, aerosol, soil, sediment, vegetation, animal tissue, etc.
1281 have been developed. The separation of iodine was mainly implemented by using
1282 a specifically designed combustion system, it allows rapid separation of iodine
1283 from various solid samples with a chemical yield up to 100%. A carrier free
1284 separation method was developed using co-precipitation to separate iodine from
1285 environmental samples and to prepare measurement target without addition of any
1286 extra iodine carrier, this is useful for the determination of natural level ^{129}I . A
1287 number of separation methods were developed for speciation analysis of iodine in
1288 air, aerosol, water, soil and sediment, iodide, iodate, gaseous organic iodine,
1289 gaseous inorganic iodine, iodine associated with different components were
1290 separated using these methods. These methods have been successfully applied in
1291 the investigation of environmental processes.
- 1292 7) A number of innovative mass-spectrometric methods have been developed for
1293 measurement of ultra-low level radionuclides, including ^{99}Tc , ^{129}I , ^{236}U , ^{239}Pu ,
1294 ^{240}Pu , and ^{237}Np . AMS measurement methods were developed for accurate
1295 determination of ultra-low level ^{129}I down to 10^6 - 10^7 atom level. Combined with
1296 carrier free iodine separation, an AMS measurement method was developed to
1297 measure ^{129}I in AgI-AgCl target with microgram level iodine ($< 5 \mu\text{g}$). A direct
1298 AMS measurement method without chemical separation of iodine was developed
1299 for rapid determination of ^{129}I in environmental samples, with this method, 40
1300 samples can be analyzed within 5 hours and the detection limit is still 2-3 orders

1301 of magnitude lower than conventional radiometric methods. New ICP-MS
1302 methods using triple-quadrupole ICP-MS and collision/reaction gas have been
1303 developed for determination of ^{239}Pu , ^{240}Pu , ^{237}Np , and ^{236}U . With this method,
1304 the interference of uranium hydrides, and tailing of ^{238}U and ^{235}U can be
1305 significantly suppressed by using $\text{NH}_3\text{-He}$ and $\text{CO}_2\text{-He}$ as reaction gasses and two
1306 quadrupole mass separators, which enable to measure ^{239}Pu in a sample with Pu/U
1307 atomic ratio lower than 10^{-11} by combining this measurement technique and
1308 chemical separation.

1309 8) A series of analytical methods have been developed for the determination of
1310 difficult to measure radionuclides (e.g. ^3H , ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{63}Ni , ^{90}Sr , ^{93}Mo ,
1311 ^{94}Nb , ^{129}I , ^{135}Cs , and isotopes of Pu, Np, Am and Cm) in various radioactive
1312 waste for decommissioning of nuclear facilities and waste repository. Special
1313 efforts were given to ensure reliability in the determination of volatile
1314 radionuclides (e.g. ^3H , ^{14}C , ^{36}Cl , ^{99}Tc , ^{129}I), simple operation and rapid separation
1315 for reducing the radiation exposure and analytical time. Some sequential
1316 analytical procedures were proposed to determine all required radionuclides in
1317 one sample, to further reduce the analytical time, the sample amount, and
1318 consequently the radiation exposure. These methods have been successfully used
1319 in the characterization of decommissioning waste from the research and power
1320 reactors in Denmark and Sweden.

1321

1322 **Acknowledgements**

1323 The author thanks the colleagues and students in Radioecology and Tracer Studies (RAS)
1324 group in the Center for Nuclear Technologies, Technical University of Denmark, Dr.
1325 Sven P. Nielsen, Mr. Qingjiang Chen, Dr. Per Roos, Dr. Jixin Qiao, Dr. Szabolcs Osváth,
1326 Mr. Liuchao Zhu for their contributions in the development of the analytical methods
1327 summarized in this papers. Dr. Keliang and Prof. Wangsuo in Lanzhou University are
1328 appreciated for their contributions in the development of some methods and suggestions

to this paper. The author is grateful to Dr. Luyuan Zhang, Ms. Yanyun Wang, Dr. Ning Chen, Dr. Qi Liu, Dr. Weichao Zhang, Dr. Maoyi Luo, Dr. Shan Xing, Dr. Yukun Fan and prof. Weijian Zhou for their contribution in the development of the analytical methods for ^{129}I and its chemical species in environmental samples and AMS measurement methods for ^{129}I . The author also likes to thank prof. Zhifang Chai, prof. Jan Kucera, prof. Nora Vajda, prof. Phil Warwick, and prof. Amares Chatt for their great and continuous support and collaboration. This work was partly supported by NKS, the Ministry of Science and Technology of China (No. 2015FY110800), the National Natural Science Foundation of China (No. 11875261, 91643206, 11605206, 41603125), Chinese Academy of Sciences (132B61KYSB20180003), and National Research Program for Key Issues in Air Pollution Control (DQGG0105-02).

References

1. IAEA, Power Reactor Information System (PRIS), <https://www.iaea.org/pris/>
2. UNSCEAR (2000) Sources, Effects and Risk of Ionizing Radiation. UNSCEAR 2000 Report to the General Assembly, Annex C: Exposures from Man-made Sources of Radiation (New York): 195–204
http://www.unscear.org/docs/publications/2000/UNSCEAR_2000_Annex-C-CORR.pdf
3. UNSCEAR (2013) Sources, Effects and Risk of Ionizing Radiation. UNSCEAR 2013, Volume I, Report to the General Assembly, Scientific Annex A: Level and effect of radiation exposure due to the nuclear accident after the 2011 great east-Japan earthquake and Tsunami. New York 2014,
http://www.unscear.org/docs/reports/2013/13-85418_Report_2013_Annex_A.pdf
4. Gray J, Jones SR, Smith AD (1995). Discharge to the environment from the Sellafield site, 1952-1992., J. Radiol. Prot., 15 (1995), 99-131

- 1355 5. IRRIN (1999), Inventaire des rejets radioactifs des installation nuceairs, Groupe
1356 Radioecologie Bord Contentin, Vol.1
- 1357 6. Hou XL, Hansen V, Aldahan A, Possnert G, Lind OC, Lujaniene G (2009)
1358 Speciation of Iodine-129 in the Environment. Anal Chim Acta. 632:181-196
- 1359 7. Xu Y, Gu P, Zhao J, Wang L, Xiao XZ, Zhang GH, Han F (2017) Comprehensive
1360 evaluation of cesium removal by CuFC adsorption: the effects of initial
1361 concentration, CuFC dosage and co-existing ions in solution. J Radioannal Nucl
1362 Chem Lett. 311:531-540. DOI:10.1007/s10967-016-5049-1
- 1363 8. Park JH, Chang BU, Kim YJ, Seo JS, Choi SW, Yun JY (2008) Determination of
1364 low ^{137}Cs concentration in seawater using ammonium 12-molybdophosphate
1365 adsorption and chemical separation method. J Environ Radioact. 99:1815-1818.
1366 doi:10.1016/j.jenvrad.2008.07.006
- 1367 9. Olatunji MA, Khandaker MU, Mahmud HNME, Amin YM (2015) In fluence of
1368 adsorption parameters on cesiumuptake from aqueous solutions- a brief review. RSC
1369 Advances. DOI: 10.1039/c5ra10598f
- 1370 10. Chen QJ, Hou XL, Nielsen SP, Dahlgaard H, Yu Y (2002) Separation of Sr from Ca,
1371 Ba and Ra in the determination of radiostrontium by means of simple precipitation
1372 using $\text{Ca}(\text{OH})_2$, $\text{Ba}(\text{Ra})\text{Cl}_2$ or $\text{Ba}(\text{Ra})\text{SO}_4$. Anal Chim Acta. 466 (1): 109-116
- 1373 11. Shi KL, Hou XL, Roos P, Wu WS (2011) Determination of Technetium-99 in
1374 environmental samples: a review. Anal Chim Acta. 709:1-20
- 1375 12. Shi K, Hou XL, Roos P, Wu WS (2012) Stability of technetium and
1376 decontamination of Ru and Mo in determination of ^{99}Tc in environmental solid
1377 samples by ICP-MS. Anal Chem. 84:2009-2016
- 1378 13. Chen QJ, Dahlgaard H, Nielsen SP (1994) Determination of ^{99}Tc in seawater at
1379 ultra-low level. Anal Chim Acta. 285:177-180

- 1380 14. Chen QJ, Aarkrog A, Nielsen SP, Dahlgaard H, Lind B, Kolstad AK, Yu YX (2001)
1381 Procedures for determination of Pu, Am, Np, U, Th, ^{99}Tc , ^{210}Po - ^{210}Po in
1382 environmental materials, Risø report, Risø-R-1263, 2001.
1383 <http://130.226.56.153/rispubl/NUK/nukpdf/ris-r-1263.pdf>
- 1384 15. Shi K, Qiao JX , Roos P, Wu WS, Hou XL (2012) Rapid determination of
1385 technetium-99 in large volume seawater samples using sequential injection
1386 extraction chromatographic separation and ICP-MS measurement. *Anal Chem.*,
1387 2012, 84(15)6783-6789
- 1388 16. Hou XL, Jansen M, Nielsen SP (2007) Use of $^{99\text{m}}\text{Tc}$ from a Commercial $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$
1389 Generator as Yield Tracer for the Determination of ^{99}Tc at Low Levels. *Applied*
1390 *Radiation and Isotopes*. 65:610-618
- 1391 17. Qiao JX, Hou XL, Miró M, Roos P (2009). Determination of plutonium isotopes in
1392 waters and environmental solids: A review, *Analytica Chimica Acta*. 652: 66-84
- 1393 18. Qiao JX, Hou XL, Miró M, Roos P (2010) Rapid and simultaneous determination of
1394 neptunium and plutonium isotopes in environmental samples by extraction
1395 chromatography using sequential injection analysis and ICP-MS *Journal of*
1396 *Analytical Atomic Spectrometry*. 25(11):1769-1779
- 1397 19. Wang ZT, Yang GS, Zhang J, Cao LG, Yu HJ, Zhu YB, Tagami K, Uchida S (2015)
1398 Effect of ashing temperature on accurate determination of plutonium in soil samples.
1399 *Anal Chem*. 87:5511-5515. DOI: 10.1021/acs.analchem.5b01472
- 1400 20. Luo MY, Xing S, Yang YG, Song LJ, Ma Y, Wang YD, Dai XX, Happel S. (2018)
1401 Sequential analyses of actinides in large-size soil and sediment samples with total
1402 sample dissolution. *J Environ Radioact*. 187:73-80.
1403 <https://doi.org/10.1016/j.jenvrad.2018.01.028>
- 1404 21. Vajda N, Kim CK (2011) Determination of transuranium isotopes (Pu, Np, Am) by
1405 radiometric techniques: A review of analytical methodology. *Anal Chem*. 83:4688-
1406 4719. DOI: 10.1021/ac2008288

- 1407 22. Chen QJ, Dahlgard H, Nielsen SP, Aarkrog A (2002) Pu-242 as tracer for
1408 simultaneous determination of Np-237, Pu-239, Pu-240 in environmental samples. J
1409 Radioanal Nuc Chem. 253:451-458
- 1410 23. Qiao JX, Hou XL, Miró M, Roos P (2011) Reliable determination of ^{237}Np in
1411 environmental samples using ^{242}Pu as a potential tracer. Talanta. 84(2):494-500
- 1412 24. Qiao JX, Hou XL, Miró M, Roos P (2011) High throughput sequential injection
1413 method for simultaneous determination of plutonium and neptunium in
1414 environmental solids using microporous anion exchange chromatography, followed
1415 by ICP-MS detection, Anal Chem. 83(1):374-381
- 1416 25. Qiao JX, Hou XL, Miró M, Roos P (2013) Method for Determination of
1417 Neptunium in Large-Sized Urine Samples Using Manganese Dioxide
1418 Coprecipitation and ^{242}Pu as Yield Tracer. Anal Chem. 85:1889-1895
- 1419 26. Wang ZT, Zheng J, Ni Y, Men W, Tagami K, Uchida S (2017) High performance
1420 method for rapid determination of Pu isotopes in soil and sediment samples by sector
1421 field inductively coupled plasma mass spectrometry. Anal Chem. 89:2221-2226
- 1422 27. Hou XL, Zhang DX (2018) Determination of I-129 in environmental solid samples
1423 using pyrolysis separation and accelerator mass spectrometry measurement. J.
1424 Radioanal Nucl Chem. 317:487-499
- 1425 28. Hou XL, Wang YY (2016) Determination of ultra-low level ^{129}I in vegetation using
1426 pyrolysis for iodine separation and accelerator mass spectrometry measurement. J
1427 Anal At Spectrom. 31:1298-1310
- 1428 29. Hou XL, Dahlgard H, Rietz B, Jacobsen U, Nielsen SP, Aarkrog A (1999)
1429 Determination of iodine-129 in seawater and some environmental materials by
1430 neutron activation analysis. Analyst. 124:1109-1114
- 1431 30. Zhang LY, Hou XL, Xu S (2015) Speciation analysis of ^{129}I and ^{127}I in aerosol using
1432 sequential extraction and mass spectrometry detection. Anal Chem. 87(13):6937-
1433 6944

- 1434 31. Hou XL, Zhou WJ, Chen N, Zhang LY, Liu Q, Luo MY, Fan YK, Liang WG, Fu
1435 YC (2010) Determination of Ultralow Level $^{129}\text{I}/^{127}\text{I}$ in Natural Samples by
1436 Separation of Microgram Carrier Free Iodine and Accelerator Mass Spectrometry
1437 Detection, Anal Chem. 82(18):7713-7721
- 1438 32. Dang HJ, Hou XL, Roos P, Nielsen SP (2012) Release of iodine from organic matter
1439 in natural water by $\text{K}_2\text{S}_2\text{O}_8$ oxidation for ^{129}I determination. Anal Method.
1440 DOI:10.1039/c2ay25958c
- 1441 33. Luo MY, Hou XL, He CH, Liu Q, Fan YK (2013) Speciation analysis of ^{129}I in
1442 seawater by carrier free AgI-AgCl coprecipitation and AMS measurement. Anal
1443 Chem. 85(7):3715-3722
- 1444 34. Saiz-Lopez A, Plane JMC, Baker AR, Carpenter LJ, Von Glasow R, Gomez Martin
1445 JC, McFiggans G, Saunders RW (2012) Atmospheric chemistry of iodine. Chemical
1446 Reviews. 112:1773-1804. DOI:10.1021/cr200029u
- 1447 35. Hou XL, Dahlgaard H, Nielsen SP (2001) Chemical speciation analysis of ^{129}I in
1448 seawater and a preliminary investigation to use it as a tracer for geochemical cycle
1449 study of stable iodine. Mar Chem. 74:145-155
- 1450 36. Xing S, Hou XL, Aldahan A, Possner G, Shi KL, Yi P, Zhou WJ (2017) Water
1451 circulation and marine environment in the Antarctic traced by speciation of ^{129}I and
1452 ^{127}I . Sci Rep. 7:7726, DOI:10.1038/s41598-017-07765-w
- 1453 37. Liu D, Hou XL, Du JZ, Zhang LY, Zhou WJ (2016) I-129 and its species in the East
1454 China Sea: level, distribution, sources and tracing water masses exchange and
1455 movement. Sci Rep. 6; 36611, DOI: 10.1038/srep36611
- 1456 38. Hou XL, Fogh CL, Kucera J, Andersson KG, Dahlgaard H, Nielsen SP (2003)
1457 Iodine-129 and Cesium-137 in Chernobyl Contaminated Soil and Their Chemical
1458 Fractionation. Sci Total Environ. 308(1-3):97-109

- 1459 39. Qiao JX, Hansen V, Hou XL, Aldahan A, Possnert G (2012) Speciation analysis of
1460 ^{129}I , ^{137}Cs , ^{232}Th , ^{238}U , ^{239}Pu and ^{240}Pu in environmental soil and sediment. Applied
1461 Radiation and Isotopes. 70(8):1698-1708
- 1462 40. Luo MY, Hou XL, Zhou WJ, He CH, Chen N, Liu Q, Zhang LY (2013). Speciation
1463 and migration of ^{129}I in soil profiles. J Environ Radioact 118:30-39
- 1464 41. Englund E, Aldahan A, Hou XL, Petersen R, Possnert G (2010) Speciation of iodine
1465 (^{129}I and ^{127}I) in lake sediments, Nucl Instr Method B. 268(7-8):1102-1105
- 1466 42. Hou XL, Roos P (2008) Critical Comparison of Radiometric and Mass
1467 Spectrometric Methods for the Determination of Radionuclides in Environmental,
1468 Biological and Nuclear Waste samples. Anal Chim Acta. 608:105-139
- 1469 43. Hou XL (2018) Liquid scintillation counting for determination of radionuclides in
1470 environmental and nuclear application. J Radioanal Nucl Chem. 318:1597-1628.
- 1471 44. Xing S, Zhang WC, Qiao JX, Hou XL (2018) Determination of ultra-low level
1472 plutonium isotopes (^{239}Pu , ^{240}Pu) in environmental samples with high uranium,
1473 Talanta 187:357-364
- 1474 45. Liu Q, Hou XL, Zhou WJ, Fu YC (2015) Accelerator mass spectrometry analysis of
1475 ultra-low-level ^{129}I in carrier-free AgI-AgCl sputter targets. Journal of the American
1476 Society for Mass Spectrometry. 2015, 26(5):725-733
- 1477 46. Liu Q, Zhao XL, Hou XL, Burr G, Zhou WJ, Fu YC, Chen N, Zhang LY (2016)
1478 Preliminary Investigation on the Rapid and Direct AMS Measurement of I-129 in
1479 Environmental Samples without Chemical Separation. Radiocarbon. 58:147-156
- 1480 47. Hou XL (2005) Determination of ^{14}C and ^3H in Reactor Graphite and Concrete for
1481 Decommission, Applied Radiation and Isotopes, 62:871-882
- 1482 48. Hou XL (2011) Analysis of Urine for Pure Beta Emitters: Methods and Application,
1483 Health Phys. 101(2):159-169

- 1484 49. Hou XL (2007) Radiochemical analysis of radionuclides difficult to measure. J
1485 Radioanal Nucl Chem. 273:43-48
- 1486 50. Hou XL (2018) Tritium and ^{14}C in the Environment and Nuclear Facilities: Sources
1487 and Analytical Methods. J. Nucl. Fuel Cycle Waste Technol. 2018, 16: 1738-1894.
- 1488 51. Hou XL, Østergaard LF, Nielsen SP (2007) Determination of ^{36}Cl in Nuclear Waste
1489 from Reactor Decommissioning, Anal Chem. 79:3126-3134
- 1490 52. Hou XL (2005) Determination of ^{63}Ni and ^{55}Fe in nuclear waste and environmental
1491 samples. Anal Chim Acta. 535:297-307
- 1492 53. Hou XL, Olsson M, Togneri L, Englund S, Vaaramaa K, Askeljung GC,
1493 Gottfridsson O, Hirvonen H, Öhlin H, Forsström M, Anders F, Lampen M, Hatakka
1494 A (2016) Present status and perspective of radiochemical analysis of radionuclides in
1495 Nordic countries. J Radioanal Nucl Chem 309(3):1283-1319
- 1496 54. Hou XL (2005) Radiochemical determination of ^{41}Ca in reactor concrete for
1497 decommissioning. Radiochim Acta. 93:611-617
- 1498 55. Chen QJ, Nielsen SP, Aarkrog A, Dahlgård H, Duniec S (1993) Distribution of
1499 plutonium isotopes in cooling water from a PWR. J Nucl Sci Technol. **30**:164-170
- 1500