



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

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

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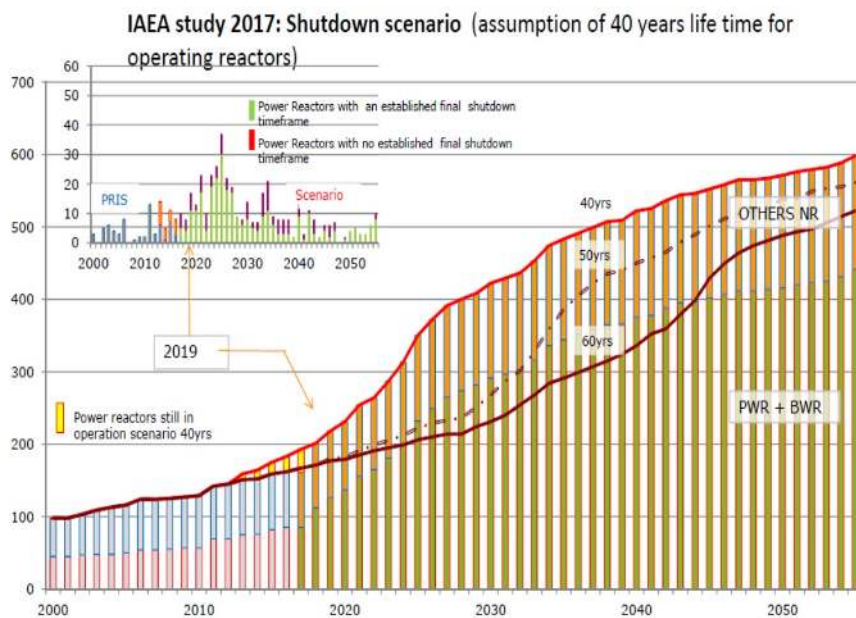
33 Radioanalytical methods for low-level radionuclides; mass spectrometry; speciation
34 analysis; environmental process tracing; decommissioning;

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](#)

61 shows the number of nuclear power reactors closed and to be closed in the world [1].
62 These closed nuclear facilities have to be well decommissioned to release the sites for
63 other purpose. In all processes of decommissioning, including preparation by background
64 radioactivity investigation of the site, cleanout by removal of spent nuclear fuel,
65 decontamination by removal of contaminant from the surface of the facilities and devices,
66 dismantling by cutting, demolition, waste removal and site clearance, waste depository by
67 classification of the produced waste and site release by measurement of the site, various
68 radionuclides in the relevant materials have to be determined for suitable treatment and
69 final repository of the produced wastes, management of the decommissioning process and
70 evaluation of the decommissioning quality. For these purposes, the analysis of various
71 decommissioning samples for their radiological and chemical characterization is the most
72 important issue. Among them, the determination of various difficult-to-measure
73 radionuclides is the major challenge, because of complicated and unknown composition
74 of sample matrix, significant difference in the radioactive level of radionuclides,
75 instability of some volatile radionuclides, and complicated chemical properties and
76 chemical species of some radionuclides. Since 2000, our laboratory has developed a
77 series of radioanalytical methods for determination of difficult-to-measure radionuclides
78 (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
79 decommissioning samples such as concrete, graphite, metals, resin, filters, etc. These
80 methods have been successfully applied in the characterization of decommissioning
81 waste of research and power reactors, hot cells and other nuclear facilities, as well as
82 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

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

103 Up to now, two large nuclear accidents happened in April 1986 in Chernobyl NPP and in
104 March 2011 in Fukushima Daiichi NPP (FDNPP) have released large amount of
105 radionuclides to the atmosphere, causing a relative high radioactive deposition in the
106 Europe during Chernobyl accident and in Japan during the Fukushima accident. FDNPP
107 has also discharged some fraction of liquid radioactive substance to the sea, caused
108 significantly increased radioactivity in the seawater off Fukushima [3]. In addition, some
109 relative small scale accidents were also occurred and released some radionuclides to the
110 environment. The accident of a graphite reactor fire at Windscale (UK) in 1957 had
111 released 1×10^{15} Bq of ^{131}I , 9.4×10^{13} Bq of ^{90}Sr to the atmosphere. An explosion in a
112 plutonium production plant in Kyshtym (USSR) in 1957 released 2×10^{15} Bq of ^{90}Sr and
113 3×10^{13} Bq of ^{137}Cs . Accidents of aircrafts carried nuclear weapons happened in
114 Palomares (Spain) in 1966 and in Thule (Greenland) in 1967 have released some amount
115 of plutonium and americium to the environment. A satellite (SNAP-9A) with ^{238}Pu as
116 fuel fell down and burned over Indian Ocean in 1964 and released 6.3×10^{14} Bq of ^{238}Pu
117 to the atmosphere, and another satellite fueled with a nuclear reactor fell down and burned
118 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
119 atmosphere.

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

126 substance to the seas and atmosphere [4, 5]. Compared with the above three sources, the
 127 amount of radionuclides discharged to the environment from the operation of nuclear
 128 reactors, isotope production and medical application in the hospital is minor (UNSCEAR
 129 2000). [Table 1](#) presents the amount of major long-lived radionuclides released to the
 130 environment from the nuclear weapons tests, reprocessing plants (Sellafield and La
 131 Hague) and nuclear accidents in Chernobyl and Fukushima. It can be seen that the major
 132 contribution of the anthropogenic radionuclides in the environment (excluding those
 133 remained in the spent nuclear fuel and stored as nuclear waste) is the atmospheric nuclear
 134 weapons tests, they caused a deposition of anthropogenic radionuclides all over the
 135 world. [Fig. 2](#) shows temporal variation of the measured ^{137}Cs and ^{90}Sr concentrations in
 136 aerosol samples collected at Risø, Denmark from 1950's to the present. The highest
 137 levels of ^{137}Cs and ^{90}Sr in the aerosol were observed in early 1960's when large numbers
 138 of atmospheric nuclear weapons tests were conducted in 1961-1962 by USA and USRR.
 139 Declined levels of ^{137}Cs and ^{90}Sr with some small peaks were observed afterwards
 140 because some atmospheric nuclear weapons tests were conducted by UK, France and
 141 China, which completely ceased in 1980. This caused a continuously decreased level of
 142 ^{90}Sr in the aerosol. Two peaks of ^{137}Cs levels were clearly observed in 1986 and 2011,
 143 which were attributed to the releases from Chernobyl and Fukushima accidents,
 144 respectively.

145

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

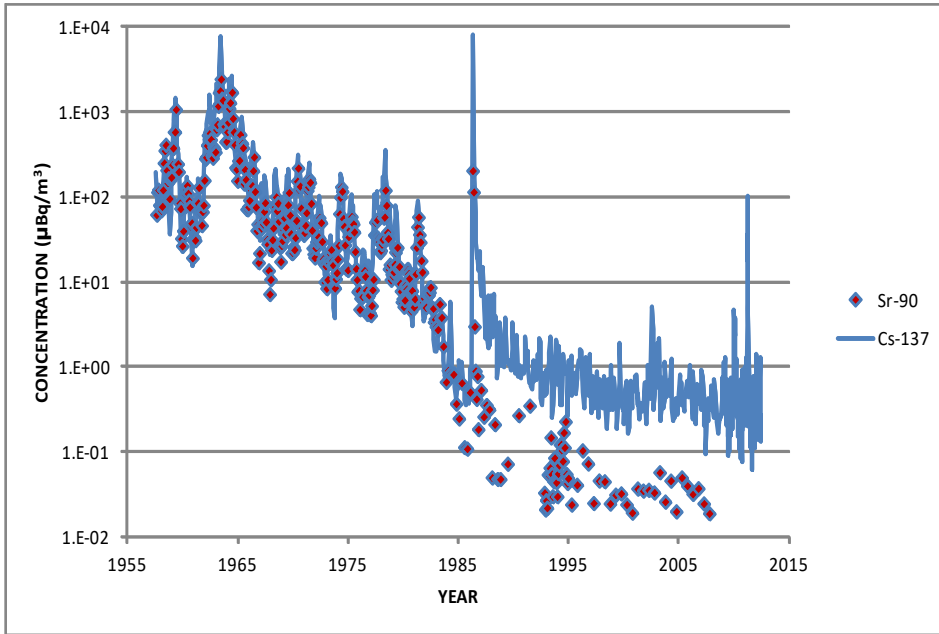
Nuclide	Released activity, 10^{15} Bq			
	Nuclear weapons tests	Reprocessing	Chernobyl accident	Fukushima accident
^{137}Cs	1280	17.45	85	15
^{90}Sr	850	3.39	10	0.9
^{144}Cs	1.04×10^6	0.51	116	

^{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.

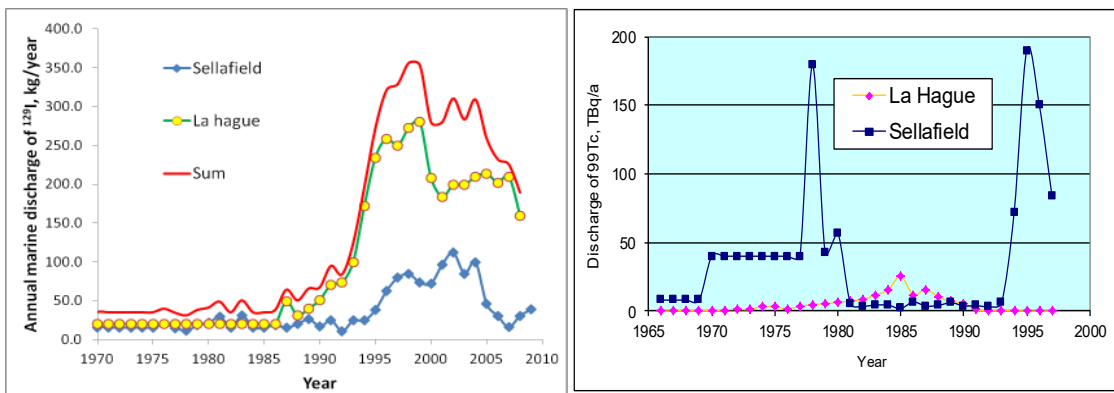
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168

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

171



172

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

175

176 **Determination of ultra-low level radionuclides in the environment**

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

193 *Chemical separation of radionuclides from environmental samples*

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

205 *Separation of cesium from water samples for the determination of ^{134}Cs , ^{135}Cs , ^{137}Cs .*
206 Selective adsorption is the most often applied method for separation of cesium from big-
207 size water sample up to 1000 liters. Powder of ammonium molybdophosphate (AMP) and
208 potassium cupriferricyanide ($\text{K}_2\text{CuFe}(\text{CN})_6$, KCuFC) are the most often applied
209 adsorbents for this purpose [7, 8]. AMP was used to separate cesium from water
210 (seawater or fresh water) in acidic medium, the sample is often acidified to pH2 on-site
211 during sample collection using HCl. AMP powder is directly added to the sample
212 solution (stable cesium or ^{134}Cs is added as chemical yield tracer) and mixed by stirring
213 for 1-2 hours. After settling for a few hours (or overnight), the AMP powder is separated
214 by discarding the supernatant, and collecting the sludge AMP on a filter paper. ^{134}Cs and
215 ^{137}Cs adsorbed on the AMP powder are then measured using an HPGe gamma detector.
216 The chemical yield is measured by determining stable cesium in the sample solution
217 before and after separation, or ^{134}Cs in the separated sample by gamma spectrometry and
218 compared with the spiked amount (if no ^{134}Cs is present in the samples). A high recovery
219 of more than 95% can be often obtained. ^{135}Cs as a long-lived (2.3×10^6 years) pure beta
220 emitter is also adsorbed on the AMP, for its determination, a further separation from
221 interferences such as ^{135}Ba for ICP-MS measurement has to be implemented. For some
222 water samples, a pre-filtration through a filter is necessary for removal of any suspending
223 substance/colloids in the water sample, to obtain water soluble radiocesium concentration
224 and a better chemical yield.

225 For more than 100 liters water samples, the AMP method is not suitable for operation,
226 especially on board of a scientific vessel. In this case, a cartridge impregnated with
227 potassium cupriferricyanide ($\text{K}_2\text{CuFe}(\text{CN})_6$) or other transition metal ferrocyanides (such
228 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
229 high selectivity and capacity for adsorption of cesium (K_d of 10^5) in neutral or slight
230 acidic media. For preparation of potassium cupriferricyanide cartridge, a polypropylene
231 cartridge is first impregnated to cupric sulfate solution, then to a solution of potassium
232 hexacyanoferrate (II), $\text{K}_2\text{CuFe}(\text{CN})_6$ precipitate is formed on the cartridge, which can be
233 mounted to the cartridge holder (Fig. 4) after dried. Seawater sample can be directly
234 pumped through two sequentially connected cartridges after past through a pre-filtration

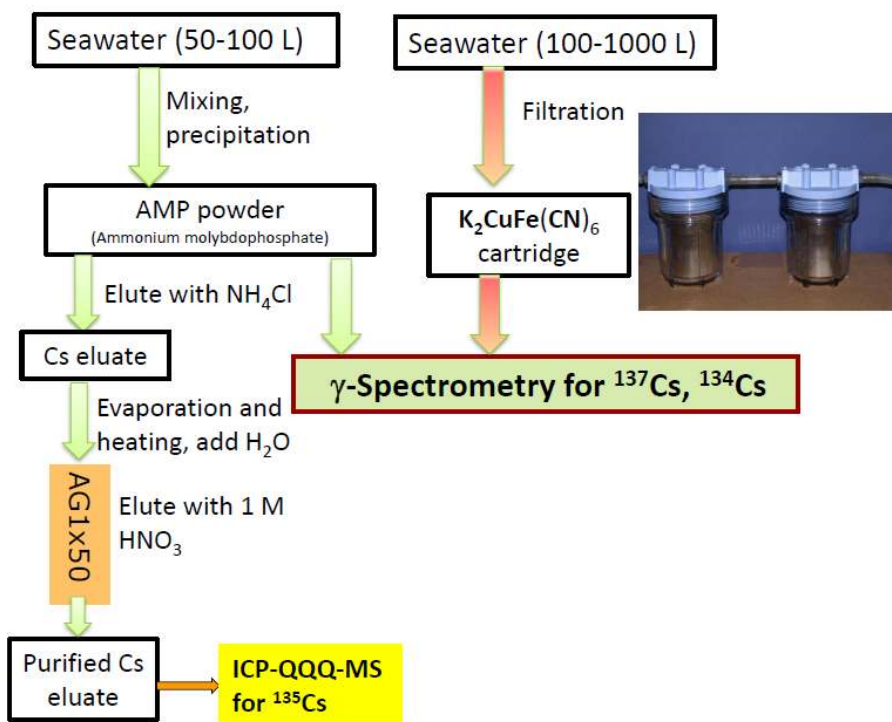
235 cartridge for removal of suspended substance. The chemical recovery can be monitored
236 using stable cesium or ^{134}Cs spiked to the sample before separation, a recovery of more
237 than 80% is often obtained for two sequential cartridges. Radiocesium on the cartridge
238 can be measured using gamma spectrometry after dried and ashed at low temperature (<
239 450 °C).

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

246

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

260



261

262 Fig. 4 Analytical procedure for determination of radiocesium (^{134}Cs , ^{135}Cs , ^{137}Cs) in
 263 water samples

264

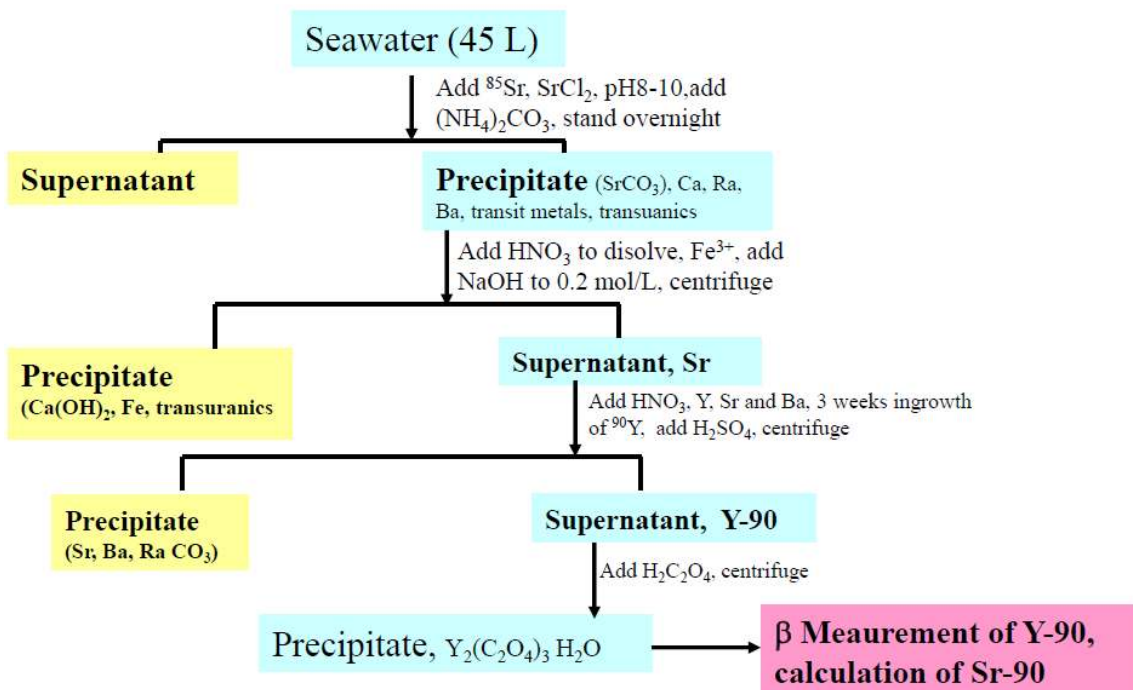
265 A number of methods have been developed to simplify the separation procedure and to
 266 improve the detection limit. In our laboratory, an analytical procedure without application
 267 of harmful fuming nitric acid and chromate was developed for analysis of large-size
 268 water samples (seawater and fresh water) for determination of ^{89}Sr and ^{90}Sr . Strontium
 269 was first separated from large volume of water (up to 100 liter) by precipitation of
 270 strontium as SrCO_3 after addition of stable strontium as carrier, and then carbonate (e.g.
 271 $(\text{NH}_4)_2\text{CO}_3$). Calcium in the sample in a high concentration was also precipitated as
 272 CaCO_3 in this step. A precipitation of hydroxide step was therefore followed to remove
 273 calcium based on lower solubility of $\text{Ca}(\text{OH})_2$ in a relative high concentration of NaOH
 274 solution (0.2-0.5 mol/l) compared to $\text{Sr}(\text{OH})_2$. ^{85}Sr (a gamma emitter) can be used as
 275 chemical yield tracer in this step. For removal of the interferences of radioisotopes of Ra,
 276 the separated strontium solution was settled for 2-3 weeks for the ingrowth of its decay
 277 daughter ^{90}Y after addition of stable yttrium. Sulfuric acid was then added to the sample

278 solution, and the formed sulphate precipitate of SrSO_4 , RaSO_4 and BaSO_4 were removed
279 by filtration, and ^{90}Y remaining in the solution was then separated by precipitation of
280 $\text{Y}_2(\text{C}_2\text{O}_4)_3$ by addition of $\text{H}_2\text{C}_2\text{O}_4$ under a slightly acidic condition. The chemical yield of
281 yttrium can be measured using yttrium spiked to the samples solution by gravimetry or
282 ICP-OES. ^{90}Y in the precipitation was measured using an ultra-low background GM
283 counter (Risø multi-counter), and ^{90}Sr concentration can be calculated according to the
284 ingrowth time and chemical yields. The overall chemical yield (including Sr and Y) is
285 normally higher than 85% [10]. Fig. 5 shows the analytical procedure of this method for
286 determination of ^{90}Sr in large volume of water samples. It should be mentioned that for
287 the analysis of fresh water samples, some amount of calcium needs to be added to
288 improve the chemical recovery of strontium in the first step. This procedure has been
289 successfully applied in our laboratory for routine analysis of environmental samples for
290 more than 15 years, and demonstrated to be robust and accurate method for determination
291 of ultra-low level ^{90}Sr in large-size samples with high strontium content.

292 The method presented above is still time consuming and applicable only for ^{90}Sr ,
293 especially because of long waiting time for ingrowth of ^{90}Y . Another method was also
294 developed for rapid determination of both ^{89}Sr and ^{90}Sr by using extraction
295 chromatographic separation. In this method, strontium in the sample leachate (from solid
296 samples, such as soil, sediment, and ash of vegetable and tissues) or small size of water
297 samples (< 2 liters) was first separated from sample matrix by precipitation of SrC_2O_4 at
298 pH2 after addition of small amount of stable strontium carrier. A $\text{Sr}(\text{NO}_3)_2$ precipitation
299 is followed to separate strontium from most of interfering radionuclides (e.g. radium and
300 barium isotopes) by addition of small amount of fuming nitric acid (<10 ml). The
301 separated $\text{Sr}(\text{NO}_3)_2$ was dissolved in water and prepared in 8 mol/l HNO_3 solution, which
302 was then loaded to a Sr-resin column (2-4 ml depending on the sample size and estimated
303 Sr content). After rinsing with 8 mol/l HNO_3 , strontium on the column was eluted using
304 0.01 mol/l HNO_3 , which was directly used for measurement of ^{89}Sr and ^{90}Y using liquid
305 scintillation counter by counting Cherenkov radiation of ^{89}Sr immediately after
306 separation, and then re-counting after 1-3 weeks for the Cherenkov radiation of $^{90}\text{Y}+^{89}\text{Sr}$,
307 to obtain both ^{89}Sr and ^{90}Sr concentrations. ^{90}Sr can be also measured by LSC with
308 addition of scintillation cocktail after the Cherenkov counting for ^{89}Sr . In this case, no

309 waiting time for ingrowth of ^{90}Y is needed and the results can be obtained in a short time
 310 (<1 day, including the chemical separation and measurement). The chemical yield of
 311 strontium in all procedure was measured by determination of stable strontium before and
 312 after separation using ICP-OES.

313

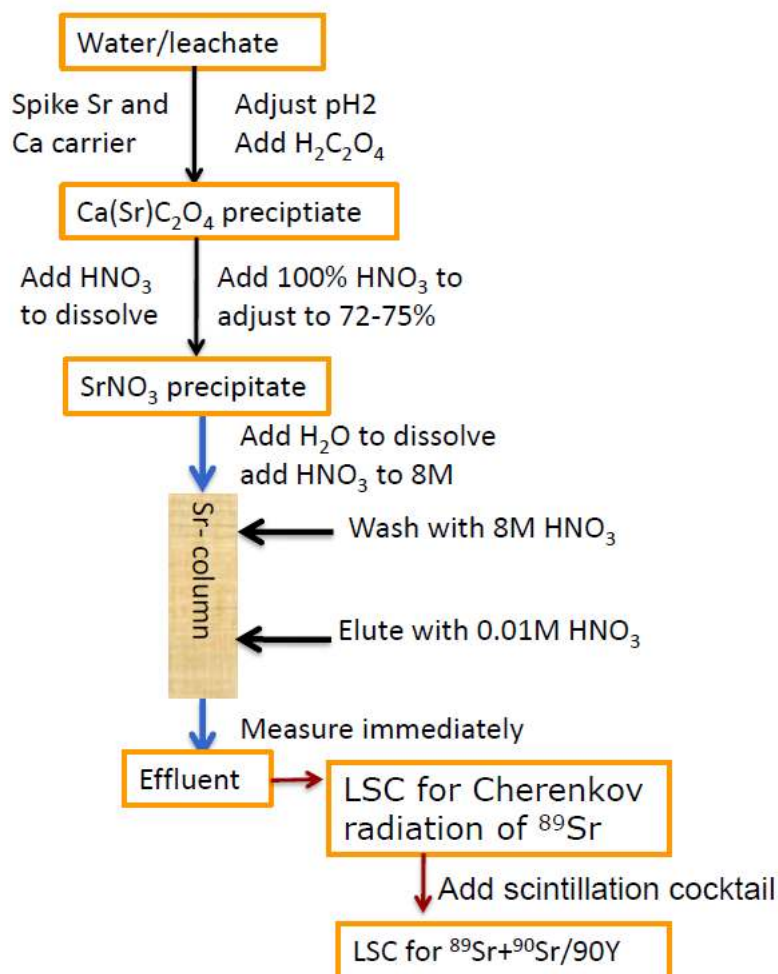


314

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

316

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



323

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

325

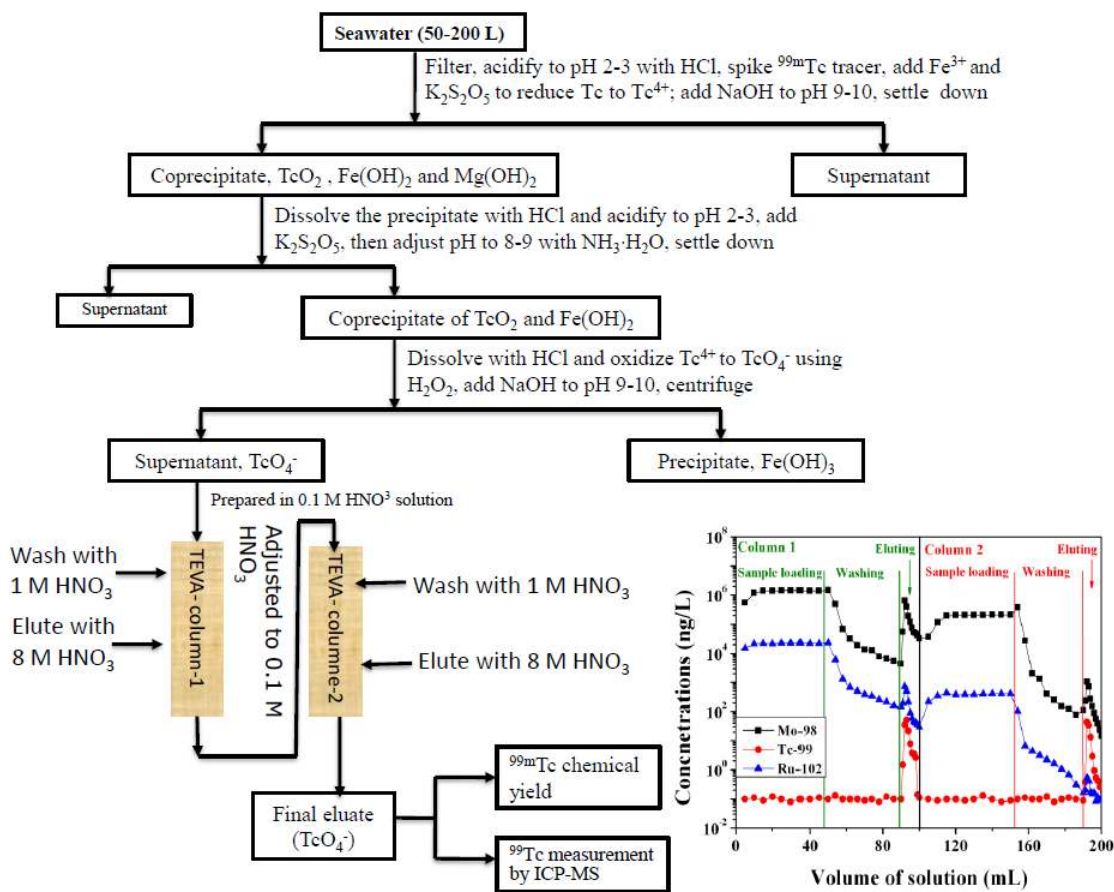
326 *Separation of technetium for determination of ^{99}Tc .* Technetium is a radioactive element
 327 without any stable isotope. ^{99}Tc is a long-lived (2.1×10^5 years) radionuclide and the
 328 major isotope of technetium occurred in the environment. Due to its high fission yield
 329 (6.1% for ^{235}U) and high mobility in the environment, it is one of the most important
 330 radionuclides in the environmental radioactivity investigation and waste repository [11].
 331 Technetium is volatile at relative high temperature, its stability in the separation
 332 procedure is critical for its determination. We have investigated the stability of
 333 technetium in different sample matrices during ashing and heating [12]. It was found that
 334 technetium is not stable in HCl medium during evaporation, while it is relative stable in

335 HNO₃ medium. Almost all technetium was lost when a technetium solution in 6 mol/l
336 HCl medium was evaporated to dryness even at 100°C. While more than 95% technetium
337 was remained when technetium in a neutral, alkaline solution or HNO₃ solution up to 8
338 mol/l was evaporated to dryness. Technetium is quite stable in brown seaweed (e.g.
339 fucus) during ashing even at 700 °C for 14 hours. While significant amount of technetium
340 was lost when it is present in soil and ashed at temperature more than 550 °C. It was
341 observed that more than 60% of technetium in soil was lost when ashing at 700°C for 6
342 hours. It is therefore recommended that the soil sample should be ashed at less than 550
343 °C for overnight (12-15 hours) to decompose organic substances before chemical
344 separation. Technetium mainly exists in Tc⁴⁺ and TcO₄⁻ forms, Tc⁴⁺ is not stable in
345 solution and easily formed TcO₂ to be associated with particles, while TcO₄⁻ is quite
346 stable in both acidic and alkaline solutions, which is also the most often occurred species
347 of technetium in oxidative media.

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

364 A separation procedure based on the co-precipitation of TcO_2 with $\text{Fe}(\text{OH})_2$ in reductive
365 condition, combined with extraction chromatographic separation using TEVA column
366 has been developed for determination of ultra-low level ^{99}Tc in seawater [15]. Seawater
367 samples up to 200 liters were first acidified with HCl to pH2, and FeCl_3 and $^{99\text{m}}\text{Tc}$ tracer
368 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
369 added to adjust pH9-10, and the formed $\text{TcO}_2\text{-Fe}(\text{OH})_2$ coprecipitate was then separated
370 by settling down for overnight followed by discarding the supernatant and filtrate the
371 precipitate. The precipitate was then dissolved with HCl and treated with H_2O_2 to convert
372 technetium to TcO_4^- . After removal iron by $\text{Fe}(\text{OH})_3$ precipitation with addition of NaOH
373 to pH8-9, the TcO_4^- in the supernatant was further purified using 2 sequentially connected
374 TEVA columns. The purpose of two TEVA columns was to improve the decontamination
375 factors to Ru and Mo , which cause high interferences for the ICP-MS measurement
376 through $^{99}\text{Ru}^+$ isobar and $^{98}\text{Mo}^1\text{H}^+$ polyatomic ion. Fig. 7 shows the analytical procedure
377 for determination of ultra-low level ^{99}Tc in large volume of seawater samples.

378 For solid samples, such as soil, sediment and seaweed, they were first ashed at 550 °C or
379 700 °C (for brown seaweed) to decompose all organic substance. Technetium was then
380 leached from the ashed samples using HCl and H_2O_2 . Technetium in the leachate was
381 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
382 technetium to Tc^{4+} and adjusted to pH8-9 to form $\text{TcO}_2\text{-Fe}(\text{OH})_2$ precipitate. ^{99}Tc was
383 then further purified using chromatography with TEVA resin and measured using ICP-
384 MS. The short-lived $^{99\text{m}}\text{Tc}$ obtained from $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator was used as chemical
385 yield tracer. Since minor amount of ^{99}Mo and ^{99}Tc is might present in the $^{99\text{m}}\text{Tc}$ eluate
386 from the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ generator, the generator needs to be pre-eluted 2-5 times to remove
387 accumulated ^{99}Tc from the generator, and the freshly eluted $^{99\text{m}}\text{Tc}$ was further purified by
388 using a Al_2O_3 cartridge filter [16]. $^{99\text{m}}\text{Tc}$ in the final solution was measured using gamma
389 spectrometry and chemical yield is calculated by comparing it to the amount of $^{99\text{m}}\text{Tc}$
390 spiked to the sample before separation.



391

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

393

394 *Separation of plutonium and neptunium for the determination of their isotopes.* The
 395 concentrations of plutonium and neptunium isotopes are normally very low in
 396 environmental samples, separation of plutonium and neptunium from big-size sample is
 397 necessary to obtain reliable analytical results. Pre-concentration of plutonium and
 398 neptunium from large volume of water (up to 200 liters) is often implemented by co-
 399 precipitation with $\text{Fe}(\text{OH})_2$, MnO_2 , or lanthanide fluoride. After removal of the suspended
 400 particles and acidification of the water to pH2 using HCl, carrier (e.g. Fe^{2+}) and chemical
 401 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
 402 stirring to reduce species of plutonium and neptunium to Pu^{3+} and Np^{4+} to ensure a better
 403 recovery. Ammonia was then added to adjust pH8-9 for co-precipitate $\text{Pu}(\text{OH})_3$ and
 404 $\text{Np}(\text{OH})_4$ with $\text{Fe}(\text{OH})_2$, which were separated by settling down for overnight, discarding

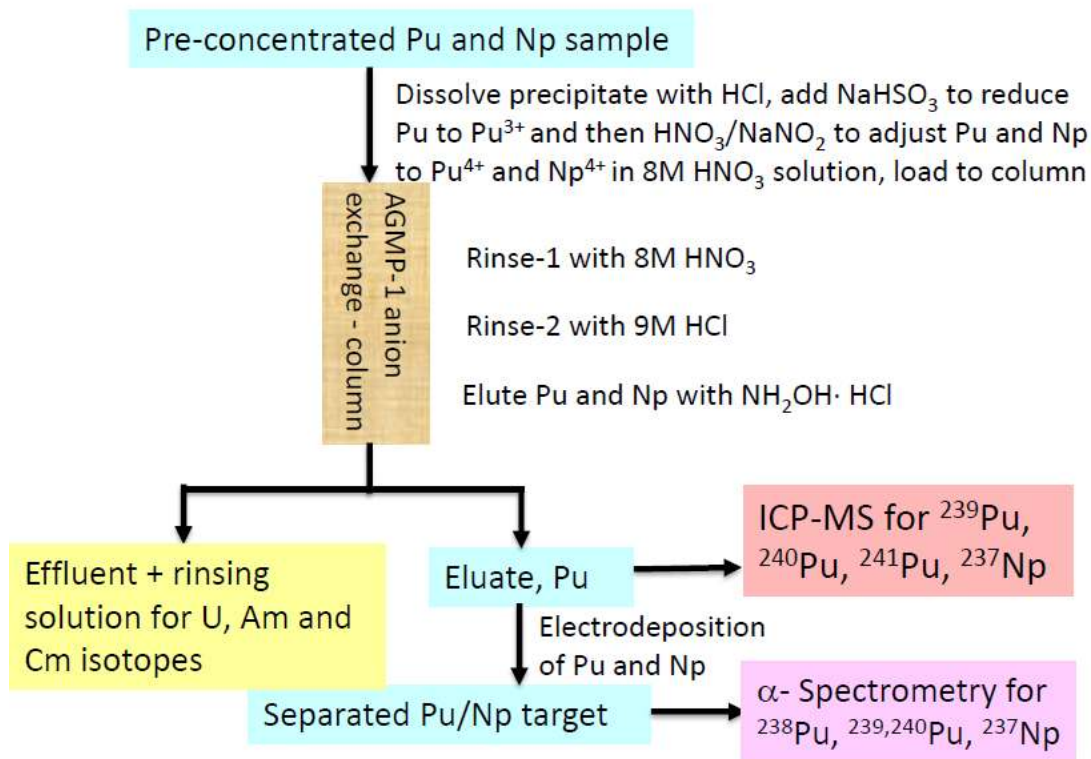
405 the supernatant and centrifuge. The precipitate was dissolved with HCl, and co-
406 precipitation was repeated by addition of ammonia to pH8-9 to remove excess of Ca and
407 Mg. The precipitate was dissolved again using HCl, and then concentrated HNO₃ or
408 NaNO₂ was added to convert plutonium to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

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

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

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

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



459

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

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

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

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

474 various solid samples such as soil, sediment, vegetation and aerosol [27, 28]. By
475 employing a modified 4-tubes Pyrolyse system (RADDEC International), four samples
476 can be treated in the same time. In this method, ^{125}I chemical yield tracer was first mixed
477 with sample in a quartz boat, up to 20 sample (soil/sediment) can be analyzed. The
478 sample boat was inserted to a quartz tube in a three zones furnace, the temperature and
479 heating sequence were programmed and precisely controlled. When the temperature of
480 the furnace was increased up to 800 °C, all iodine was released as gaseous iodine, and
481 trapped in a bubbler filled with diluted NaOH solution. The chemical yield in this process
482 was more than 95% depending on sample type. The most critical step is the
483 burning/carbonization in the analysis of samples of large amount of organic matter, such
484 as vegetation, wood, aerosol/filter and high organic sediment. The rapidly increased
485 temperature might cause quick burning of large amount of organic substance and create
486 large amount of CO_2 and other gasses in a short time. As a consequence, un-decomposed
487 materials (carbon particles) will be transported to the bubbler by the flowing gasses ($\text{N}_2 +$
488 O_2), even a splashing of the trap solution in the bubbler and small explosion of the quartz
489 tube may occur. Slowly increased temperature in the carbonization step of the sample
490 combustion was found to be an effective approach for solving this problem. A 2 °C/min
491 temperature increasing rate in 250-400°C for soil/sediment samples, and 1°C/min rate in
492 230-300 °C for vegetation/wood samples were confirmed to be suitable [27, 28].

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

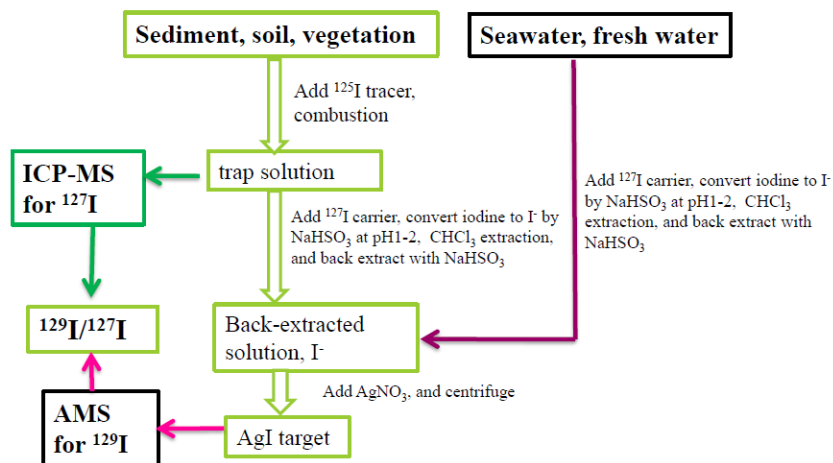
503 caused a low recovery. Therefore, the oxidative combustion was confirmed to be a more
504 effective method for releasing iodine from solid sample matrix.

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

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

527 Iodine is also present in organic form in water samples [6], direct solvent extraction and
528 AgI precipitation only separate inorganic iodine (mainly iodide and iodate). For
529 determination of total ^{129}I or organic associated ^{129}I , an oxidative decomposition method
530 was developed using strong oxidant $\text{K}_2\text{S}_2\text{O}_8$ at an increased temperature. It was found
531 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 .



535

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

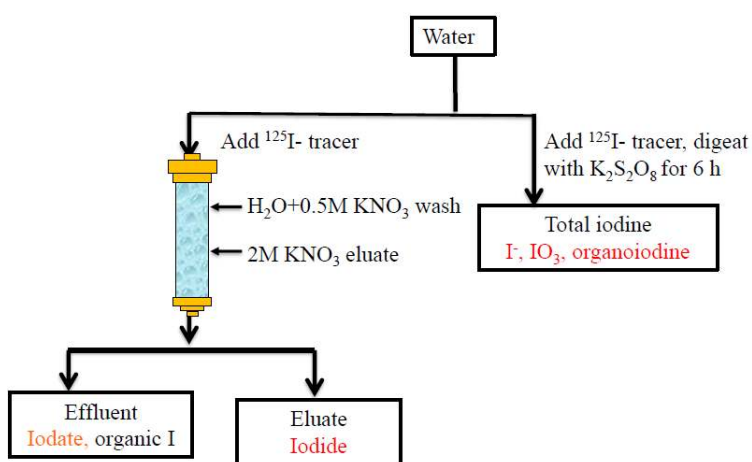
538

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 $AgI-AgCl-Ag_2SO_3$ 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 Ag_2SO_3 precipitate [33]. Ag_2SO_3 can be removed by washing the co-precipitate
 549 with HNO_3 , 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.

552 In seawater, iodine is present as iodide, iodate and minor amount of organic iodine
553 depending on the marine environment. While in fresh water samples, organic iodine
554 might accounts for a relative large fraction. In the atmosphere, iodine is present as both
555 gaseous forms and particle associate forms. The specific species of gaseous iodine in the
556 atmosphere are very complicated [34], but can be classified as gaseous inorganic iodine
557 (mainly I₂, HI, HIO, etc.) and gaseous organic iodine (mainly alkyl iodide). In aerosol,
558 soil and sediment, iodine is mainly associated to different components of the sample,
559 therefore often separated into different fractions such as water soluble, exchangeable,
560 carbonate, oxides, organic and mineral associated forms. While, in biological samples
561 including vegetation and animal tissues, iodine is mainly bound to different organic
562 compounds [6].

563 We have developed a series of methods for speciation analysis of ¹²⁹I in different
564 environmental samples. Separation method based on anion exchange chromatography
565 [35], co-precipitation [33], and solvent extraction were developed for separation of iodide
566 and iodate for the speciation analysis of iodine in water samples. The anion exchange
567 chromatographic procedure is based on the high affinity of iodide compared with iodate
568 on strong base anion exchange resin (e.g. Dowex 1 or AG1). Water samples were directly
569 loaded to an anion exchange column filled with Bio-Rad AG1-×4 resin in NO₃⁻ form.
570 Iodide was adsorbed on the column, while iodate and organic iodine passed through.
571 Small fraction of iodate remained on the column was removed by rinsing with diluted
572 (0.5 mol/l) KNO₃, iodide on the column was finally eluted with 2 mol/l KNO₃. For
573 separation of iodate, the effluent and rinsing solution were combined, acidified to pH<2
574 using HCl. Iodate in the sample was reduced to iodide by addition of KHSO₃ solution
575 and separated using the same procedure as for iodide (Fig. 10). The eluted iodine from
576 the column was further separated from matrix using solvent extraction and prepared as
577 AgI for AMS measurement [35]. A simple co-precipitation method was developed to
578 separate iodide and iodate from seawater for speciation analysis of ¹²⁹I, which is more
579 suitable for application on board of a ship. This method is based on the selective
580 coprecipitation of AgI with Ag₂SO₃ and AgCl at pH4-6, the Ag₂S₂O₃ and excessive
581 amount of AgI could be removed by washing with HNO₃ and ammonium. Addition of

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



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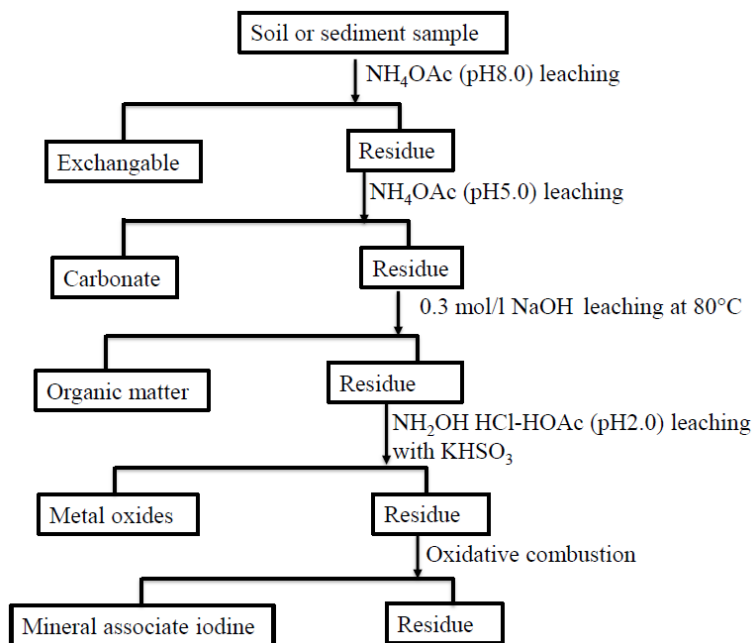
601 Fig. 10 Schematic diagram of separation procedure for speciation analysis of ¹²⁹I in
 602 water samples using anion exchange chromatography

603 A three-fraction air iodine collector was developed for separation of particle associate,
604 inorganic gaseous iodine and organic gaseous iodine from air, the collector was
605 connected to an air pump [6]. In this collector, particle associate iodine (aerosol) was first
606 collected on a glass fiber filter of 0.45 μm pore size, followed by two layer cellulosic
607 filter impregnated with NaOH for collecting inorganic gaseous iodine (HI, I₂, HOI, etc.),
608 and the organic gaseous iodine (alkyl iodide) was finally collected by an active carbon
609 cartridge, in which the active charcoal was purified by washing with NaClO and NaOH,
610 and impregnated with triethylenediamine. Iodine collected in the filter or cartridge was
611 then separated by combustion using tube furnace, and prepared as AgI for determination
612 of ¹²⁹I.

613 For speciation analysis of ¹²⁹I in aerosol, a sequential extraction followed by anion
614 exchange chromatographic method was developed in our laboratory. Iodide, iodate, water
615 soluble iodine organic and mineral associated iodine were sequentially separated, each
616 fraction of iodine was then purified and finally prepared as AgI for measurement of ¹²⁹I
617 using AMS [30]. In this method, aerosol samples cut into small pieces was first leached
618 with deionized water, and the leachate was divided into two parts, one was used for
619 determination of total water soluble ¹²⁹I by digestion with K₂S₂O₈ in acidic condition and
620 heating followed by solvent extraction. Iodide and iodate in another part of water leachate
621 were separated using anion exchange chromatographic method as described above for
622 water samples, and used to determine ¹²⁹I in iodide and iodate form. The residue filter
623 after water leaching was leached with 0.5 mol/l NaOH at 45°C. The leachate was treated
624 using the same method as that for determination of the total ¹²⁹I, i.e. digestion with
625 K₂S₂O₈ followed by solvent extraction, this fraction of ¹²⁹I was considered as organic
626 associated ¹²⁹I. Iodine still remained in the remained residue was separated by oxidative
627 combustion using tube furnace, followed by purification by solvent extraction or direct
628 AgI precipitation for determination of ¹²⁹I in the mineral fraction of aerosol. The analysis
629 of aerosol collected in Denmark showed that most ¹²⁹I is present as organic associate
630 iodine, and the water soluble ¹²⁹I is mainly present as iodide [30].

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

633 fractionation method was modified to avoid the loss of the iodine during the separation
 634 [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

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

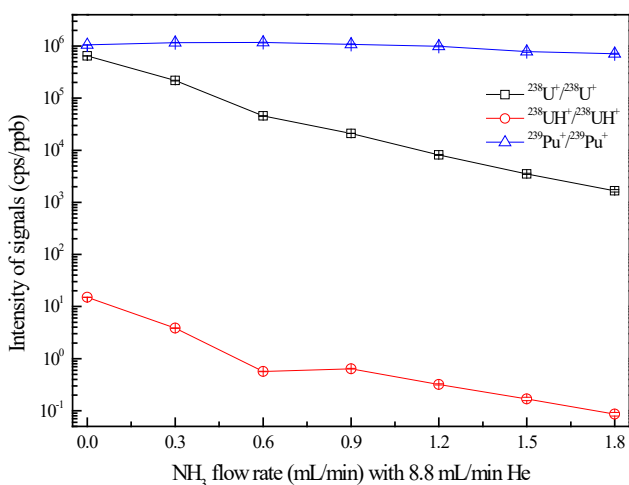
684 Many mass spectrometry techniques can be used to measure radionuclides, such as
685 inductively coupled plasma mass spectrometry (ICP-MS), accelerator mass spectrometry
686 (AMS), thermal ionization mass spectrometry (TIMS), resonance ionization mass
687 spectrometry (RIMS), secondary ion mass spectrometry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

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

710 $^{200}\text{Hg}^{40}\text{Ar}^+$, etc.). Uranium is an abundant element on the earth, the concentration of
711 uranium in the environment is normally more than 6 orders of magnitude higher than that
712 of plutonium, causing ^{238}U the major interferences in the ICP-MS measurement of ^{239}Pu
713 and ^{240}Pu . To eliminate the interference of uranium hydrides ($^{238}\text{U}^1\text{H}^+$, $^{238}\text{U}^1\text{H}_2^+$),
714 different dynamic reaction gases were investigated in our lab. It was found that simple
715 collision reaction using He cannot effectively destroy hydrides of uranium, therefore
716 could not remove its interference. By introducing O_2 as reaction gas, UH^+ and U^+ were
717 converted to oxides (UO^+ , UHO^+ , UO_2^+ or UHO_2^+), meanwhile Pu was also converted to
718 oxides (PuO^+ , PuO_2^+), the interference of uranium hydrides could not be effectively
719 eliminated in the measurement of ^{239}Pu and ^{240}Pu . Injection of ammonium into the
720 reaction cell could significantly suppress the signal of UH^+ by 2 orders of magnitude,
721 while the intensities of Pu^+ keep constant. Meanwhile, the intensity of U^+ signal was
722 reduced 3-4 orders of magnitude (Fig. 12). This indicated that ammonium as reaction gas
723 could effectively eliminate the interference of hydrides of uranium to the measurement of
724 ^{239}Pu and ^{240}Pu . This was attributed that U^+ and UH^+ reacted with NH_3 and formed
725 UNH_2^+ , but Pu^+ does not react with NH_3 [44]. This method could reduce the contribution
726 of ^{238}U to the ^{239}Pu to 1×10^{-7} . CO_2 as reaction gas was also investigated, it was found that
727 CO_2 can effectively react with UH^+ to form UO^+ ions, while Pu partly react with CO_2 to
728 form PuO^+ . At optimal condition, this method can reduce the contribution of ^{238}U to ^{239}Pu
729 to 1×10^{-8} , one order of magnitude better than NH_3 . It was also observed that injection of
730 He with NH_3 or CO_2 in to reaction/collision cell could significantly improve the
731 measurement sensitivity of plutonium isotopes by a factor of 3. This was attributed to the
732 collision focusing of He through reducing and narrowing the energy distribution of Pu^+
733 ion during transmission to the detector from the quadrupole.

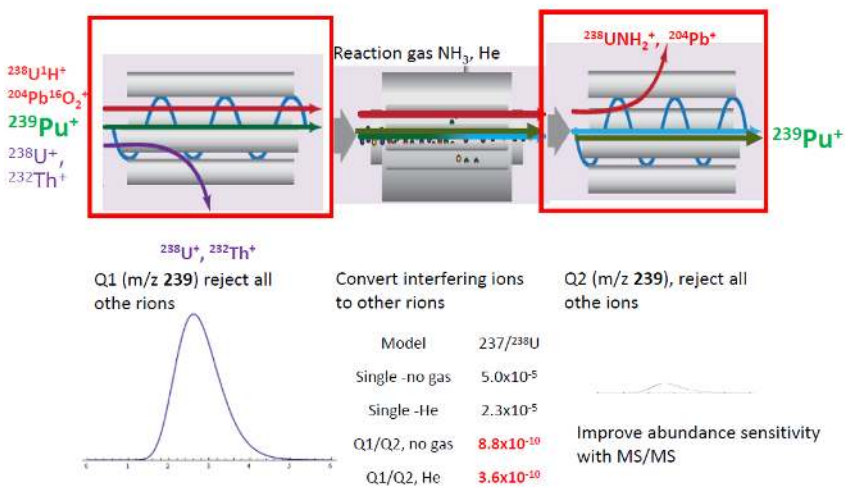
734 By employing two quadrupole mass separators in the Agilent 8800 ICP-MS, the
735 abundance sensitivity (tailing) of the ^{238}U was significantly improved. It was observed
736 that the contribution of ^{238}U to $m/z=237$ was significantly reduced to $<10^{-9}$ when two
737 quadrupole mass separators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

740 contribution of ^{238}U to $m/z=237$ was reduced to $<2\times 10^{-11}$ when $\text{CO}_2\text{-He}$ gasses were
 741 injected into the reaction/collision cell. Besides the double separation by two
 742 quadrupoles, removal of $^{238}\text{U}^+$ ions by converting U^+ to UO_2^+ or UO_2^+ ions in the reaction
 743 cell also reduced its contribution to $m/z=237$ and 239. In addition, collision focusing of
 744 $^{238}\text{U}^+$ by helium atoms in the DRC also helps to reduce the tailing contribution to
 745 $m/z=237$ and 239. A schematic mechanism of the triple quadrupole ICP-MS with $\text{NH}_3\text{-}$
 746 He as reaction gasses is illustrated in Fig. 13.



747

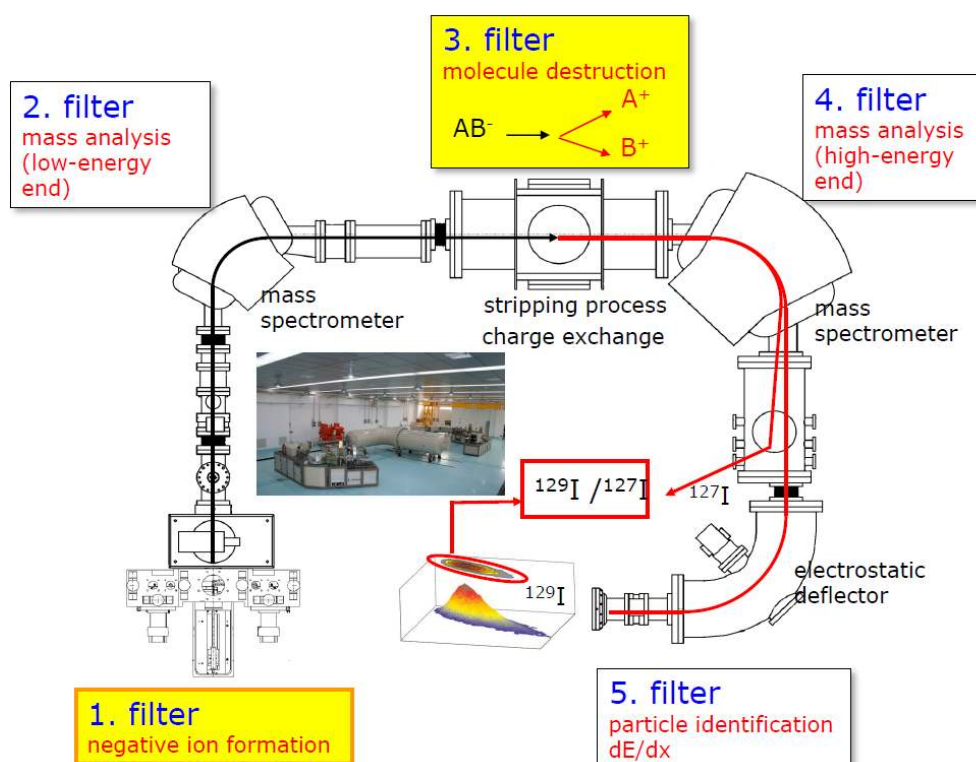
748 Fig. 12 Variation of the signal intensities of $^{238}\text{U}^+$, $^{238}\text{U}^1\text{H}^+$ and $^{239}\text{Pu}^+$ with the flow rate
 749 of NH_3 (mixed with 8.8 ml/min He) as reaction gas measured in uranium standard
 750 solution (^{238}U) and ^{239}Pu standard solution using ICP-MS/MS



751

752 Fig.13 Diagram illustrating the mechanism of triple-quadrupole ICP-MS with NH₃-He as
753 reaction gas to eliminate interferences for measurement of ²³⁹Pu

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



760

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

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

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

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

788 For the measurement of ^{129}I in surface environmental samples (with $^{129}\text{I}/^{127}\text{I}$ ratio $> 10^{-9}$),
789 0.5-2.0 mg of stable iodine carrier prepared from a low-background iodine crystal
790 (Woodward Company) was spiked to the sample after separation using combustion, or
791 directly to the water samples. The separated iodine in iodide form was precipitated as AgI
792 by addition of AgNO_3 . After dried at 70-75°C in a 1.5 ml centrifuge tube, the AgI
793 precipitate was ground to fine powder and mixed with niobium powder of 3-5 times by
794 mass, which was then pressed in a copper holder for AMS measurement of ^{129}I . In
795 general, 10 mg of mixture can be pressed into target holder, i.e. maximum 2 mg of AgI
796 can be pressed into the holder. In practice, only small fraction of sample in the target
797 holder was used for measurement due to a relative short analytical time (< 20 min.).

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

802 An AMS method using carrier free iodine target was developed for the determination of
803 ^{129}I in ultra-low level samples. In this method, no stable iodine was spiked to the sample
804 to avoid the ^{129}I background resulted from iodine carrier. Because the concentration of
805 iodine in environmental samples (except seaweed, thyroid, brine, etc.) is normally very
806 low, only small amount of iodine (<0.05 mg) can be separated from the sample, e.g. 20 g
807 soil), which is not sufficient to prepare AgI precipitate, therefore an AgI-AgCl co-
808 precipitation method was developed to prepare the target. The final AgI-AgCl precipitate
809 of 0.5-1 mg was prepared, ground, mixed with 2-5 mg of niobium powder, and pressed
810 into a niobium holder for measurement of ^{129}I using AMS. The main challenge in this
811 method is stabilization, control and precise measurement of the beam current of iodine
812 ions, because of very low current of <100 nA. With this method, samples with $^{129}\text{I}/^{127}\text{I}$
813 atomic ratio of 2.0×10^{-13} can be measured when 0.05 mg iodine is separated and used for
814 measurement. This method is therefore useful for analysis of ultra-low level ^{129}I samples,
815 e.g. deep soil, seawater, or pre-nuclear samples. For a sample with $^{129}\text{I}/^{127}\text{I}$ ratio of 1×10^{-10} ,
816 this method only needs 3 μg iodine for measurement, i.e. a small size sample is needed,
817 which is very useful for the application in which only small sample is available [31].

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

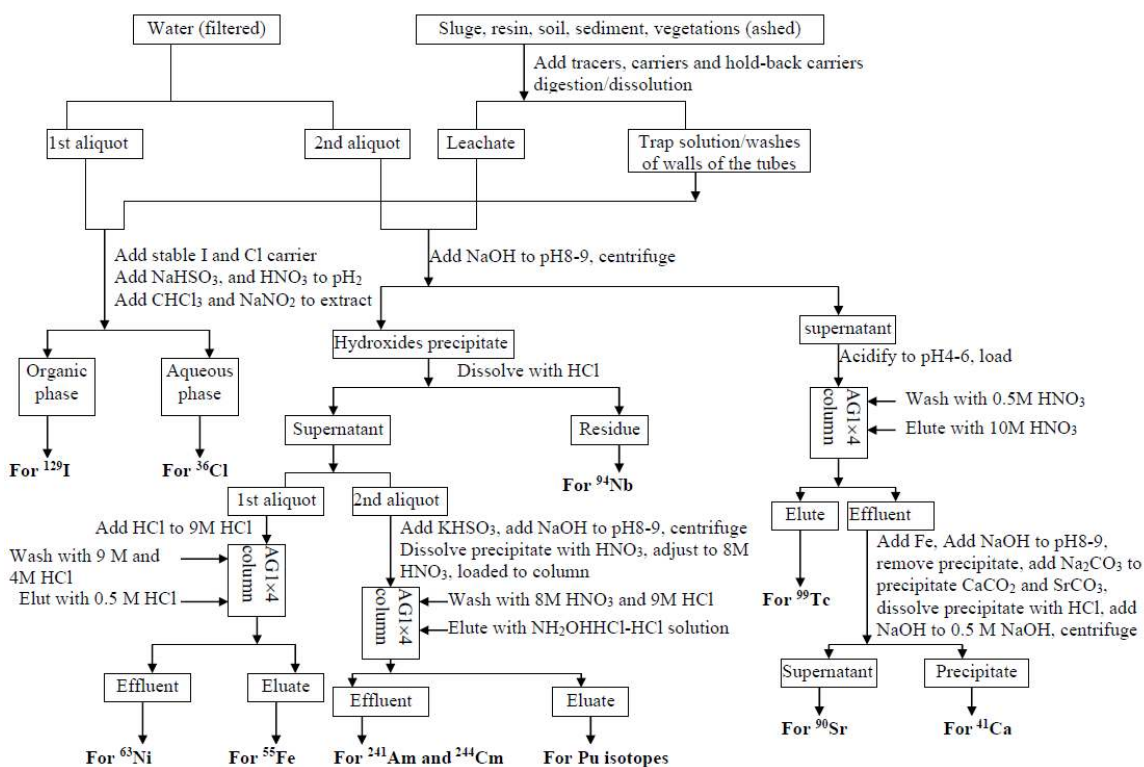
827 + AlI₃ and 3AgCl + Al = 3Ag + AlCl₃, these reactions take place when water vapor and
828 water soluble iodide/chloride are present [45].

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 ¹²⁹I in the 3MV AMS. The analytical results indicate
835 that this method is valid for the measurement of ¹²⁹I in environmental solid samples (e.g.
836 vegetation, soil, aerosol /dust) in a level of 0.1 μBq/mg ¹²⁹I with an analytical uncertainty
837 of less than 20%. For normal environmental sample with low concentration of iodine (< 5
838 μg/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, ¹⁴C, ³⁶Cl, ⁴¹Ca, ⁵⁵Fe,
848 ⁶³Ni, ⁹⁰Sr, ⁹³Mo, ⁹⁹Tc, ¹²⁹I, ²³⁷Np, ²³⁸U, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Pu, ²⁴¹Am and ²⁴⁴Cm. 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.

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



862
 863 Fig. 15 Schematic diagram of overall separation procedure of radionuclides for
 864 characterization of radioactive waste

865

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

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

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

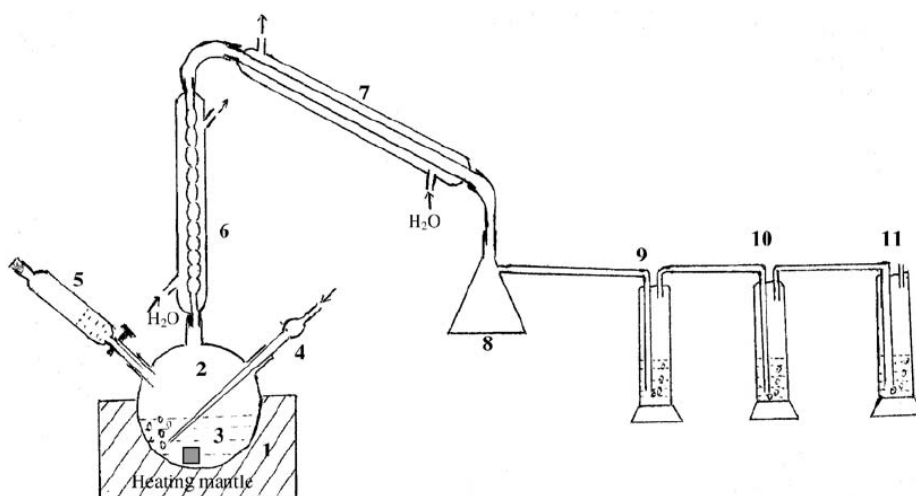
887 A combustion method using Sample Oxidizer has been developed for determination of ^3H
888 and ^{14}C in solid samples [49]. Solid samples in powder such as graphite, concrete, active
889 charcoal, soil, sediment, metal pieces (<2 mm), resin, etc. were mixed with cellulose
890 powder in a cellulose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

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

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

910 Both iodine and chlorine are volatile elements, and instable during sample treatment and
911 analysis. For water sample, solvent extraction was directly used for the separation of
912 iodine from matrix; the aqueous phase from the extraction was used for separation of ^{36}Cl
913 by AgCl precipitate. While for solid sample, a special attention has to be given to avoid
914 loss of ^{129}I and ^{36}Cl during analysis. An acid digestion method in a closed system was
915 developed to decompose graphite, iron, aluminum, stainless steel and ion exchange resin
916 for the determination of ^{129}I and ^{36}Cl (Fig. 16). In this method, the sample was first put
917 into the flask, yield carriers (stable Cl and I) were added. All apparatus in the system
918 were connected and leakage was checked. Acid or mixed acids were added through the
919 funnel (No. 5) to avoid the loss of the produced gasses. Afterwards, the sample with acid
920 was heated to dissolve the sample and release iodine and chlorine to the solution.
921 Different acid or acid mixture were used depending on the sample types. It was found
922 that mixed acids of $\text{H}_2\text{SO}_4:\text{HNO}_3:\text{HClO}_4 = 15:4:1$ were effective for completely dissolve
923 graphite, 5-8 mol/l of H_2SO_4 was effective for completely dissolve stainless steel and iron
924 without addition of any chlorine, while HNO_3 is sufficient for dissolution of aluminum,
925 lead, copper. For soil and sediment, HNO_3 can be used to leach iodine and chlorine out
926 [51]. Alkaline fusion was also used to release iodine and chlorine from soil, sediment and
927 vegetation samples [29]. For releasing iodine from ion exchange resin, NaOH and NaClO
928 leaching was a simple and sufficient method. In this case, the closed digestion system
929 was not necessary, because iodine was stable in alkaline solution in the present of NaClO.

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



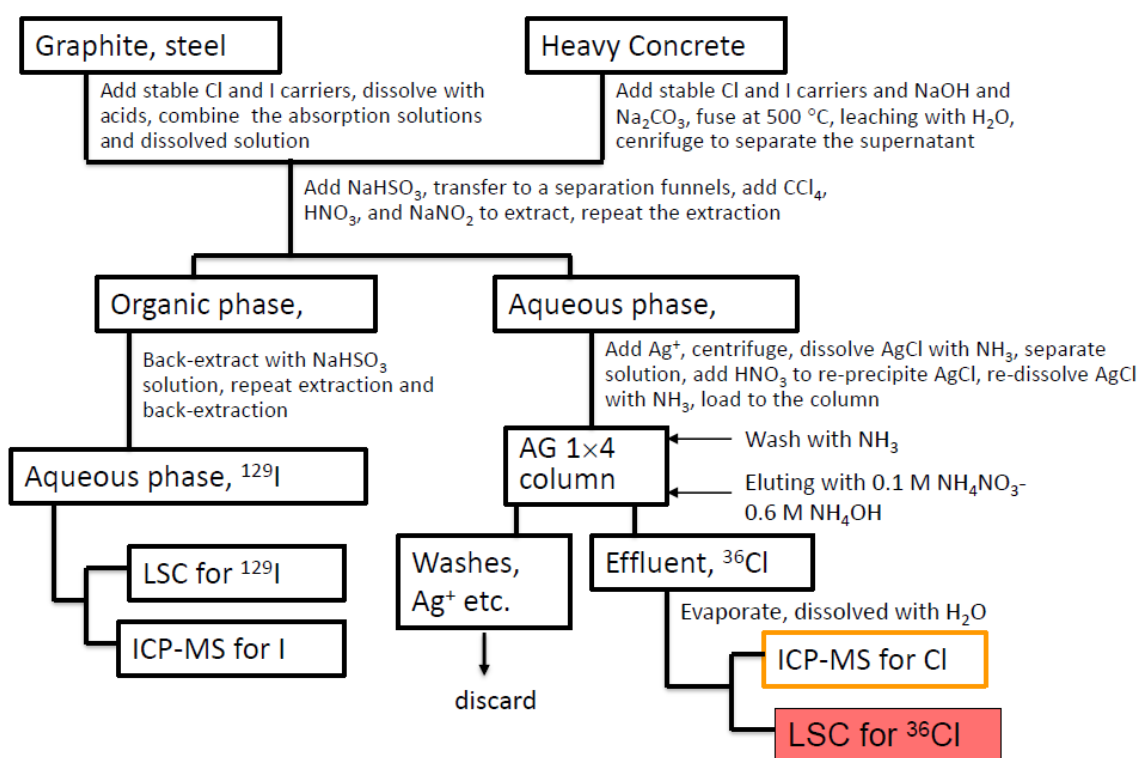
936

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

942

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

950 The AgCl precipitate was dissolved with NH₄OH and then Cl⁻ was re-precipitated as
 951 AgCl by addition of HNO₃ to pH 1-2. The formed AgCl was dissolved in 5 ml NH₄OH
 952 and loaded to an anion exchange column which has been conditioned with NH₄OH
 953 solution. After washing with NH₄OH to remove all Ag⁺, Cl⁻ adsorbed on the column was
 954 finally eluted with NH₄NO₃-NH₄OH 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 ³⁶Cl [51]. Fig. 17 shows a combined analytical procedure for
 957 determination of ¹²⁹I and ³⁶Cl in decommissioning samples.



958

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

961

962 **Determination of ⁹⁹Tc.**

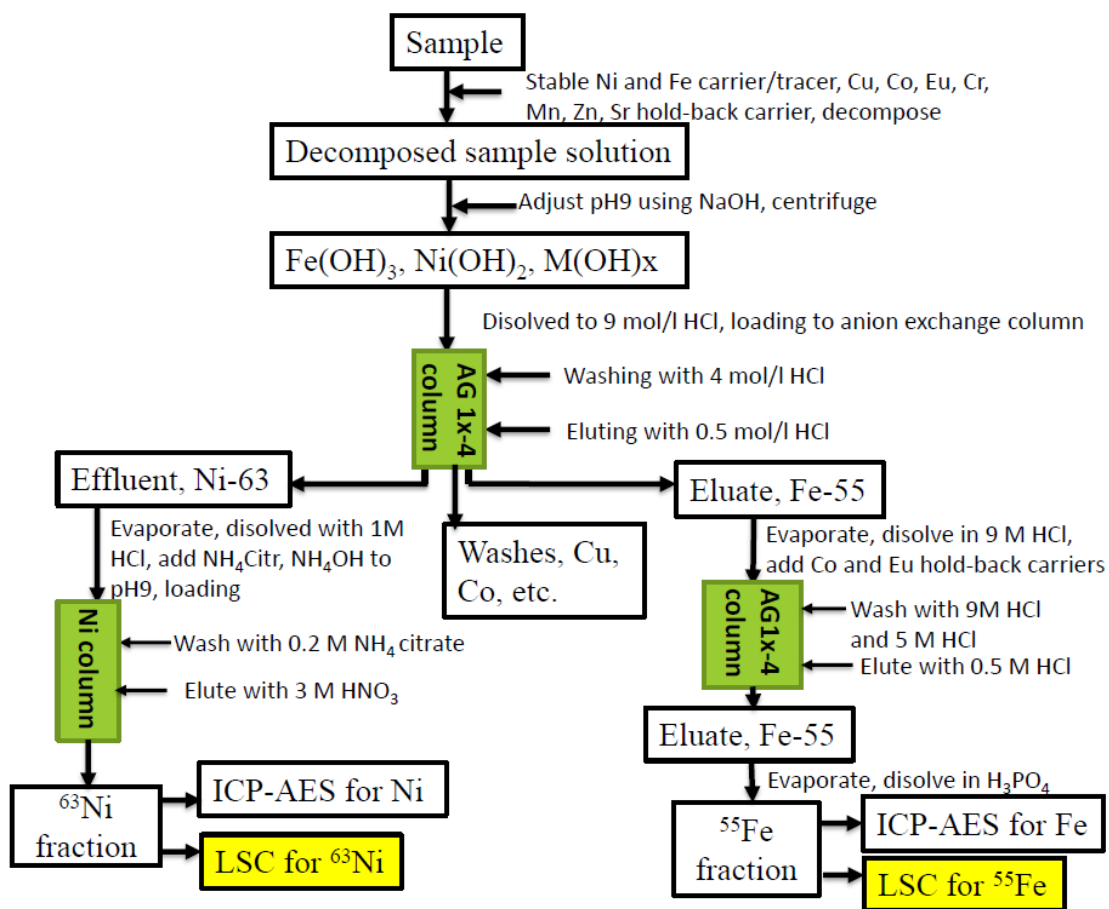
963 In oxidative condition, ⁹⁹Tc is mainly present as TcO₄⁻, therefore can be separated from
 964 matrix by anion exchange chromatography. Based on the high affinity of TcO₄⁻ on anion

965 exchange resin, ^{99}Tc was separated from most of interfering radionuclides. ^{99}Tc in water
966 or leachate of sample was first oxidized to TcO_4^- using H_2O_2 , then the solution was
967 neutralized to pH8-9 to separate the transit metals and actinides by hydroxides
968 precipitation. The supernatant was loaded to an anion exchange column (e.g. AG1×4, Cl^-
969 form) after acidified to pH4-5. The column was washed with 1.0 mol/l NaOH, H_2O and
970 0.5-1.0 mol/l HNO_3 , ^{99}Tc on the column was finally eluted using 10 mol/l HNO_3 . The
971 eluate was evaporated to 0.5-1.0 ml on a hotplate, and then diluted with 20 ml H_2O . The
972 prepared solution was loaded to a 2 ml TEVA extraction chromatographic column, the
973 column is washed with 2 mol/l HNO_3 , ^{99}Tc on the column was finally eluted with 10
974 mol/l HNO_3 . The eluate was evaporated to 0.5-1.0 ml and diluted to 5 ml with H_2O .
975 Chemical yield was measured by gamma counting of $^{99\text{m}}\text{Tc}$ spiked to the sample before
976 separation, and ^{99}Tc in the separated sample solution was finally measured using ICP-MS
977 [12, 15]. LSC can be also used for measurement of ^{99}Tc . In this case, the eluate can be
978 evaporated to near dryness at $<100\text{ }^\circ\text{C}$, and transferred to 20 ml vial with 2-3 ml water.
979 After addition of scintillation cocktail, ^{99}Tc can be measured using LSC. However, the
980 detection limit of ICP-MS for ^{99}Tc is generally better than LSC by more than one order of
981 magnitude [42].

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

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

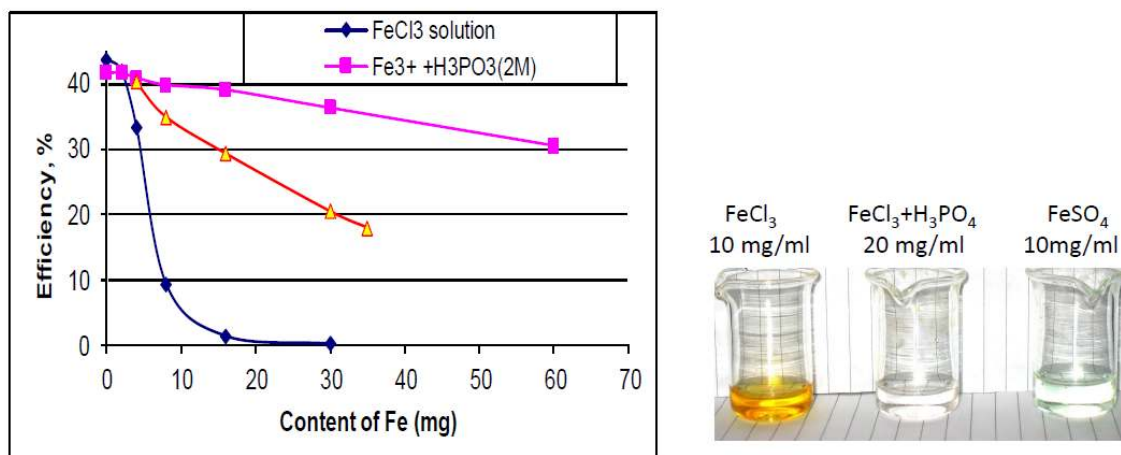
995 containing high iron or radioactive cobalt, a further purification step was added. The
 996 dried ^{55}Fe fraction was dissolved with 9 mol/l HCl, hold-back carriers (e.g. Co^{2+}) were
 997 spiked. The solution was loaded to a new anion exchange column. The column was
 998 rinsed with 5-6 mol/l HCl, and ^{55}Fe on the column was finally eluted with 0.5 mol/l HCl.
 999 The eluate was evaporated to dryness, and dissolved with 1mol/l H_3PO_4 to obtain a
 1000 colorless solution (Fig. 18). The second anion exchange chromatographic purification is
 1001 needed when ^{60}Co and ^{58}Co concentration are high and/or the iron content is high in the
 1002 sample to get a high decontamination factors for ^{58}Co and ^{60}Co . The iron in the final
 1003 solution and the original solution was measured by ICP-OES to calculate the chemical
 1004 yield. In this procedure, ^{55}Fe is normally quantitatively recovered, a chemical yield of
 1005 more than 98% was often achieved. The remaining solution was used to measure ^{55}Fe by
 1006 LSC.



1007

1008 Fig. 18 Diagram of analytical procedure for determination of ^{55}Fe and ^{63}Ni

1009 It should be mentioned, application of H_3PO_4 to dissolve $\text{Fe}(\text{OH})_3$ or Fe_2O_3 is important,
1010 otherwise a high quench color (yellow/brown) solution is obtained, causing a low LSC
1011 counting efficiency of ^{55}Fe . H_3PO_4 can not only dissolve $\text{Fe}(\text{OH})_3$ and Fe_2O_3 , but also
1012 form a colorless solution of complex of iron with H_3PO_4 , Fig. 19 shows quench curve of
1013 ^{55}Fe in different amount of Fe solution and at different media (FeCl_3 , $\text{Fe}-\text{H}_3\text{PO}_4$ or
1014 FeSO_4), a significantly improved quench level and high counting efficiency of ^{55}Fe was
1015 achieved by using H_3PO_4 .



1016

1017 Fig. 19 Quench curves of ^{55}Fe in different media against the iron content in the sample.

1018

1019 For the separation of nickel, a specific extraction resin based on dimethylglyoxime
1020 (DMG) as function group was used. Nickel can form a stable complex with DMG, Ni^{2+}
1021 loaded to the Ni-resin column can be adsorbed on the resin. However, other transition
1022 metal ions (e.g. Fe^{3+} , Co^{2+} , Cu^{2+} , etc.) can also form complexes to be adsorbed on the
1023 column. Because the complex of other transition metal with DMG are not stable, which
1024 can be removed by rinsing. For obtaining a better decontamination factor for some high
1025 radioactive radionuclides (e.g. ^{60}Co , ^{58}Co), a further separation of these transition metals
1026 is necessary. Therefore, ^{63}Ni was first separated from many other transition metals using
1027 anion exchange chromatography, most of ^{60}Co and ^{58}Co ($\text{DF} > 10^3$) can be removed in this
1028 step. However, rare earth elements could not form anions in HCl solution and entered the

1029 effluence with Ni. Since rare earth elements could not form complex with DMG, they
1030 could be well removed in the Ni-resin extraction chromatographic separation step. The
1031 effluent from the anion exchange column was evaporated to dryness, the residue was
1032 dissolved using 1.0 mol/l HCl. 1-2 ml of 1 mol/l ammonium citrate (depending on the
1033 amount of residue) was added to the solution to complex most of metals. Then ammonia
1034 solution was added to the solution to pH 8-9. The prepared sample solution was then
1035 loaded to an extraction chromatographic column (Eichrom Ni-column, 2 ml). The column
1036 was rinsed with 0.2 mol/l ammonium citrate at pH9 to remove all possible interfering
1037 radionuclides. Ni adsorbed on the column (red band) was finally eluted using 3.0 mol/l
1038 HNO₃. The eluate was evaporated to 0.1-0.3 ml on a hotplate, and transferred to a vial
1039 with 2 ml water. 0.1 ml of the final solution, as well as the original solution, were taken
1040 for the determination of Ni using ICP-OES for the chemical yield measurement. It was
1041 observed that nickel can be quantitatively recovered in this procedure with a chemical
1042 yield of >98%. ⁶³Ni in the remaining solution was measured by LSC [52]. The pre-
1043 separation of nickel from iron and cobalt was confirmed very necessary for the samples
1044 with high ⁶⁰Co and ⁵⁸Co, because the decontamination factor of Ni-column is not
1045 sufficient high to remove all radioactive isotopes of cobalt, which can cause a high
1046 interference in the measurement of ⁶³Ni [53].

1047

1048 ***Determination of ⁴¹Ca and ⁹⁰Sr.***

1049 Calcium-41 is a long-lived (1.3×10^5 years) radionuclide decaying by electron capture,
1050 without any gamma or beta rays emission. LSC is the most suitable method for its
1051 measurement by counting its low-energy Auger electrons. ⁴¹Ca is a neutron activation
1052 product, mainly produced in concrete biological shield, which contains high
1053 concentration of calcium and is exposed to neutrons. ⁹⁰Sr is one of the important fission
1054 products because of its high fission yield, and therefore an important radionuclide in the
1055 decommissioning of nuclear facilities. ⁹⁰Sr is a pure beta emitter, and therefore needs to
1056 be separated from all other radionuclides before measurement, especially from
1057 radioisotopes of alkaline earth metals (e.g. ¹³¹Ba, ^{228,226}Ra). In some heavy concrete used

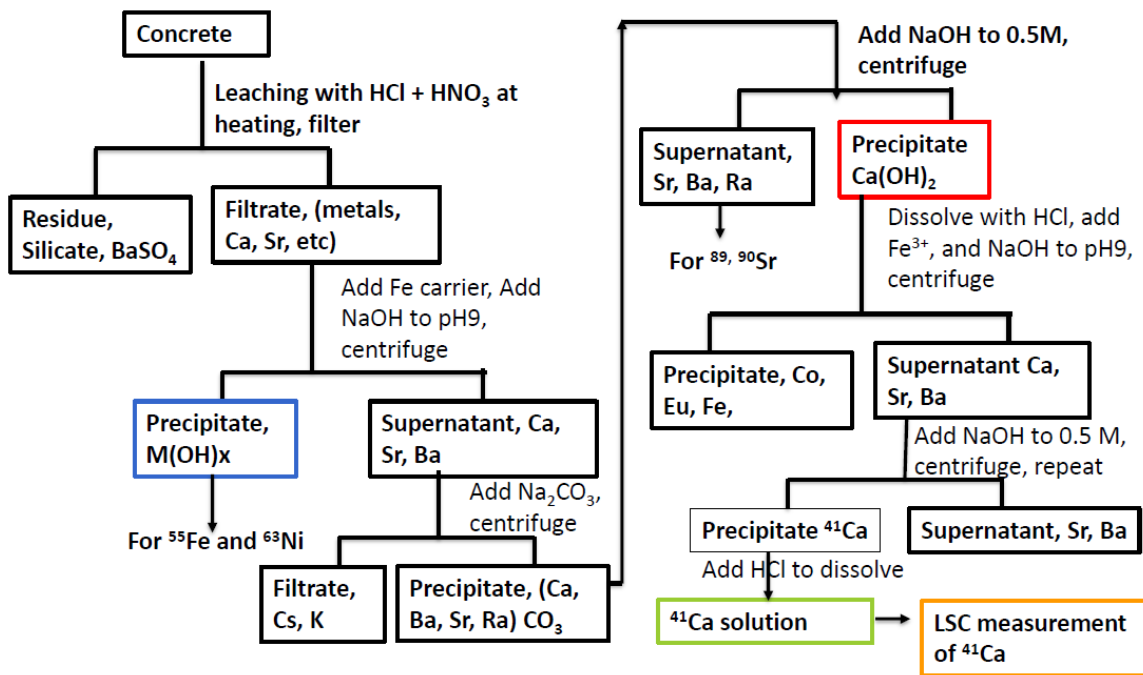
1058 in nuclear reactors, BaSO₄ was added to obtain a better shield of radiation, the separation
1059 of ¹³¹Ba is one of major challenge in the analysis of such type of samples. We have
1060 developed a simple precipitation method for separation of calcium from matrix and
1061 interfering radionuclides, as well as to separate calcium from strontium [54]. In this
1062 method, calcium and strontium were first released from concrete to solution. Both acid
1063 leaching and alkaline fusion were investigated, and found acid leaching using *aquia regia*
1064 can release almost all calcium and strontium from concrete, and more simple compared to
1065 alkaline fusion. Meanwhile, most of BaSO₄ can be removed because of its insolubility in
1066 acid solution. Sr²⁺ and Ca²⁺ carriers, Fe³⁺ hold back carrier and ⁸⁵Sr tracer were added to
1067 the sample before separation. The leachate was then neutralized to pH8-9, all transit
1068 metals (e.g. Fe, Co, Eu, etc.) and actinides were precipitated and removed from calcium
1069 and strontium. The supernatant containing calcium and strontium was used for further
1070 separation of ⁴¹Ca and ⁹⁰Sr.

1071 Na₂CO₃ solution was added to the supernatant, which was heated to 95 °C and keeping
1072 for 1 hour. The formed precipitate of Ca and Sr as carbonate was separated by centrifuge.
1073 The precipitate was dissolved with HCl, and 2 mg of Fe³⁺, Co²⁺, and Eu³⁺ were added,
1074 and then the NaOH was added to adjust pH to 8-9. The Fe(OH)₃ precipitate was removed
1075 by centrifuging, 6 mol/l NaOH was added to the supernatant to 0.5 mol/l NaOH, and the
1076 precipitate of Ca(OH)₂ was separated by centrifuging. The supernatant was used for the
1077 separation of ⁹⁰Sr. The Ca(OH)₂ precipitate was dissolved with HCl, 2 mg of Fe³⁺. Co²⁺
1078 and Eu³⁺ were added and pH adjusted to 8-9 using NaOH again. The precipitate was
1079 removed by centrifuge, and 6 mol/l NaOH was added to the supernatant to 0.5 mol/l of
1080 NaOH. Ca(OH)₂ precipitate was then separated by centrifuging. This dissolution and
1081 precipitation step were repeated. The final obtained Ca(OH)₂ precipitate was dissolved
1082 using HCl. The chemical yield was measured by determination of stable calcium in the
1083 final solution and the solution before separation. ⁴¹Ca in the final solution was measured
1084 by LSC counting [54]. An overall recovery of more than 85% was obtained, and
1085 decontamination factors to all interfering radionuclides were more than 5×10⁴. Fig. 20
1086 shows the analytical procedure for ⁴¹Ca in concrete.

1087 To the supernatant from the first Ca(OH)₂ precipitation step, HCl is added to adjust pH2.
1088 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].

1099



1100

1101 Fig. 20 Schematic diagram of analytical procedure for ^{41}Ca

1102

1103 *Determination of isotopes of plutonium, americium and curium*

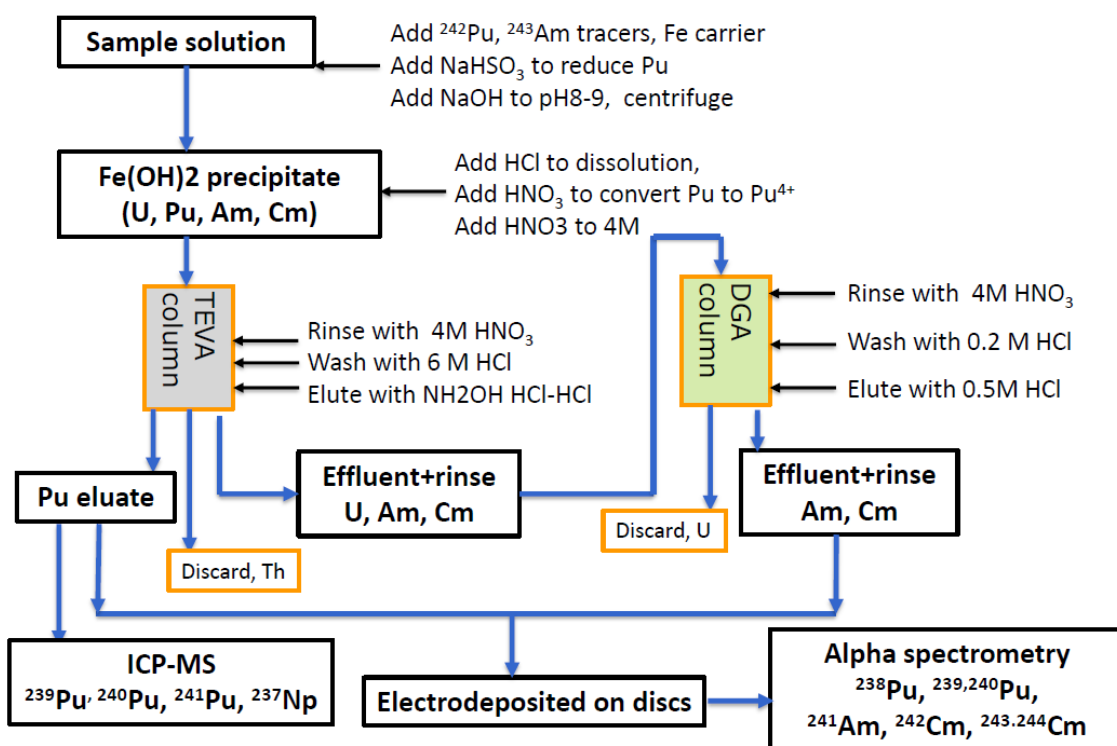
1104 The major isotopes of plutonium in the environment and decommissioning waste are
1105 ^{238}Pu , ^{239}Pu , ^{240}Pu and ^{241}Pu , they are the important alpha and beta emitters and have to be
1106 determined in the decommissioning of nuclear facilities. Separation of plutonium mainly
1107 relies 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 (AG1×4, 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

1135 together and reported as $^{243}\text{Cm}+^{244}\text{Cm}$ ($^{243,244}\text{Cm}$). Americium and curium are often
1136 presented as Am^{3+} and Cm^{3+} , they cannot form anion complexes with HNO_3 and HCl in
1137 aqueous solution due to the small ion radius and strongly bound water molecules, but
1138 could form anion complexes in non-aqueous media. To the effluent from the ion
1139 exchange separation of Pu , Fe^{3+} was added, and NH_3 was added to pH8-9 to form co-
1140 precipitates of Am and Cm hydroxides with $\text{Fe}(\text{OH})_3$. The precipitate was dissolved
1141 using concentrated HNO_3 . 30% H_2O_2 was added and the solution stirred for 2 minutes.
1142 CH_3OH was added to the solution to prepare the sample in 93% CH_3OH -1.0 mol/l HNO_3
1143 solution. The solution was then loaded to an anion exchange column (AG1×4, Cl^- form).
1144 The column was rinsed with 1.0 mol/l HNO_3 -93% CH_3OH and 0.1mol/l HCl -0.5 mol/l
1145 NH_4SCN -80% CH_3OH , followed by 1.0 mol/l HNO_3 -93% CH_3OH to remove interfering
1146 radionuclides and lanthanides. Am and Cm on the column were finally eluted using 1.5
1147 mol/l HCl -86% CH_3OH solution. The eluate was evaporated to dryness, concentrated
1148 HNO_3 was added to the residue and digested for 30 min on a hotplate and then
1149 evaporated to dryness. The residue was dissolved with 10 ml of 0.05M H_2SO_4 , and the
1150 solution was transferred to an electrodeposition cell to electrodeposit Am and Cm on a
1151 stainless steel disk. ^{241}Am and ^{244}Cm on the disc were finally measured by alpha
1152 spectrometry. ^{243}Am on the disc was also measured and used as chemical yield tracer for
1153 correction of the measured concentration of ^{241}Am and $^{234,244}\text{Cm}$ [14]

1154 A new analytical procedure using extraction chromatography was developed in our lab
1155 for separation of plutonium, americium and curium in the nuclear waste samples (Fig.
1156 21). The sample solution was first acidified using HCl , ^{242}Pu and ^{243}Am tracers, Fe^{3+}
1157 carriers were spiked, and then NaHSO_3 was added to reduce plutonium to Pu^{3+} . NaOH
1158 was added to the sample solution to adjust pH8-9 to co-precipitate Pu^{3+} , Am^{3+} and Cm^{3+}
1159 hydroxides with $\text{Fe}(\text{OH})_2$. The precipitate was dissolved with HCl and concentrated
1160 HNO_3 was added to oxidize Pu^{3+} to Pu^{4+} . The sample solution was prepared in 4 mol/l
1161 HNO_3 medium, and loaded to two sequential connected columns of TEVA and DGA, the
1162 columns were then rinsed with 4 mol/l HNO_3 . $\text{Pu}(\text{NO}_3)_2^-$ was adsorbed on TEVA
1163 column, while Am^{3+} and Cm^{3+} passed through the TEVA column, and adsorbed on DGA
1164 column by forming complex with the functional group of tetra-n-octyldiglycolamide on

1165 the DGA column. Afterwards, the two columns were disconnected, TEVA column was
 1166 used for separation of plutonium, and DGA column was used for separation Am and Cm.
 1167 The TEVA column was rinsed with 6 mol/l HCl, and plutonium on the column was then
 1168 eluted using 0.5 mol/l NH₂OH·HCl–2 mol/l HCl solution. The DGA column was rinsed
 1169 with 0.2 mol/l HCl, and Am and Cm were eluted using 0.5 M HCl. The separated
 1170 plutonium and Am+Cm fractions were prepared using the same method described above
 1171 for the determination of plutonium isotopes using ICP-MS and alpha spectrometry for
 1172 ²³⁸Pu, ²⁴¹Am, and ^{243,244}Cm.

1173



1174

1175 Fig. 21 Schematic diagram of analytical procedure for determination of isotopes of
 1176 plutonium, americium and curium using extraction chromatography

1177

1178 ***Determination of other radionuclides.***

1179 In our laboratory, the methods for the determination of ^{93}Mo , ^{94}Nb , and ^{135}Cs in the
1180 decommissioning wastes were also developed, and the methods for the determination of
1181 other radionuclides, such as ^{79}Se , ^{93}Zr , ^{126}Sn , and ^{151}Sm are under development. Although
1182 the concentrations of these radionuclides are very low in most of decommissioning waste,
1183 but their long half-lives make them also important in view of waste repository.

1184 The separation of ^{93}Mo and ^{94}Nb was implemented using ion exchange chromatography
1185 followed by a purification using alumina column. After spiked the yield tracers of stable
1186 Mo, Nb and Zr and hold-back carriers, such as stable Co, Ni and Eu, the sample was
1187 prepared in 0.02 mol/l HF and loaded to a strong acidic cation exchange chromatographic
1188 column. Mo, Zr and Nb present as anions MoO_4^{2-} , ZrF_6^{2-} or NbF_6^- passed through the
1189 column, while cations including transition metals, alkali and alkaline earth metals were
1190 adsorbed on the column and removed. The effluent from the column was then loaded to a
1191 TEVA column, MoO_4^{2-} , ZrF_6^{2-} and NbF_6^- were adsorbed on the column. After rinsing
1192 with 0.02 mol/l HF solution, Zr was first eluted using 7 mol/l HCl-0.5 mol/l HF solution,
1193 Mo was eluted with 4 mol/l HF solution, and Nb was eluted with 1 mol/l HNO_3 solution.
1194 The Nb fraction was directly used for measurement of ^{94}Nb by gamma spectrometry after
1195 evaporated to < 5 ml. Zr fraction can be used for determination of ^{93}Zr after a further
1196 purification. The Mo fraction was evaporated to dryness and converted to HNO_3 medium
1197 by addition of HNO_3 and evaporated to dryness, and the residue was dissolved in 1.0
1198 mol/l HNO_3 solution. The prepared solution was then loaded to an alumina column, after
1199 rinsing the column with 1.0 mol/l HNO_3 , 0.1 mol/l HNO_3 , water and 0.01 mol/l ammonia.
1200 MoO_4^{2-} adsorbed on the column was finally eluted with 25% ammonium. The eluate was
1201 evaporated to dryness and the residue was dissolved in water, which was transferred to a
1202 20 ml vial for LSC measurement of ^{93}Mo . The chemical yield was obtained by
1203 measurement of stable Mo and Nb in the separation sample and the spiked sample
1204 solution using ICP-OES.

1205 For the determination of ^{135}Cs , the sample solution was prepared in a neutral or slight
1206 acidic medium. Ammonium molybdophosphate (AMP) powder was added and mixed
1207 with the sample solution, AMP powder adsorbed cesium was separated by filtration.
1208 Cesium on the AMP powder was then leached out with 5 mol/l NH_4Cl solution. By this

1209 way, most of radionuclides can be removed because of the specific adsorption of cesium
1210 on the AMP powder. The leachate was then loaded to a cation exchange chromatographic
1211 column (e.g. Bio-Rad AG 1×-50), Cs⁺ was adsorbed on the column. After rinsing with
1212 H₂O and 0.1 mol/l HNO₃, Cs⁺ was eluted with 1.0 mol/l HNO₃. In this step, most of Ba
1213 was removed. The eluate was then evaporated to dryness and prepared in 5 ml of 0.5
1214 mol/l HNO₃ for ICP-MS of ¹³⁵Cs using a triple-quadrupole ICP-MS (Agilent 8800) with
1215 N₂O as reaction gas to eliminate the interferences including isobar (e.g. ¹³⁵Ba⁺).
1216 Meanwhile, ¹³⁷Cs can be also measured by ICP-MS. In this case, no external chemical
1217 yield tracer is needed, ¹³⁷Cs can be used as an internal yield tracer. ¹³⁷Cs in the samples
1218 was first measured using gamma spectrometry, the concentration of ¹³⁵Cs was calculated
1219 using the measured ¹³⁵Cs/¹³⁷Cs ratio by ICP-MS and the ¹³⁷Cs concentration in the
1220 sample measured by gamma spectrometry. For the sample containing high level
1221 radioactivity of other radionuclides (e.g. ⁶⁰Co), ¹³⁷Cs can be determined by measurement
1222 of the AMP powder adsorbed cesium from the sample, in which ⁶⁰Co and many other
1223 radionuclides were removed.

1224 The methods presented in this work have been successfully used for the characterization
1225 of various radioactive wastes from the decommissioning of research reactors in Denmark
1226 (DR-1, DR-2 and DR-3) and Australia, nuclear power reactors in Barsebäck, Sweden,
1227 and other nuclear facilities such as hot cells in Denmark. Meanwhile they were also used
1228 for characterization of radioactive waste from the operation of nuclear power plants (e.g.
1229 concentrate, ion exchange resin, etc.) in Finland. [Table 2](#) list the sample amount required
1230 for analysis and the minimum detectable activity (MDA) of our methods for the difficult-
1231 to measure radionuclides. This is mainly for the clearance samples (less contaminated).
1232 For the samples directly exposed to neutrons or highly contaminated ones, e.g. graphite,
1233 metals from reactor tank or first circulation system, ion exchange resin for purification of
1234 reactor water, small sample (0.05- 0.5 g) is required depending on the radioactive level,
1235 while the MDAs for the corresponding radionuclides (in unit of Bq/mBq) are similar as
1236 listed in the table.

1237

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	³ H	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 μBq/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	³ H	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 μBq/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 ¹⁴C) 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. .

1244 **Conclusions**

1245 This paper presents the progress in the development of Radioanalytical methods for
1246 determination of radionuclides in ultra-low level samples in the environment, and
1247 analytical methods for the characterization of radioactive waste from decommissioning of
1248 nuclear facilities, the main achievements are briefly summarized below.

1249 1) A series of radioanalytical methods have been developed and updated for
1250 determination of low-level anthropogenic and naturally occurring radionuclides in
1251 various environmental and biological samples for environmental radioactivity
1252 investigation, environmental process and oceanographic tracing.

1253 2) A number of highly selective pre-concentration methods using AMP powder
1254 adsorption and $K_2CuFe(CN)_6$ impregnated cartridge filtration were developed
1255 and applied for separation of cesium from 100-1000 liter water for determination
1256 of low-level ^{134}Cs and ^{137}Cs using gamma spectrometry. With further purification
1257 using ion exchange chromatography combined with triple quadrupole ICP-MS
1258 and N_2O as reaction gas, a method was also developed for determination of ^{135}Cs
1259 in environmental samples.

1260 3) A simple method was developed for separation of strontium from large volume of
1261 environmental water samples (up to 100 L) and more than 20 g soil by
1262 precipitation without using highly toxic fuming nitric acid and chromate. By
1263 removal of Sr and Ra by sulfate precipitation and separation of yttrium as oxalate,
1264 ^{90}Sr was determined by measurement of its decay daughter of ^{90}Y . A rapid
1265 method based on extraction chromatography using Sr-resin was also developed
1266 for determination of ^{89}Sr and ^{90}Sr in samples of low strontium content, especially
1267 decommissioning samples, both ^{89}Sr and ^{90}Sr were determined using Cherenkov
1268 counting and LSC.

1269 4) The stability of technetium in separation processes were investigated, a method
1270 was developed to separate technetium from large size environmental samples
1271 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
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1321

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