Tritium and ^{14}C in the Environment and Nuclear Facilities: Sources and Analytical Methods

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Tritium and ^{14}C are two most important radionuclides released from nuclear facilities to the environment, and ^{14}C contributes dominant radiation dose to the population around nuclear power plants. This paper presents an overview of the production, pathway, species and levels of tritium and ^{14}C in nuclear facilities, mainly nuclear power plants. The methods for sampling and collection of different species of tritium and ^{14}C in the discharge gas from the stack in the nuclear facilities, atmosphere of the nuclear facilities and environment are presented, and the features of different methods are reviewed. The on-line monitoring methods of gaseous tritium and ^{14}C in air and laboratory measurement methods for sensitive determination of tritium and ^{14}C in collected samples, water and environmental solid samples are also discussed in detailed. Meanwhile, the challenges in the determination and speciation analysis of tritium and ^{14}C are also highlighted.

Keywords: Tritium, Carbon-14, Source term, Production, Monitoring, Speciation analysis

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1. Introduction

Tritium and ^{14}C are important radionuclides from a nuclear regulatory perspective in order to protect man and environment, since these radionuclides generally are the major contributors to the activity released to the environment from nuclear facilities. Especially, ^{14}C is one of the dominating radionuclides released from nuclear facilities concerning dose to the public [1]. The methods for release limitation are difficult especially for tritium, and monitoring reports indicates large uncertainties in analyses due to the unreliable sampling and analytical methods.

Knowledge on source terms, analytical methods for monitoring their level in nuclear facilities and environment and method for release limitation of theses radionuclides is of vital importance for a reliable analysis, review and development of regulations.

For a nuclear power plant, the thermal power affects the amount of ^{14}C and tritium produced and released. In addition to normal operation of nuclear power plants, ^{14}C and tritium are also important radionuclides during decommissioning, handling, and processing of radioactive waste.

This paper aim to summarize and review the sources of tritium and ^{14}C in the environment and the methods for sampling and determination of tritium and ^{14}C species in nuclear facilities and environment, meanwhile to discuss the main challenges and forthcoming development in these areas.

2. Sources and ^{14}C and tritium in the environment

Both tritium and ^{14}C are nature occurred radionuclides. However, human nuclear activities since 1945 have released large amount of these radionuclides to the environment, causing significantly increased levels in the environment. The production of tritium and ^{14}C and their pathway to the environment are presented below.

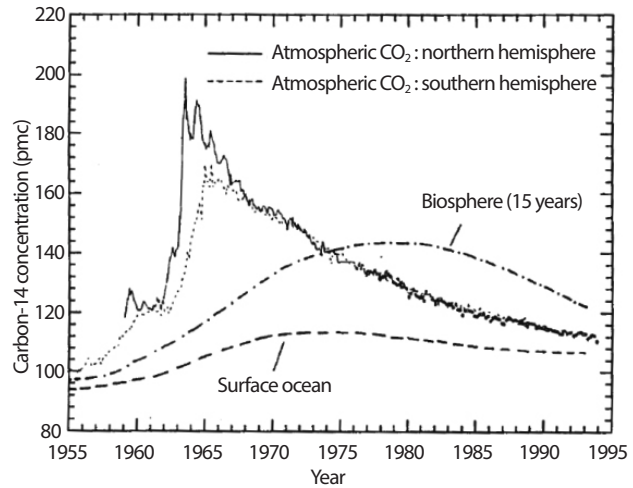Fig. 1. Concentration of ^{14}C in the atmosphere. pmc refers to the unit of ^{14}C, i.e. percent of modern carbon, representing the proportion of radiocarbon atoms in the sample compared to that present in the year 1950 AD [2].

2.1 Production of ^{14}C and its pathways to the environment

2.1.1 Production of ^{14}C in the nature and nuclear weapons testing

In nature, ^{14}C is mainly produced in the upper atmosphere by cosmic ray reaction with nitrogen through ^{14}N(n, p) ^{14}C. It has been estimated that the annual production rate of ^{14}C by this process is 1.4×10^6 GBq, and the total inventory of ^{14}C in the atmosphere was estimated to be 1.4×10^8 GBq, but much large in the deep ocean of 1.0×10^{10} GBq [2].

Large amount of ^{14}C has been produced in the atmospheric nuclear weapons tests in 1945-1980, mainly by the reactions of neutrons produced in the nuclear weapons testing with the nitrogen in the atmosphere through ^{14}N(n, p) ^{14}C. In addition, a small fraction of ^{14}C was also produced by ternary fission reaction of uranium and plutonium during weapons testing. It has been estimated that a total of 2.2×10^8 GBq ^{14}C was released to the atmosphere by nuclear weapon testing, causing a significantly increased concentration of ^{14}C in the atmosphere in 1950s-1960s (Fig. 1), when a large number of atmospheric nuclear weapons testing was conducted [2].

Table 1. The major neutron activation reactions and reaction cross sections for production of ^{14}C in nuclear reactor [3, 4]

Reaction	Natural abundance of target isotope	Cross section of neutron reaction (barn)		
		Thermal neutron	Resonance integral (epithermal neutron)	Fission neutron
$^{17}O(n, \alpha)^{14}C$	0.038%	0.235	0.106	0.095
$^{14}N(n, p)^{14}C$	99.6%	1.82	0.818	0.0355
$^{13}C(n, \gamma)^{14}C$	1.1%	$1.37×10^{-3}$	$5.93×10^{-4}$	$5.16×10^{-5}$

2.1.2 Production and pathways of ^{14}C in nuclear reactors

During the operation of a nuclear reactor, ^{14}C is mainly produced by neutron activation reactions of ^{17}O, ^{14}N, ^{13}C, and to some extent ^{15}N and ^{16}O, in the nuclear fuel elements, construction materials, moderator and coolant, as well as by ternary fission reaction of uranium and plutonium in the nuclear fuel. Table 1 lists the major production reactions of ^{14}C in the nuclear reactors.

Presently the major anthropogenic source of ^{14}C is the nuclear industry including nuclear power reactors and nuclear spent fuel reprocessing plants through atmospheric releases and water discharges. In the nuclear power reactors, a large fraction of ^{14}C is produced in the nuclear fuel due to high neutron flux and high concentration of oxygen. But, it mainly remains in the fuel elements and cladding material as solid waste or partly released during reprocessing. ^{14}C produced in the other construction materials is mainly treated as solid waste during decommissioning. ^{14}C produced in the moderator and coolant is therefore the major source of ^{14}C released to the environment during the operation. For the graphite moderator used in the gas cooled and graphite moderated reactors (GCRs) and the light water cooled and graphite moderated reactor (LWGRs/RBMK), the major fraction of ^{14}C produced in the graphite is presents as solid waste, and a small fraction might be released in gaseous form to the environment. ^{14}C produced in the coolant (light or heavy water) is mostly released to the atmosphere or discharged as liquid waste. Some of ^{14}C in the coolant water can be trapped in ion exchange resin and treated as

solid waste. It has been estimated that about $1.1×10^{15}$ Bq ^{14}C is produced yearly in the nuclear power plants all over the world, in which about $1.1×10^{14}$ Bq·y^{-1} ^{14}C is released to the atmosphere as gaseous form from all operating nuclear power plants, meanwhile about $3.7×10^{14}$ Bq·y^{-1} ^{14}C in both gaseous and liquid forms is released from the reprocessing plants [5]. The production rate and pathway of ^{14}C in the nuclear power plants vary with the type of power plants related to the enrichment of uranium in the fuel, the concentrations of oxygen and nitrogen in the fuel, structural materials, moderator and coolant.

Light water reactors (LWRs) are the most popular nuclear power reactor, accounting for two third of the nuclear power reactors, including pressurized water reactor (PWR) and boiling water reactor (BWR). In LWRs, ^{14}C in the coolant water is mainly produced through $^{18}O(n, \alpha)^{14}C$ reaction due to the lower nitrogen concentration. Based on an assumption of 0.1 ppm N_2 in coolant water in the BWR and 0.054 ppm in the coolant in PWR, it was estimated that more than 99% of ^{14}C is produced from ^{18}O in LWRs, and a production rate of 580 GBq/GW$_e$/y for 2500 MWth BWR (core specific calculation) and 350 GBq/GW$_e$/y for 2775 MWth PWR (core-specific calculation) [6, 7]. It should be mentioned that application of N_2 as annular gas in some BWRs significantly increases the production of ^{14}C in the coolant of the BWR because of $^{14}N(n, p)^{14}C$ reaction. ^{14}C produced in the fuel is mainly retained in the fuel elements; however, it might be leached out to the coolant through the cladding material such as stainless steel. In this case, it will become an important source of ^{14}C released to the environ-

ment. ^{14}C produced in the coolant and fuel in the nuclear power plants is distributed as gas and water-soluble form. Leakage of plant systems will eventually lead to release of ^{14}C to the environment. Therefore, the pathway and distribution of ^{14}C in the system is important for establishment of control measure.

In the PWRs, the reactor coolant also acts as moderator and is circulated in a closed loop (primary circuit). Because the coolant water in the close loop is separated from the water/steam in the secondary circuit, ^{14}C produced in the coolant water is not significantly dispersed to the secondary circuit. PWRs operate under reducing condition in the presence of excessive hydrogen, causing the major part of ^{14}C produced in the coolant to be in the form of organic compounds such as methane, acetate and formate (75-95%) with a small fraction of inorganic form as $^{14}CO_2$ and ^{14}CO (5-25%) [2, 4]. Due to boric acid addition and buffering in the coolant, a small portion of produced $^{14}CO_2$, ^{14}CO and organic ^{14}C remains dissolved, while most of $^{14}CO_2$, ^{14}CO and ^{14}C-methane leaks to the air space in the reactor, which are released from the coolant system at different steps. Most of the gaseous ^{14}C is released by venting of the volume control tank (air ejector) to the atmosphere. An ion exchange system is connected to the primary circuit to purify the coolant by removal of most of corrosion products. A fraction of dissolved ^{14}C produced in the coolant water is also removed in the ion exchange resin, mainly the organic compounds, supposed to be acetate, formate, and carbonate [4]. It was reported that a majority of the organic ^{14}C compounds in the reactor coolant (60%) is gaseous compounds (i.e. methane), and the remaining 40% of organic ^{14}C is dissolved non-volatile organic compounds (e.g. formate and acetate). It should be noted that ion exchange resin can only remove small fraction of dissolved ^{14}C in the coolant (6-10%), therefore, some extent of ^{14}C is discharged to the environment in liquid form. The majority of ^{14}C release is the gasses from the primary off-gas treatment system (volume control tank), accounting for about 70% of the total release, other pathways include steam generator blowdown tank vent exhaust,

fuel handling building ventilation exhaust, turbine gland seal condenser exhaust, etc. A normalized ^{14}C release from PWRs was estimated to be 130 GBq/GW(e)/y [2].

In boiling water reactors (BWRs), the heat generated in the reactor core is transferred to the coolant. Due to no pressure, the coolant is boiled to form a mixture of water and steam. The created steam is directed to the turbines, and condensed in the condenser. After purification in the ion exchange column, the water is recycled back to the reactor vessel. Therefore, ^{14}C and other radionuclides produced in the coolant reach to the turbines. Meanwhile, compounds of corrosion products are concentrated in the coolant water and deposited onto the surface of fuel elements (crud formation), causing a relative high production of ^{14}C in the coolant of the BWRs. The ^{14}C produced in the coolant is also the major source of ^{14}C released from BWRs. Unlike PWRs, the single circuit in the BWRs generates a continuous releases of ^{14}C through stack. Due to non-reductive condition in the coolant of BWRs, ^{14}C produced in the coolant is mainly in $^{14}CO_2$ form, with a small fraction in organic hydrocarbon form (5-20%). Therefore, the ^{14}C released from BWRs is mainly in $^{14}CO_2$ form. A small fraction of ^{14}C dissolved in coolant (HCO_3^-) can be removed in the ion exchange purification system. However, it has been reported that only a very small fraction of ^{14}C in the coolant of BWR (<1%) is removed in the ion exchange resin [7]. Therefore, some portion of ^{14}C is also discharged in liquid form. Besides the major release pathways of gaseous ^{14}C from BWR stacks in the form of CO_2, other systems including the turbine gland seal condenser exhaust, reactor building purge exhaust, and turbine building ventilation system exhaust also release small portion of ^{14}C produced in coolant. The typical ^{14}C release rate from a BWR was estimated to be about 260 GBq/y, which is higher than that in the PWRs [2]. ^{14}C releases to the environment from the nuclear power production in LWRs are estimated to be about 50% of the total production in BWR and 30% in PWR, the remaining part remains in the nuclear fuel and other solid waste.

In heavy water reactors (HWRs), heavy water (D_2O)

Table 2. Chemical forms of ^{14}C (relative percentage of each form) in airborne releases from different type of water reactors [2]

Reactor type	$^{14}CO_2$, %	^{14}CO, %	^{14}C in hydrocarbons, %
PWR (USA and Europe)	5-25	--	75-95 (CH_4 and C_2H_6)
BWR (USA and Europe)	80-95	--	5-20
HWR (Bruce unit 7, Canada)	65.5-72.8	0.2-3.7	26.7-34.4
HWR (Gentilly 2, Canada)	77.9-97.5	0.01-0.09	2.5-22.0

is used as coolant and/or moderator, the CANDU reactor is the commercial HWR .There are also many research reactors using heavy water as coolant and graphite as moderator for obtaining high quality thermal neutron spectra for experiment. In CANDU reactors, nuclear fuel elements in fuel channels are inserted in the reactor tank filled with heavy water moderator, the fuel is cooled by heavy water (coolant) pumped through the closed pressure tube (primary circuit) to transfer heat to steam generator where steam is produced in the secondary circuit containing light water. The annulus between each pressure tube and its outer tube is filled with CO_2 gas to insulate the cool moderator from the heat transfer system [4]. ^{14}C in HWR is mainly produced in the moderator, coolant system, fuel elements and annulus gas system. Due to the enriched ^{17}O in the heavy water, the production of ^{14}C in HWR is normally higher than in LWRs. Most of ^{14}C is trapped in the ion exchange resin in the heavy water purification system, causing a high ^{14}C concentration of 1.7-7.9 TBq·m^{-3} in the ion exchange in the moderator purification system. The release of gaseous ^{14}C is mainly from moderator system with a small fraction from the annulus system using CO_2. However, when N_2 is used as annulus gas, higher production rate and release of ^{14}C is expected. The airborne ^{14}C releases from two Canadian CANDU (600 MW(e)) reactors were reported to be 121-720 GBq/y in Point Lepreau and 277-2920 GBq/y from Gentilly 2 nuclear power reactors [8]. In the CANDU reactor, most of the airborne ^{14}C is released in $^{14}CO_2$ form (65.5-97.5%), a relatively small fraction in the form of organic hydrocarbon (2.5-34.4%), and very small fraction in

^{14}CO form (0.01-3.7%) [2]. Table 2 presents the forms of airborne ^{14}C released from different type of reactors.

In Magnox, AGRs (gas cooled graphite moderated reactors) and RBMK reactors, graphite is used as moderator. In Magnox and AGRs, CO_2 gas is used as coolant, whereas light water is used as coolant in RBMK reactors. In RBMK, the reactor space is filled with helium-nitrogen mixture gases to prevent graphite oxidation.

In the graphite reactors, ^{14}C is mainly produced in the graphite moderator through ^{13}C(n, γ)^{14}C and ^{14}N(n, p)^{14}C reaction. However, most of the produced ^{14}C remains in the graphite during the operation of the reactor, and is not released to the atmosphere. During operation of AGR, some ^{14}C produced in the graphite might be released as CO_2 coolant gas because of corrosion of graphite and isotope exchange between CO_2 coolant and graphite, which increases the ^{14}C concentration in the coolant gas. Meanwhile nitrogen impurity in the gas coolant is another source of ^{14}C in the coolant, the concentration of nitrogen in the CO_2 coolant gas is a key issue for the ^{14}C content in the coolant gas. A large portion of gaseous ^{14}C releases from gas cooled reactors come from the purification of the CO_2 circuits by leakage or during periodic routine purge. Of the totally produced ^{14}C in Magnox reactors and AGRs, only 3% and 6% is released, respectively. Gaseous ^{14}C released from a Magnox type reactor in France (Chinon 2 reactor, 200 MW(e)) was reported to be 370 GBq·y^{-1}. In RBMK reactors, most of the released gaseous ^{14}C is produced by the ^{14}N(n, p)^{14}C reaction, caused by the large amounts of nitrogen in the graphite block. It is assumed that the major part of ^{14}C re-

Table 3. Production and releases of ^{14}C from different types of power reactors [2]

Reactor type	Installed capacity MW(e)	Gaseous discharge (GBq/y)	Liquid discharge (GBq/y)	Solid waste (GBq/y)
PWR	1000	129.5	1.3	647.5
BWR	1000	259.0	1.3	1165.5
HWR	600	3108	small	703
Magnox	480	373.7	small	2982.2
AGR	660	255.3	small	2479

leased from RBMKs is in ^{14}CO$_2$ form. It is estimated that in total 1000±300 GBq/GW(e)/y ^{14}C is released from RBMK reactor.

Table 3 summarizes the ^{14}C release from different types of nuclear power reactors, it can be seen that HWR has the highest gaseous release of ^{14}C, and only a very small fraction of ^{14}C is discharged in liquid.

2.2 Production of tritium and its pathways to the environment

2.2.1 Production of tritium in the nature and nuclear weapons testing

In nature, tritium (^{3}H) is mainly produced by cosmic ray reaction of nitrogen (^{14}N(n, ^{3}H)^{12}C) and oxygen in the upper atmosphere, the produced tritium is converted to water (HTO) and reaches to the earth's surface through precipitation. An estimated annual production rate of tritium is 1.48×10^8 GBq. With the radioactive decay of tritium, a steady state inventory of tritium in the earth surface is 2.59×10^9 GBq [2], causing a concentration of tritium in precipitation of 0.6-1.2 Bq·L^{-1} before nuclear era. A large amount of tritium was produced and released to the environment during atmospheric nuclear weapons testing in 1945-1980, it is estimated that 2.96×10^{11} GBq of tritium was released to the environment by this way, causing the tritium concentration significantly increased on the earth. This tritium is mainly produced by neutron activation reaction of Li through ^{6}Li(n, α)^{3}H and ^{7}Li(n, nα)^{3}H) in hydrogen bombs. The contribution
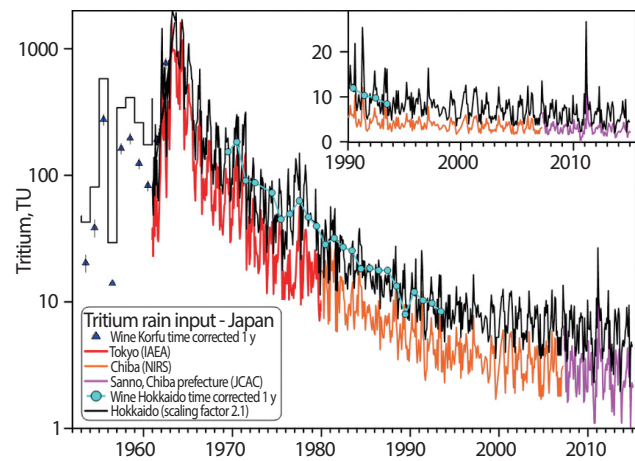

Fig. 2. Tritium time series in precipitation in Japan. The precipitation input curve is constructed using tritium data of Kofu wine (1952–1960), IAEA Tokyo station (1961–1975), Chiba NIRS (1976–2007), and Chiba JCAC (2008–present). The inset shows tritium time series from 1990 to 2016 [9]. TU= 0.118 Bq·L^{-1}
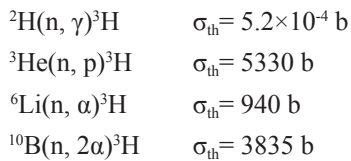
from ternary fission reactions of ^{235}U and ^{239}Pu is minor because of very small fission yield of tritium. The reaction of neutrons with nitrogen and deuterium (^{14}N(n, ^{3}H)^{12}C, ^{2}H(n, γ)^{3}H) in the atmosphere also contribute the tritium during explosions . Underground nuclear weapons tests seem to add little tritium to the atmosphere. Due to the relative short half-life of tritium (12.32 y), the last fraction of the tritium released during nuclear weapon tests has been decayed, and the present tritium concentration in the precipitation without direct contamination has also ready reach to about 1 Bq·L^{-1}. Fig. 2 shows the variation of tritium in the atmosphere from 1950's to 2016 in Japan.

Table 4. Typical release rates (GBq·y[-1]) of tritium from different types of nuclear power reactors [2]

Reactor type	Gaseous discharge	Liquid discharge
PWR (Zr cladding)	3.70×10^3	2.59×10^4
BWR	1.85×10^3	3.70×10^3
HWR	7.40×10^5	1.85×10^5
GCR	7.40×10^3	1.11×10^4

Table 5. Historical value for normalized releases of tritium and ^{14}C from nuclear power reactors (TBq/(GWa)) [1]

Period	PWR	BWR	GCR	HWR
Tritium(gas)				
1980-1984	5.9	3.4	5.4	670
1985-1989	2.8	2.1	8.1	690
1990-1994	2.3	0.94	4.7	650
1995-1997	2.4	0.86	3.9	330
1998-2002	2.1	1.6	3.3	874
[14]C (Gas)				
1980-1984	0.35	0.33	0.35	6.3
1985-1989	0.12	0.45	0.54	4.8
1990-1994	0.22	0.51	1.4	1.6
1995-1997	--	--	--	--
1998-2002	0.22	0.53	1.3	1.2
Tritium (liquid)				
1980-1984	27	2.1	96	290
1985-1989	25	0.78	120	380
1990-1994	22	0.94	220	490
1995-1997	19	0.87	280	340
1998-2002	20	1.8	402	817

2.2.2 Production and pathways of tritium in the nuclear reactors

In nuclear reactors, tritium is mainly produced by the following neutron activation reactions:

^{2}H(n, γ)^{3}H σ_{th}= 5.2×10^{-4} b
^{3}He(n, p)^{3}H σ_{th}= 5330 b
^{6}Li(n, α)^{3}H σ_{th}= 940 b
^{10}B(n, 2α)^{3}H σ_{th}= 3835 b

Tritium is therefore mainly formed in the following components in the nuclear reactors:

1) Water coolant and moderator (LWRs, Li and B impurities)
2) Heavy water coolant and moderator (HWRs, ^{2}H, Li and B)
3) Helium coolant (HTRs, ^{3}He)
4) Graphite moderator (GCRs, Li)
5) U and Pu fuel (Li, fission reaction)
6) Boron control rods (some reactors)
7) Reactor core materials (Li)

Among these components, tritium produced in fuel, boron control, graphite and reactor core materials is mainly retained inside the fuel elements or materials and not released to the environment until reprocessing or decommissioning/melting. Small portion of tritium produced in the fuel might diffuse through the cladding material, such as stainless steel into the coolant. Transfer of tritium from the graphite moderator to the coolant may occur because of corrosion of the graphite.

Tritium produced in the coolant is partly or entirely releases in the discharge streams to air or discharged water depending on the practical management of the gas releases and waste water in the nuclear power plants. The tritium released to the air might be in tritiated water (HTO or ^{1}H^{3}HO) vapor or hydrogen gas (HT or ^{1}H^{3}H), and tritium discharges in liquid are mainly in water form (HTO). The typical discharge rates of tritium from various types of reactors are presented in Table 4. The production and release pathways of tritium in major types of reactor are discussed below.

In light water reactors (LWRs), besides the production of tritium in the fuel by ternary fission, which is remained in the fuel elements until reprocessing, most of tritium in LWRs is produced in the coolant water from boron and lith-

Table 6. Estimated average annual collective doses of tritium and ^{14}C due to discharges from nuclear power plants from the period 1998-2002 [1]

Nuclide	Quantity	PWR	BWR	GCR	HWR	LWGR	FBR
tritium (gas)	Total release (PBq)	0.39	0.11	0.017	0.11	0.20	0.02
	Collective dose (man Sv)	0.82	0.22	0.036	0.23	0.43	0.041
tritium (liquid)	Total release (PBq)	3.7	0.12	2.1	10	0.006	0.0007
	Collective dose (man Sv)	2.4	0.078	1.3	6.7	0.04	0.0004
[14]C (gas)	Total release (PBq)	0.041	0.035	0.007	0.015	0.01	
	Collective dose (man Sv)	10	9.5	1.8	4.1	2.8	0.00005

ium. In PWRs, the production of tritium in the coolant is mainly from boron because of addition of boric acid for reactivity control. In BWRs, boron control rods are an important source of tritium. In LWRs, tritium is often discharged to the environment without additional trapping due to less production rate. Table 5 shows the tritium releases per energy production from PWRs and BWRs in 1980-2002. The different methods for reactivity control causes the higher tritium releases from PWRs compared to the BWRs.

Compared to light water reactor, large amount of tritium is produced in heavy water coolant and moderator in HWRs through the $^2H(n, \gamma)^3H$ reaction, with an estimated production rate of 8.9×10^7 GBq/GW$_{(e)}$/y [2]. Because of the high thermal neutron flux in the reactor core compared to the fuel channels, the fraction of tritium formed in the heavy water coolant is smaller than that in the moderator. The estimated concentration of tritium in the moderator is 3640 GBq/kg after 40 years operation, while only 81 GBq/kg tritium exists in the coolant for the same operation time.

The major part of the tritium produced in the heavy water moderator and coolant remains in the heavy water, but a minor part of heavy water might be released from the system to the reactor building or escape during detritiation process of heavy water. The HWRs are the reactor type with the highest releases of tritium among all types of reactors (Table 5) due to high production of tritium in the heavy water moderator and coolant.

In graphite reactors, tritium is mainly produced in the graphite from lithium impurity through $^6Li(n, \alpha)^3H$ because of high cross section of this reaction (940b). Tritium produced in the graphite might be released to the atmosphere by corrosion of the graphite. In addition, tritium might also be produced in the water vapor present in the reactor core. The vapor is transferred from the reactor core by the coolant gas (CO_2) and finds its way to the liquid discharges.

In RBMK, the reactor space is filled with helium-nitrogen mixture gases to prevent graphite oxidation. Because of the very high cross section of 5330b for reaction $^3He(n, p)^3H$, a high amount of tritium in the RBMK is produced, causing a high release of tritium from RBMK reactors.

Table 5 and 6 summarized the releases of tritium and ^{14}C from different types of reactors, and the estimated radiation doses. It can be seen that radiation dose from ^{14}C is much higher than tritium in most types of nuclear power reactors.

2.3 Releases of tritium and ^{14}C from nuclear fuel reprocessing plants

Tritium and ^{14}C produced in the nuclear fuel are removed during the reprocessing. All ^{14}C and tritium in the fuel are released during the shearing and dissolution step, while most of tritium and ^{14}C in the cladding materials still remain in the undissolved cladding. Around half of ^{14}C releases as off gas during dissolution of the fuel, most of it is trapped in scrubbing solution, and small portion is released to the atmosphere. About half of tritium enters into the dis-
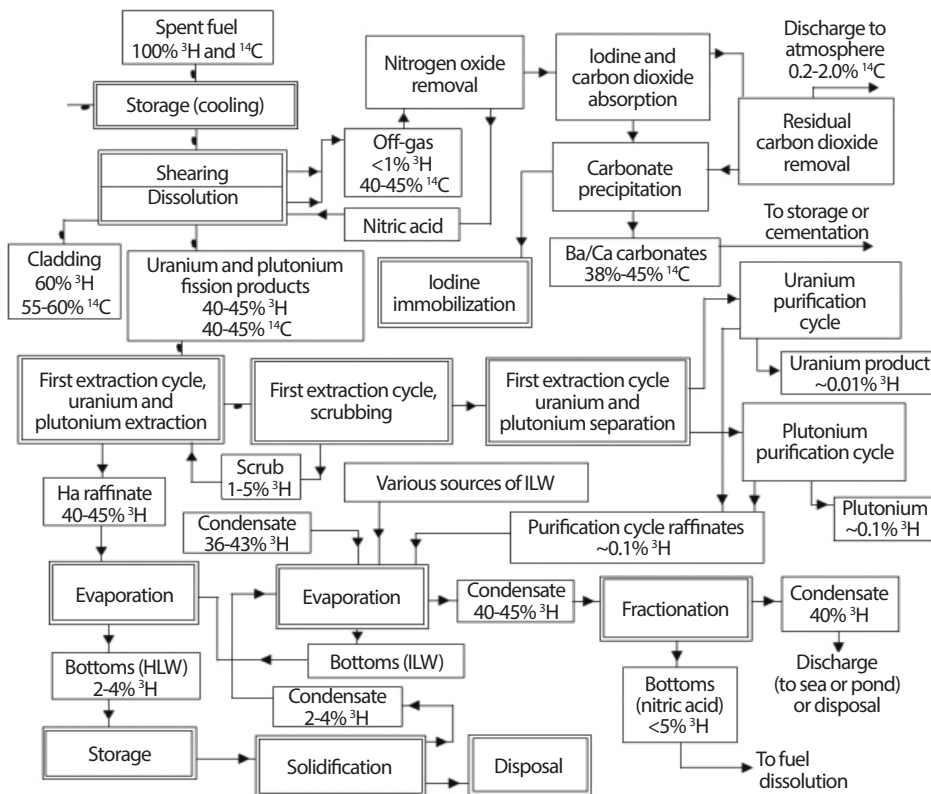
Fig. 3. Simplified flow chart of tritium and ^{14}C in a PUREX reprocessing plant for treatment of LWR fuel. The percentages of tritium and ^{14}C in different process products are shown (Modified from [1]).

solution of the fuel, and is separated as liquid waste. The distribution of ^{14}C and tritium in the reprocessing plants is shown in the Fig. 3.

2.4 Releases of tritium and ^{14}C from nuclear accidents and other nuclear facilities

Up to now, two major nuclear accidents in Chernobyl in 1986 and in Fukushima in 2011 have releases large amounts of radioactive substance to the environment, including tritium and ^{14}C. The damaged nuclear reactor in Chernobyl accident is a RBMK type reactor, due to the high production of tritium and ^{14}C in this type of reactor and burning of graphite during accident, large fraction of tritium and ^{14}C was released to the atmosphere. It was reported that large

fraction of ^{14}C released during the accident were in gaseous form (CO and CO$_2$) due to the burning of graphite at high temperatures (up to 3000℃), which was dispersed to a large area in the world. Total ^{14}C released to the environment was estimated to be 44 TBq (about 24% of the total inventory of reactor core) [10]. which is relative small compared to the nuclear weapons tests, but comparable to an annual releases from all PWRs in the world. Significantly increased ^{14}C level in the air was observed in Finland after the Chernobyl accident [11]. In addition, aerosol ^{14}C (mainly in fine graphite particles) was also released, which mainly deposited in local region of Chernobyl, which had been changed into organic carbon by assimilation via microorganisms in the past decades [12]. There is no report on the tritium releases from the Chernobyl accident. Since high production

of tritium in the graphite and He coolant in the RBMK type reactor, it is expected that a relative large amount of tritium was released to the environment. Based on the fission yield of ^{137}Cs and ^{3}H and the released ^{137}Cs, a release of 37 TBq tritium from Chernobyl accident was estimated [13]. This might be a high underestimation, because tritium in RBMK is mainly produced through neutron activation of lithium impurity in graphite and He in cooling tube, which was released through explosion and burning of graphite. A low (20 Bq·L^{-1}), but about 7 times increased tritium level was observed after the Chernobyl accident in the precipitation in Finland which received high Chernobyl fallout [11], but no remarkable increased tritium level in precipitation was observed after the Chernobyl accident in Germany, Ireland and Japan [13]. However, it might be still very small compared to the releases from the nuclear weapons tests, and even to the releases from HWRs.

Fukushima accident in 2011 has released large amount volatile radionuclides (e.g. [131]I, ^{137}Cs, [134]Cs, radioactive Xe) to the environment; tritium and ^{14}C should be also released. Since the damaged reactors in Fukushima Daiichi NPP are boiling water reactors, the production and inventory of tritium and ^{14}C in these reactors are much low compared to the RBMK reactor in Chernobyl accident, the released tritium and ^{14}C should be much less compared to that from Chernobyl accident. No report on the estimated amount of tritium and ^{14}C releases from the Fukushima accident is available. The measurement of ^{14}C in tree rings showed a slightly increased ^{14}C level only in the local region (<15 km from the damaged reactor in Fukushima Daiichi NPP) [14]. Increased tritium concentration of up to 6 Bq·L^{-1} was measured in the precipitation in Japan within a few weeks after the Fukushima accident. However, this is very quickly decreased to background level after 2 month [15].

Tritium was widely applied in medical research by labelling tritium to different organic compound, it might also release some amount of tritium to the air in forms of tritium gas (HT), organic gas tritium, and to rivers and marine system in liquid form, but it is only a small contribution compared to the total tritium on the earth [45]. The potential huge source of tritium will be production and application of tritium in fusion device (reactors) in the near future. In the fusion reactor, up to a few tens of kilogram of tritium (and deuterium) will be used. The release of a small fraction of these tritium during production, storage and operation of the power reactor might cause significant increased concentration of tritium in the environment (1g = 360 TBq tritium), which might be a big challenge in the limitation of its releases in the future.

In summary, tritium and ^{14}C are naturally produced in the atmosphere by cosmic ray. In the human nuclear activities, tritium is mainly produced through neutron activation reactions of [3]He, [6]Li, [10]B and ^{2}H in the nuclear reactors, and ^{14}C is mainly produced from neutron activation of ^{14}N, [17]O and [13]C. Tritium and ^{14}C released to the environment from the nuclear power reactors are mainly produced in the reactor coolants, and gases. The nuclear fuel and cladding materials contains large fraction of tritium and ^{14}C produced in the reactors due to high neutron flux, but they mainly remain inside these materials. The nuclear weapons tests in the 1950's and 1960's have been the major source of tritium and ^{14}C in the environment, which have declined significantly and is close to the natural level in normal environment until present time. The releases from the nuclear power plants are now become one of the major sources of tritium and ^{14}C in the environment, especially in the vicinity of the NPPs. Both tritium and ^{14}C are released from nuclear facilities to the environment in gaseous releases and liquid discharges. The majority of tritium is discharged to the environment through liquid discharges, while gaseous ^{14}C is the major way to be released to the environment from the nuclear power plants. Due to the different production ways, HWRs release much higher tritium per energy production, especially in liquid discharges, to the environment compared to other types of nuclear power reactors. While, light water reactors (PWRs and BWRs) release more gaseous ^{14}C to the environment per power production compared to other types of power reactors.

3. Approaches and setup for monitoring ^{14}C and tritium in nuclear facilities and environment

Monitoring of ^{14}C and tritium released from the nuclear facilities is important to the managers and operators of the nuclear facilities, as well as to the regulators and public to demonstrate that the radioactive emission is within acceptable limits. Tritium and ^{14}C are released to the environment in both gaseous and liquid discharges and in different forms. Reliable methods for sampling/collection of tritium and ^{14}C are critical for accurate monitoring the releases and environmental level of these two radionuclides.

There are normally two systems for monitoring ^{14}C and tritium releases from the nuclear facilities, discharge and environmental monitoring systems. The discharge monitoring systems are used to directly measure tritium and ^{14}C in airborne and liquid discharges before release to the environment; environmental monitoring systems are intended to measure the environmental level of these two radionuclides by analysing environmental samples, such as atmosphere, surface water, and environmental samples surround the nuclear facilities; the two systems are complementary. Environmental monitoring provides the accurate assessment of radiation exposure to the public, discharge monitoring provides direct data on the total amount of radionuclides and their species released from the nuclear facilities. Therefore, both systems are often operated in parallel.

3.1 Monitoring of ^{14}C in air, concerning collection efficiency of different forms of [14]C

Gaseous ^{14}C is normally released from the nuclear facilities through stacks in different species, $^{14}CO_2$, ^{14}CO, and hydrocarbon (C_nH_m). Table 2 presents the relative percentages of different species of ^{14}C released from different nuclear power reactors. In PWRs, most of ^{14}C was released as hydrocarbon, mainly CH_4 and C_2H_6, while in other types of power reactor (BWRs, HWRs, graphite reactor), ^{14}C is

mainly released as $^{14}CO_2$. Releases in ^{14}CO form accounts for very small fraction for all types of power reactors. The species of ^{14}C in the atmosphere are also mainly in three forms $^{14}CO_2$, ^{14}CO and hydrocarbon. However, the species of hydrocarbon in the atmosphere are more complicated than that in the stack of nuclear facilities. The percentages of different forms of ^{14}C in the atmosphere depends on its sources and the environmental conditions. Besides the direct releases of ^{14}C from the nuclear facilities, ^{14}C in the atmosphere also include the recycling of ^{14}C in the ecosystem, i.e. re-emission of ^{14}C accumulated in the environmental media including vegetation as well as soil and water. Meanwhile, constant production of natural ^{14}C in the upper atmosphere through cosmic rays is also a major source to the atmosphere in the present.

The methods for collection of ^{14}C from the stack of the nuclear facilities and from the atmosphere therefore depend on the requirements and purposes. There are three common used methods: (1) only collection of $^{14}CO_2$; (2) collection of all forms of ^{14}C in one sample; (3) collection of different species of [14]C.

3.1.1 Collection of $^{14}CO_2$ from the stacks and atmosphere

$^{14}CO_2$ in air and stack of a nuclear facility can be collected by two types of methods, active and passive collection. Passive sampler is just simply exposure of a collector to air, $^{14}CO_2$ is absorbed in the regents in the collectors, NaOH pellet, NaOH solution and filter paper impregnated with NaOH as absorbent have been used for passive collection of $^{14}CO_2$ in the air. 4 mol·l^{-1} NaOH solution putting into plastic tray, covered with nylon mesh to prevent from drop of suspending particles in the air into the NaOH solution, and filter paper wetted with 0.8 mol·l^{-1} NaOH solution have been used at Chalk River Laboratory, Canada for collecting $^{14}CO_2$ from air. This system is suitable for short term sampling because the NaOH solution will be saturated if it is exposed for a long time [27, 61]. Compared to NaOH impregnated filter paper, NaOH pellets as absorbent is easy

to handle and transport and have been applied for collect [14]CO_2 from stack of nuclear reactors [16, 17]. However, it should be mentioned that the passive method only provides a relative level of ^{14}C, and cannot give a precise concentration of [14]CO_2 in the air or stack gas. Some calibrations are needed to convert the measured ^{14}C value into the concentration of [14]CO_2 in the air or stack gas, but normally with a relative high uncertainty. It is therefore not often used.

The active sampling is the most often used method for collecting [14]CO_2 from the stack of nuclear facilities and from air. In this method, gas/air is pumped from the sampling site through a bubbler filled with absorbent or tube filled with molecular sieve. The most often applied absorbents are NaOH solution (0.8-4.0 mol·l^{-1}), NaOH pellet and organic amine (such as CarboSorb provided by PerkinElmer). The sampling efficiency depends on many parameters, such as the design of the bubbler, flow rate, absorbent components and concentration, as well as volume of the absorbent solution and gas/air collected. The flow rate should be kept low to allow a sufficient contact time of the gas/air with the absorbent solution. Bubbler with micro-pores sintered glass on the bottom is often applied to distribute the input gas/air into small bubbles for a better contact of the gas/air with absorbent. Two sequentially connected bubblers are often employed to ensure a quantitative collection of [14]CO_2. Compared with NaOH solution, CarboSorb solution has better compatibility with organic scintillation cocktails, and therefore low quenches effect in liquid scintillation counting (LSC) measurement of [14]C. Molecular sieve tube has been reported to be an effective approach for collecting CO_2 from air and stack gas with a good collecting efficiency, it is also easy to operate in the field and transport afterwards. In addition, it has a high capacity and can be operate for a long time, therefore suitable for sampling a large volume of air samples [18]. The main drawback of this technique is that [14]CO_2 adsorbed on the molecular sieve cannot be directly measured; it has to be released from the molecular sieve and trap the [14]CO_2 into CarboSorb or NaOH solution again for measurement using LSC, or converted to other forms

such as graphite for accelerator mass spectrometry (AMS) measurement of [14]C. For collecting [14]CO_2 in stack gas in nuclear facilities, NaOH solution and CarboSorb absorbers are the effective and the most often used methods, whereas, molecular sieve method is an effective method for collecting [14]CO_2 from large volume of air sample.

3.1.2 Collection of all species of gaseous ^{14}C from the stacks and atmosphere

The major fraction of gaseous ^{14}C released from PWRs is in hydrocarbon form, while the fraction of gaseous ^{14}C from other types of nuclear power reactors released as hydrocarbon is in 2-35%. Measurement of only [14]CO_2 will underestimate ^{14}C level in the stack gas and air, although the radiation risk of ^{14}C in hydrocarbon form is smaller than that of [14]CO_2, due to less absorption of hydrocarbon by vegetation and intake by humans through inhalation. Therefore, all species of ^{14}C are often collected from stack gas in many nuclear power plants, especially PWRs. The major method for collection of all species of ^{14}C is based on the conversion of all ^{14}C to [14]CO_2, and then trapping the formed [14]CO_2 using the same methods as for collecting [14]CO_2 from air. Hydrocarbon is normally converted to CO_2 by oxidation combustion with O_2 flowing and catalyst, in this case [14]CO is also converted to [14]CO_2. In practice, this is implemented by pumping stack gas or air through a tube which is filled with catalyst and heated in an oven to 400-800℃, where all species of hydrocarbon and [14]CO are converted to [14]CO_2. The off gas from the tube is then trapped in a bubbler filled with NaOH or amine. The most often used catalyst is Pt/Pd material, it has been reported that more than 99.7% of hydrocarbon can be converted to [14]CO_2 using Pd as catalyst and heated at 600℃ [19]. CuO has also been used as catalyst/oxidant to convert hydrocarbon and CO to CO_2 under heating at 600℃, and the formed CO_2 is then trapped in monoethnolamine. The oxidation and CO_2 collection efficiency by this method are >99.3% and >97.5%, respectively [20]. In this method, O_2 flow is not necessary, since CuO provides oxygen for the oxidation. Some commercial

instruments for collecting all [14]C (e.g. V3H14C (VF, Czech Republic) have been applied in some nuclear facilities [17, 21, 22, 23, 24, 25, 26, 27, 62].

3.1.3 Collection of different species of gaseous ^{14}C from the stacks and atmosphere

For better understanding the components of ^{14}C species released from the nuclear facilities and in the atmosphere and estimating the impact of ^{14}C to the ecosystem and public, different species of ^{14}C are collected and measured. In many systems for monitoring ^{14}C from stack of nuclear facilities, gas or air is passed through two devices separately, one is used to trap [14]CO_2, and the other for all species of [14]C. The difference between the values obtained by the two devices is the content of ^{14}C in hydrocarbon and CO forms. The results obtained by this method are general reliable if the ^{14}C fraction of hydrocarbon and CO forms is not very small compared to [14]CO_2. However, if the sum of the hydrocarbon and CO fractions are less than 5% of the total ^{14}C, the uncertainty of the analytical results for these two species will be relative big.

A sequential collection system has also been proposed and applied for collecting different species of ^{14}C from the stack of nuclear facilities or atmosphere. In this case, gas or air first passes through a [14]CO_2 bubbler where CO_2 is completely trapped, the off gas from the first bubbler passes through a tube filled with catalyst (e.g. Hopcalite, Cab-O-Sil, Packard Instruments, The Netherlands) at ambient temperature where [14]CO is converted to [14]CO_2, which is then trapped in the second CO_2 bubbler; afterwards the off gas from the second bubbler passes through anther tube filled with Pd/Pt catalyst which is heated in an oven at 400-800℃ to convert hydrocarbon to [14]CO_2, which is trapped in the third CO_2 bubbler. By this setup, three species of ^{14}C can be sequentially collected. In this system, it is important that the trapping efficiency for [14]CO_2 has to be sufficiently high to avoid any cross over from the front one to the following one, especially for [14]CO fraction, which normally accounts for a small percentage (<1%). By optimization of bubbler
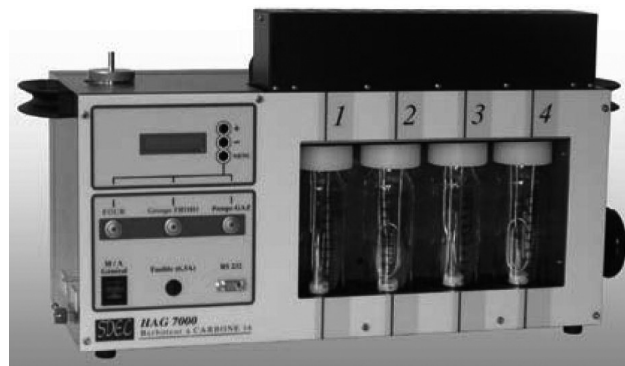

Fig. 4. HAGUE 7000 ^{14}C sampler for collecting [14]CO_2 and hyrocarbon-14 plus [14]CO. The bubblers 1 and 2 filled with NaOH or CarboSorb solution are sequentially connected for trapping [14]CO_2 from the air; the bubblers 3 and 4 are used to trap the converted [14]CO_2 from hydrocarbon and [14]CO.

design and adjustment of flow rate, a trapping efficiency of >99.9% have been obtained for [14]CO_2 [19].

Because the [14]CO species accounts for a very small fraction of ^{14}C, it is often collected with hydrocarbon. In this case, the gas or air first passes through a [14]CO_2 bubbler where CO_2 is completely trapped, the off gas from the first bubbler passes through a tube filled with Pd/Pt catalyst and heated in an oven at 400-800℃ to convert both hydrocarbon and [14]CO to [14]CO_2, which is trapped in the second CO_2 bubbler. By this setup, two fractions of ^{14}C, [14]CO_2 and hydrocarbon plus [14]CO are collected. Fig. 4 shows a commercial available system (Hague 700 ^{14}C sampler, SDEC, France) for sequentially collecting [14]CO_2 and [14]CO plus hydrocarbon-14 .

For low-level air samples, a sequential collection of [14]CO_2 and [14]C_nH_m is often implemented by passing through the air to a collection column and a furnace followed by the second column. The first column is filled with molecular sieve for trapping CO_2, the off gas from the first column passes through a tube filled with platinum catalyst, which is heated in a furnace to convert hydrocarbon and possible CO to CO_2, which is then trapped in the second molecular sieve column. The two columns are transported to laboratory for further separation of trapped CO_2 by heating and

re-trapping the released ${}^{14}CO_2$ in NaOH or CarboSorb solution for LSC measurement of ^{14}C.

3.2 Monitoring tritium in air concerning separation of different species of tritium

Many types of tritium monitors have been developed to measure gaseous tritium in stack exhaust gas from the nuclear facilities. Ionization chambers (e.g. Tyne Room Tritium-in-air monitor, Tyne Engineering Inc. Canada) is often used for such monitors, proportional counter (e.g. LB 110 tritium monitor, Berthold Technologies GmbH & co. KG, Germany) and solid scintillation detector are also employed in this types of monitors. However, these systems are not sensitive, with a detection limit of 0.1-10 kBq·m^{-3}. In addition, such monitors cannot well separate other radionuclides such as ^{14}C, radioactive noble gases, etc. therefore not very accurate when the concentrations of the other gaseous radionuclides are high. These monitors are not suitable to measure low-level tritium in the gas discharge from nuclear facilities and environmental air. Collection of tritium from large volumes of discharge gas or air has to be implemented for determination of low-level tritium and its species.

In the discharge gas from nuclear facilities and environmental air, tritium occurs as tritiated water vapor (HTO, DTO, T_2O), tritium gas (HT, DT, T_2) and hydrocarbon. The gaseous tritium released from most of the nuclear facilities is mainly in tritiated water form (HTO), especially in HWRs. Tritium in tritium gas (HT, T_2) and hydrocarbon species has a slow exchange with hydrogen in the vegetation, and are accumulated in vegetation and humans to a less degree. These species of tritium are consequentially less important than tritiated water (HTO) in view of radiation protection. Therefore, tritiated water (HTO) is more often measured in the reactor building and discharge gas in the stack of the nuclear facilities. For this purpose, the discharged gas from the stack or air in the reactor building is passed through a condenser or a dryer such as silica gel, tritiated water vapor is collected in the condenser or

adsorbed in the silica gel. The water adsorbed in the silica gel is further converted to liquid water by heating it and condensing the released water vapor. The separated tritiated water is directly used for LSC measurement of tritium.

The total tritium in the discharge gas is also often collected and monitored. In this case, the discharge gas or air first passes through a tube filled Pt catalyst, which is heated in a furnace to 400-800℃ to convert tritium gas and hydrocarbon tritium to HTO. The tritium in the tritiated water form is then trapped by a condenser or dryer. Bubblers has also been used for trapping tritiated water vapor, an ethylene glycol and tritium free water mixture is better than only water as trapping solution in the bubbler to minimize evaporative losses in longer term sampling. Since the trapping efficiency of water bubbler is normally not very high, three sequential bubblers are used to obtain a better recovery of tritium. For air samples with high content of other radionuclides, a purification of the trap solution is needed. Distillation or purification through an ion exchange cartridge (mix bed ion exchange resins) is sufficient good to remove most of interfering radionuclides.

For determination of different species of tritium in the discharge gas or air, the discharge gas or air first passes through a condenser or dryer, the off gas passes through a tube filled with platinum catalyst at ambient temperature to convert HT to HTO, which is then trapped in the second condenser or dryer. The remaining hydrocarbon species in the gas is passed through a tube filled with Pt/Pd catalyst and heated to 400-800℃ in a furnace to convert the organic species of tritium (hydrocarbon) to HTO, which is then trapped in the third condenser or dryer. The collected three fractions of tritium are then measured using LSC. HT can also be converted to tritiated water by passing gas over a heated CuO catalyst [2]; in this case, no oxygen is needed. Since HT and organic gas tritium species normally accounts for a very small fraction of tritium in the discharge and atmosphere, they are often combined as one fraction, i.e. the first tube filled with catalyst and heated following one trapper to collect the converted HTO from both HT and

organic gas tritium. A commercial tritium sampler (Fig. 5) is available for collection of two fractions of tritium: tritiated water and HT.

For analysis of air with low concentration of tritium, such as the environmental air, a large volume of air is needed. In this case, molecular sieve is often used to replace the condenser or dryer to collect tritiated water [28]. The collected three fractions of tritiated water in molecular sieve columns are transported to laboratory to separate the trapped tritiated water in each column by heating followed by condenser for tritium measurement [29].

For on-line measurement of different species of tritium in the stack discharge with high level of tritium concentration, two ionization chamber monitors can be used. In the sampling line, a desiccant cartridge is inserted between the two ionization chamber monitors for trapping the tritiated water from the gas stream. The second monitor measures the concentration of tritium gas and hydrocarbon tritium, and the first monitor measure all the species of gaseous tritium. The difference between two monitors gives the concentration of tritiated water [2].

The tritium samplers discussed above require the use of an air pump and flow meters to delivery certain volume of air/gas to the sampler in order to give concentrations of the total tritium or different species of tritium. A passive diffusion tritium sampler has also been developed and used for monitoring tritium level [30, 31]. This type of tritium sampler consists of a 20 ml LSC vial with a lid modified to contain a stainless steel insert with a diffusion orifice in the centre. HTO vapor in the air diffuses through the orifice and is trapped in the water in the vial. The amount of water vapor trapped into the vial is controlled by the diffusion rate of the orifice, exposure time and other parameters of the air components. The trapped tritiated water in the vial is directly measured using LSC after added scintillation cocktail. This method is less expensive and simple in operation, which is very suitable for field use for monitoring the outdoor air tritium level. The detection limit of this method is reported to be as low as 1 Bq·m^{-3} for over one-

Fig. 5. Marc 7000 Tririum sampler for collecting HTO and HT. The bubblers (No. 1 and 2) cooled to 5-15 ℃ are used to collect HTO . A tubular oven equipped with Pd alumina catalyst pellet heated to 200-500℃ to convert HT (as well as hydrocarbon) to HTO, which is collected in bubblers 3 and 4.

month exposure [32, 33]. However, the results obtained are not quantitative since the level of tritiated water trapped is influenced by many parameters.

3.3 Combined system for monitoring both tritium and ^{14}C in air

Gaseous tritium and ^{14}C in air can be sampled simultaneously in a combined system. In such a system, air is pumped through sequentially connected collectors or tubes. The first collector is a condenser/dryer/bubbler filled with ethylene glycol and water mixture/or a molecular sieve for trapping tritiated water vapor, the second collector is a bubbler containing NaOH or CarboSorb solution or another molecular sieve to trap $^{14}CO_2$. The off gas then passes through a tube filled with platinum with oxygen gas flow and heated in a furnace, where HT is converted to tritiated water, hydrocarbons are converted to HTO and $^{14}CO_2$, and ^{14}CO is converted to $^{14}CO_2$, the off gas passes through the following collectors, the third collector is a condenser/dryer/bubbler filled with ethylene glycol and water mixture/or a molecular sieve for trapping the formed tritiated water vapor, and the fourth collector is a bubbler contain NaOH or CarboSorb solution or another molecular sieve
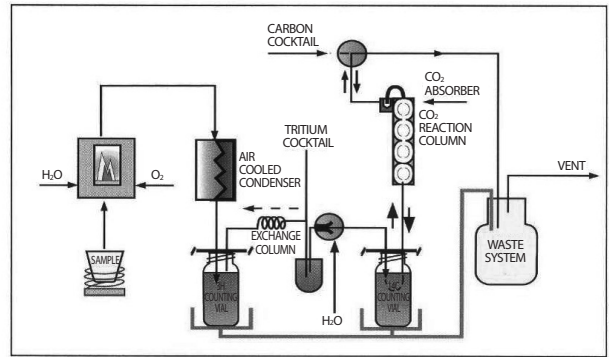
Fig. 6. A tritium and ^{14}C sampler (V3H14C, VF a.s., Czech Republic) for collecting tritium and ^{14}C in two fractions. The system includes two parallel lines, the first line equipped with heated platinum catalyst, and the second line without. Each line consists 3 bottles filled with silica gel absorber to trap tritiated water and 3 bottles filled with NaOH solution to trap [14]CO$_2$. Therefore, the first line is used to collect all species tritium and ^{14}C, while the second line is used to collect tritiated water and [14]CO$_2$.

(a)

(b)

Fig. 7. Schematic diagram of combustion system for separating Tritium, ^{14}C and other volatile radionuclides from solid samples. a) Sample Oxidizer; and b) tube furnace.
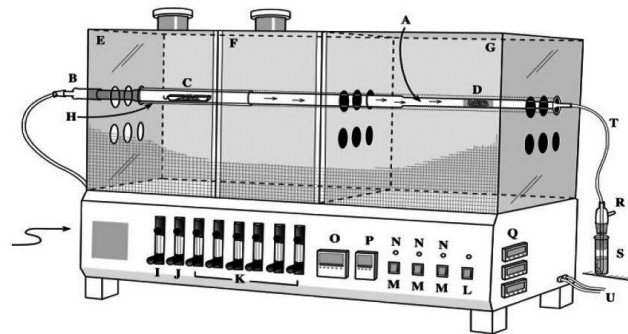
to trap the formed [14]CO$_2$. The tritium collected in the first and third collector is used to measure tritiated water and organic tritium plus tritium gas after separation of the tritiated water from the collector. The trap solutions in the second and fourth collectors are used to measure [14]CO$_2$ and hydrocarbon-14 plus [14]CO, respectively, after a further separation or purification. Some commercial systems are available for combined collection of different species of tritium and [14]C (Fig. 6), which have been used in some nuclear facilities for monitoring gaseous tritium and [14]C.

3.4 Monitoring of ^{14}C in water, speciation analysis of ^{14}C in water

Large amount of ^{14}C is produced in the reactor water (coolant and moderator), which forms the major source of ^{14}C in the discharge gas from the nuclear facilities. How-

ever, only a small fraction of the volatile species of [14]C ([14]CO$_2$, [14]CO and volatile hydrocarbon-^{14}C) escapes from the reactor water and is released through the stacks. Other fractions of ^{14}C is stable under reactor operation condition and remains in the reactor water. Some of the reactor water might be discharged into rivers or seas from the nuclear facilities, which cause an elevated concentration of ^{14}C in the environmental water samples. In principle, the chemical species of ^{14}C in the environmental water contaminated by the discharges from the nuclear facilities should be the same as its sources. However, some new species of ^{14}C might be formed during natural processes involving biological activities, and the distribution of the ^{14}C species in the environmental water might be changed. In general, ^{14}C in the reactor water and environmental water normally exist
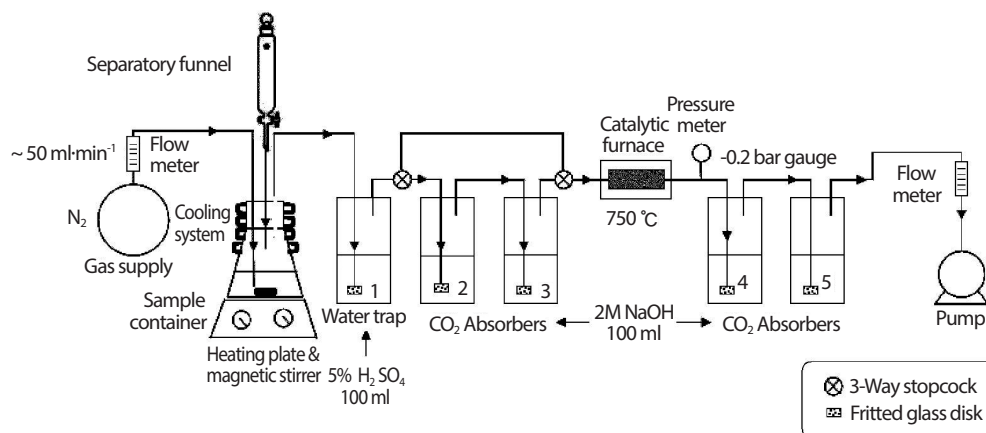
Fig. 8. Diagram of system for sequential separation of ^{14}C species in water sample [6]. Bubbler 2, 3 and 4, 5 are filled with 2 mol·l^{-1} NaOH for trapping [14]CO_2, the bubbler 1 is filled with diluted H_2SO_4 for trapping tritium and other volatile radionuclides (e.g. [131]I), CuO is used as catalyst in the furnace for convert CO and organic carbon to CO_2.

as dissolved gaseous [14]C (volatile hydrocarbons), inorganic carbon (mainly carbonate/biocarbonate) and water soluble organic compounds [2, 6].

Some methods have been reported for the determination of ^{14}C and its species in the reactor water [34, 35, 36, 37, 38, 39]. In general, three types of methods were used to separate ^{14}C and its species: combustion, wet oxidation using strong oxidative reagents ($K_2S_2O_8$ with $AgNO_3$ in acidic media or CrO_3 and H_2SO_4) and acid digestion (H_2SO_4). The combustion method is normally used to determine the total soluble ^{14}C in the water after evaporating the water to dryness; acid digestion is used to separate ^{14}C in carbonate/bicarbonate form; while wet oxidation for decomposing organic compounds is used for separation of ^{14}C in both organic and carbonate forms. The released ^{14}C is adsorbed in NaOH or CarboSorb solution for LSC measurement. For separation of volatile species of ^{14}C in water samples (e.g. CH_4, C_2H_6), a combustion method can be used by purging volatile species of ^{14}C from the water, which pass through a tube filled with catalyst (Pt/CuO) and heated in a furnace at 400-800℃ to convert all volatile organic carbon (hydrocarbon) to [14]CO_2, which is trapped in a NaOH bubbler [27]. For determination of all soluble ^{14}C using combustion method, the water is first adjusted to pH 8-9 using Na_2CO_3 and/or

NaOH followed by evaporation to dryness. The residue is then transferred to a boat that is placed in a tube furnace for combustion or combusted using sample oxidizer (Fig. 7). The water sample is first evaporated to a small volume (<5 ml), and then transferred to a boat to avoid that residues attach to the surface of the beaker, causing loss of some residue during transferring the entire residue to the boat. There are two types of commercial combustion systems available for separation of total ^{14}C in the residue: Pyrolysis based tube furnace (Raddec International, Southampton, UK) [40] and Sample Oxidizer (PerkinElmer, USA) [41]. Sampler Oxidizer can rapidly separate ^{14}C from residue in 2-3 min/sample compared to Pyrolysis of about 4 hours for each batch (4-6 samples). However, the tube furnace system (pyrolysis based system) can treat a large size sample up to 20 g, compared to only less than 1 g samples in Sample Oxidizer system. Schematic diagram of two systems (Fig. 7) shows the separation principle and structure of the system. In wet oxidation method for separation of organic ^{14}C or all soluble ^{14}C, some ^{14}C might be released as [14]CO or volatile organic species during the wet oxidation process. A combustion furnace with catalyst can be applied before trapping [14]CO_2 in order to ensure the collection of all soluble [14]C.

Two methods have been proposed for determination of different species of ^{14}C. One method use two systems; one is used to separate the entire ^{14}C employing wet oxidation at acidic media, and another one use acid digestion to separate carbonate. The difference between the ^{14}C results from the two systems is the fraction of organic ^{14}C [4]. If the fraction of organic ^{14}C is relative small (<5% of the total ^{14}C), the results of organic ^{14}C from this method might be inaccuracte (e.g. with an uncertainty more than 100%). Another method is to sequentially separate each species of ^{14}C and collecte them individually in an integrated system [6, 7].

Fig. 8 shows the schematic diagram of the system for sequential separation of ^{14}C species in water samples [6]. The system consists of 6 parts: (1) the gas supply to purge gas (N_2) to the system; (2) Reaction vessel where the water sample is put in a flask which can be heated by a hot plate and stirred, a separatary funnel is connected to the sample flask to add acid to the water, and a cooling/condensor to convert the evaporated water vapor to liquid and return to the sample container funnel; (3) three bubblers, the bottle No.1 contains diluted H_2SO_4 for trapping tritiated water and other volatile radionuclides (e.g. radioactive isotopes of iodine, chlorine, technetium, etc.), bottle No. 2 and 3 are filled with NaOH solution for trapping $^{14}CO_2$, the bottle No. 3 is a backup of the bottle No. 2 to ensure completely trapping of $^{14}CO_2$; (4) catalytic furnace, a tube filled with catlyst/oxidant (CuO) which is heated in a furnace, ^{14}CO and organic carbon compounds are converted to $^{14}CO_2$ in this part; (5) two bubblers for trapping $^{14}CO_2$, among them the bottle No. 5 is a backup of the bottle No. 4 to ensure complete trapping of $^{14}CO_2$; (6) a vacumm pump to suck gas from the system.

The separation of ^{14}C species in water is carried out in three steps: 1) for volatile species of ^{14}C, the water sample is purged from the bottom of the sample container using a flow of N_2, the volatile carbon compounds are purged out from the water and transferred through the system, oxidized forms of carbon (CO_2) are absorbed in the bottle No. 2, while other forms of carbon compounds pass through the catalytic furnace where organic carbon is converted to CO_2, which is then trapped in the bottle No. 4, the solutions in bottle No. 2 and 4 are used for measurement of volatile species of ^{14}C, and solution in all bubblers are replaced with new trap solution before the second step; 2) acid stripping for separation of carbonate species, the system is first evacuated to 0.2 bar using the vacumm pump, and carrier gas (N_2) is then purged through the system, H_2SO_4 is added from the separatary funnel to the water sample, the acidified water is purged for 1 hour. CO_2 released from the sample is trapped in bottle No. 2 and 3, which is used to measure ^{14}C in carbonate fraction. (3) wet oxidation for soluble organic species of ^{14}C, after the previpus two steps, the gas flow from the sample flask is switched to the connection to the catalytic furnace, and 5% $K_2S_2O_8$ and 4% $AgNO_3$ solution are then added to the water sample flask, the water is then heated to 95℃ and stirred for 2 hous, gasses released from the sample as CO_2 and CO flow through the catlystic furnace to convert all species of ^{14}C to $^{14}CO_2$, which is trapped in bottle No. 4 and 5, and used for measurement of soluble organic ^{14}C.

This system can also be used for separation of ^{14}C species in environmental water or wastewater discharged from the nuclear facilities.

3.5 Monitoring of tritium in water, concerning organic and inorganic tritium

In reactor water, liquid discharge and environmental water samples, tritium exists dominantly as tritiated water (HTO or T_2O). While, in the liquid discharge and the environment, a small fraction of tritium might occur in organic forms. The determination of tritium in water is straightforward and easy by LSC. However, because the decay energy of tritium (maximum energy of beta particle is 18.6 keV), quench effect has to be considered before measurement, such as peroxide, alkaline or acidic medium and high salt content. A specific quench correction can be used for the determination of the specific samples when the tritium

concentration is sufficiently high, otherwise purification is normally needed. Distillation is the most often applied and simplest method for purification of water samples for tritium measurements. The water sample is first neutralized before distillation to remove acids and volatile compounds. For the water sample with relative high content of organic compounds, active charcoal is added to adsorb the soluble organic compounds, which is then removed by filtration, the filtrate is further purified by distillation. The tritium in the organic form, which is absorbed in active charcoal, can be further separated by oxidation combustion (Fig. 7) to convert the organic compounds to tritiated water for measurement. This method has also been used for speciation analysis of tritium and ^{14}C in urine samples [42].

The tritium concentration in environmental water is normally too low to be directly measured by LSC, an enrichment system is normally used to enrich tritium from water samples. The enrichment system of water is based on the electrolysis of water, in which hydrogen water (H_2O) is electrolyzed to H_2 and O_2 gases before tritiated water (T_2O and HTO), and HTO is remained and enriched, which is used for measurement by LSC. By this way, an enrichment factor of 30-50 can be reached depending on the initial volume of the water and the final water volume [43, 44].

3.6 Combined system for monitoring both tritium and ^{14}C in water

In the most cases, both tritium and ^{14}C in the liquid discharge and environmental water are required to be monitored. The system used for ^{14}C can also be used for tritium. For the measurement of total tritium and ^{14}C, the water sample can be treated by wet oxidation; ^{14}C in both inorganic and organic forms is converted to CO_2 to be trapped for ^{14}C measurement, while tritium remaining in the liquid sample is further purified by distillation for measurement of tritium in the distilled water. Meanwhile the speciation analysis of tritium in the water can also be carried out by using the same systems as for speciation analysis of ^{14}C in

water. Tritium in tritiated water form is obtained by measurement of the distillated water from the original water sample. The total tritium is obtained by the further purification of the wet oxidation treated water samples by distillation. The difference between the total tritium and tritiated water fraction is the organic tritium. It should be mentioned that the organic tritium fraction in the liquid discharge and environmental water is normally too small to be significant in view of radiation protection.

3.7 Separation of tritium and ^{14}C in solid waste and environmental samples

For the determination of tritium and ^{14}C in solid samples such as ion exchange resin, water evaporates, concrete, graphite, metals, soil, sediment and vegetation, oxidation combustion is often used. In this technique, the samples are combusted at high temperature (850-1000°C) under O_2 flow and with Pt or CuO catalyst. Regardless of its species, all tritium in the sample is converted to water vapor, which is released from the sample and collected by a condenser or water/diluted acid trapping. Meanwhile, ^{14}C in both inorganic and organic forms is converted to CO_2, which is released from the sample and trapped in an alkaline solution such as CarboSorb or NaOH. The separated tritium in water and ^{14}C in trap solution are measured by LSC after mixing with scintillation cocktails, respectively. Pt or CuO catalyst is used to convert any CO to CO_2, since CO cannot be effectively trapped in alkaline solution.

Two combustion systems have been used for this purpose: Pyrolysis based tube furnace (Raddec International, Southampton, UK) [40] and Sample Oxidizer (PerkinElmer, USA) [41]. Sampler Oxidizer (Fig. 7) can rapidly separate tritium and ^{14}C from solid samples in 2-3 min/sample compared to Pyrolysis of about 4 hours for each batch (4-6 samples). However, the tube furnace system can treat larger samples, up to 20 g for concrete, soil and metal and, 5 g for biological samples, compared to only less than 1 g concrete, soil and metal, and 0.5 g biological samples

in Sample Oxidizer system. Besides these samples, the Sample oxidizer has also been used to analyze oil, bitumen and plastic samples. The results showed that both inorganic and organic forms of tritium and ^{14}C could be quantitatively separated from samples using these two systems.

In ion exchange resin, ^{14}C exists in both inorganic (mainly carbonate) and organic forms (i.e. organic compounds). A sequentially extraction/digestion method similar to the method used for reactor water has been used to separate inorganic and organic ^{14}C in ion exchange resin and processing water from nuclear reactor [6, 7].

In the reactor bio-shield concrete, tritium might be present as strong bound species, which is produced inside the crystal of minerals in the concrete during exposure to neutrons. Meanwhile tritium water (HTO) released from the reactor, especially the reactors which use heavy water as coolant, might also bind to concrete in HTO form. Based on the different volatility of tritium species, they can be separated by heating/combustion at different temperatures. Tritium water (HTO) associated to concrete can be liberated at 100℃. While strongly bound tritium produced by neutron activation of concrete cannot be released at temperature <300℃, and have to be combusted at >700℃ [40].

In the Danish research reactor DR-3, due to leakage of heavy water from the reactor tank, the reactor bio-shield concrete was contaminated by heavy water with high HTO content in addition to tritium produced in the bio-shield concrete during reactor operation. A concrete core from DR-3 was sampled under cooling using nitrogen gas from liquid nitrogen container, in order to investigate the distribution of tritium species. The sampled concrete core was immediately cooled and stored at -20℃ until analysis. Before the analysis, the concrete core was cooled by immersing the concrete in a plastic bag into liquid nitrogen, and then sliced to about 1 cm slice. The slice was then immediately crushed to powder (<0.5 mm), and transferred to a round bottom flask. The concrete powder in the flask was quickly connected to a heating and condensing system. The flask was heated using a heating mantle at 200±20℃ for

2 hours. The released tritium water (HTO) was condensed in the condenser and receiver by cooling, and transferred into a vial by rinsing the condenser tube and receiver using tritium free water for tritium measurement. The remained concrete powder was further analyzed using the Sample Oxidizer system for strongly bound tritium by combustion at >1000 ℃ [41].

In metals used in the nuclear facilities, tritium mainly originates from adsorption from the air as HT or HTO or local production through neutron activation reactions of B (^{10}B (n, 2α)^{3}H, Li (^{6}Li(n, α) ^{3}H) and N (^{14}N(n, ^{3}H) ^{12}C). It is proposed that when the metal is exposed to tritium (HT or HTO), tritium enters metals by diffusion with a rate controlled by the metal composition and surface feature, and tritium is normally trapped in hydrated oxide. While in irradiated metals, tritium forms internally through neutron capture reactions with boron and lithium inside the metal bulk. It was found that the adsorbed tritium can be released at temperature of lower than 400℃, while release of internally produced tritium in the metal needs to be heated at higher temperature of 600-900℃ [63]. For the sample containing both adsorbed and local produced tritium, the distribution of tritium might be highly heterogeneous, a careful sampling and sample preparation should be given to obtain a representative sample for tritium analysis.

Tritium species in biological samples including food are also an interesting issue, which is related to the estimation of radiation exposure through food consumption, which is also a key issue in the investigation of the transfer pathway of tritium from soil and air to vegetation. Species of tritium in sediments is also an interesting issue regarding to sources, transfer and accumulation of tritium in the environment [45]. Speciation analysis of tritium in biological samples and sediment mainly focus on tritiated water, water exchangeable and non-exchangeable organic tritium. Tritiated water in fresh biological and sediment samples can be separated by freeze-drying or distillation. Water exchangeable tritium is separated from dried samples by leaching using tritium-free water [46]. The non-exchangeable organic

Table 7. Tritium and ^{14}C in air and tea leaves around Qinshan NPP, China [49]

Year	Air		Tea leaves	
	tritium (mBq·L^{-1})	[14]C(mBq·L^{-1})	tritium (Bq·kg^{-1})	[14]C (Bq·kg^{-1})
2004	1.27	0.50	12.3	36.7
2005	0.81	0.49	9.2	26.9
2006	1.28	0.65	5.0	26.2
2007	1.13	0.66	6.0	26.1
2008	2.28	0.50	13.6	30.3
2009	1.58	0.46	1.5	24.5
2010	1.41	0.41	<MDC	18.8
2011	1.90	0.50	1.6	16.8
Background	0.21	0.40		

tritium remains in the leached samples is finally separated by a combustion method using sample oxidizer or tube furnace (Fig. 7). The tritiated water can also be extracted by water leaching using tritium -free water, based on quick exchange of tritium water in the biological samples and sediment with leaching water. Experiment has shown that tritiated water adsorbed in silica gel, concrete and brick can be quickly leached out by water [46, 47, 48]. However, the water exchangeable organic tritium will also be extracted, and a combined fraction of water exchangeable tritium is obtained [45].

In the environment around some of the NPPs, tritium and ^{14}C in air and foodstuff are monitored in the routine monitoring program. Table 7 shows reported levels of tritium and ^{14}C in air and tea leaves collected in the agriculture land around the Qinshan NPP, China (with 9 units, among them 2 units are CANDU type reactors) [49].

In summary, three methods have being used for monitoring ^{14}C and tritium in the gaseous releases and atmosphere, i.e. [14]CO$_2$, total ^{14}C, and different species of ^{14}C and HTO , total tritium and different species of tritium. Because tritium is mainly discharged as HTO vapor in the gaseous form, HTO is often determined in the gaseous discharge from nuclear facilities in routine monitoring program. The

species of ^{14}C in gaseous discharges vary depending on the type of reactor, monitoring of different species of ^{14}C, mainly [14]CO$_2$ and hydrocarbon-14, is in general implemented in the gaseous discharges from nuclear facilities. [14]CO$_2$ is mainly trapped in NaOH solution or organic amine in a bubbler. A trapping efficiency of >99% for [14]CO$_2$ is obtained in this method. HTO is often collected using a condenser or silica gel dryer. For speciation analysis of ^{14}C, the gas from the stack first passes through a bubbler with NaOH to trap [14]CO$_2$, and then the off gas passes through a furnace tube filled with CuO or Pt/Pd catalyst and heated to 400-800℃ to convert hydrocarbon and CO to CO$_2$, which is then trapped in the second bubbler. A combined system is also used to monitoring both ^{14}C and tritium in the gaseous discharges using the same principles. For atmosphere samples, the concentrations of ^{14}C and tritium are normally low and molecular sieves are often used for collecting [14]CO$_2$ and HTO, respectively. In this case, a long sampling period is applied to collect sufficiency amount of tritium and ^{14}C for measurement. In the reactor water and liquid discharges, ^{14}C mainly exists as dissolved gaseous [14]C (volatile hydrocarbons), inorganic carbon (mainly carbonate) and water-soluble organic compounds. Three types of methods have been used to separate ^{14}C and its species

in the water samples, combustion, wet oxidation using a strong oxidative reagents and acid digestion. The combustion and wet oxidation methods are used to determine the total soluble ^{14}C in the water after evaporating the water to dryness. Acid digestion is used to separate the ^{14}C in carbonate form. By using acid digestion followed by wet oxidation, both inorganic and organic ^{14}C can be separated. Systems with a tube furnace or a sample Oxidizer with CuO or Pd/Pt catalyst has been used for separation of ^{14}C and tritium in solid samples. In the liquid discharges and environmental water samples, the water form of tritium dominates, with only a small fraction of organic tritium forms. Tritium in water form is separated by distillation and measured by LSC. The organic associated tritium can be separated using tube furnace or sample Oxidizer.

Although a number of methods for speciation analysis of tritium and ^{14}C in the discharges from the nuclear facilities and environment have been developed and some commercial instruments are available. The methods developed a few decades ago are still used. In these methods, only [14]CO_2 and HTO in gaseous discharges and total ^{14}C and HTO in liquid discharges are monitored. It is a challenge to update and replace the old methods by the state of the art methods of speciation analysis of tritium and ^{14}C in order to provide a more useful and comprehensive information of tritium and ^{14}C released from the nuclear facilities for precise estimation of radiation dose to the critical population.

4. Analytical methods for measurement of ^{14}C and tritium

The most often used techniques for off-line measurement of tritium and ^{14}C is liquid scintillation counting (LSC). Among other techniques, accelerator mass spectrometry (AMS) is the most sensitive technique for the detection of ^{14}C, and is often used for analysis of non-nuclear samples but normally not used for samples from nuclear facilities such as discharges, resin and waste.

Noble gas mass spectrometry is the most sensitive technique for measurement of tritium in very low levels (< mBq), which is based on the measurement of [3]He, the decay daughter of tritium. Helium in the sample is first removed by vacuum and the sample in a tight container is kept for a few months for ingrowth of tritium from tritium decay, the produced [3]He is separated and measured using noble gas mass spectrometry. However, this method is not used for analysis of discharge and waste samples from nuclear facilities. Ionization chamber and proportional counter are often used for directly measurement of gas tritium (HT, T_2) and [14]C ([14]CO_2, CH_4), and they are often used in the most of on-line monitors for tritium and [14]C.

4.1 Measurement of tritium using LSC

Tritium in water form is normally prepared as purified water for measurement using LSC. To improve the counting efficiency, water is filtered, neutralized and distilled to remove the chemicals to reduce the quench effect. A scintillation cocktail is mixed with the purified water for LSC measurement, a better compatible cocktail is normally selected to use bigger volume of water and to obtain a better counting efficiency, and finally a good detection limit. For determination of tritium in environmental samples, 10 ml water sample is often used and mixed with 10 ml scintillation cocktail for LSC measurement. In this case, a detection limit of 1-2 Bq·L^{-1} can be obtained using ultra-low level LSC (e.g. Quantulus 1220, PerkinElmer, USA). For improvement of detection limit, a high capacity LSC (e.g. AccuFLEX LSC-LB7, HITACHI ALOKA, Japan) with 145 ml vial can be used. In this case, up to 70 ml water sample can be used, and a detection limit down to 0.3 Bq·L^{-1} can be reached.

4.2 Measurement of ^{14}C using LSC

[14]C collected or separated from samples is normally absorbed in NaOH or CarboSorb trap solution, solid ab-

sorbent such as Ascarite (NaOH immobilized in a solid support), NaOH pellets or molecular sieve. CarboSorb and diluted NaOH solution can be directly mixed with scintillation cocktail for LSC measurement, but a relative high quench level is normally obtained when directly mixing 2-4 mol·l^{-1} NaOH with scintillation cocktail, and therefore a less counting efficiency will be obtained. Therefore, ^{14}C absorbed in NaOH solution, NaOH pellet and immobilized NaOH solid is normally further separated. This is normally achieved by two methods. NaOH pellet is dissolved in water, excessive BaCl$_2$ is added to the NaOH solution, ^{14}C is precipitated as BaCO$_3$, which is separated by centrifuge and washed by water. The BaCO$_3$ precipitate is dispersed in scintillation cocktail for LSC measurement, which reduce the quench level, meanwhile ^{14}C can also be purified by removal of other radionuclides in the solution during precipitation [50, 51, 52]. However, the BaCO$_3$ powder mixed with scintillation cocktail can cause some level of physical quench. Another method is to release ^{14}C absorbed in NaOH as CO$_2$ by addition of acid (H$_2$SO$_4$) under N$_2$ purging, the released [14]CO$_2$ is trapped in CarboSorb (an amine solution), which is then mixed with specific scintillation cocktail for LSC measurement. [14]C adsorbed in molecular sieve and Ascarite can be released as [14]CO$_2$ by heating, and the released gaseous [14]CO$_2$ is trapped in CarboSorb for LSC measurement after mixed with scintillation cocktail.

NaOH or CarboSorb trap solution for ^{14}C cause a relative high quench in the LSC measurements, relative small samples can be analyzed with this method. Therefore, the detection limit of this method is not sufficient low for the determination of ^{14}C in low-level environmental samples. The measurement of low level ^{14}C using LSC can also be carried out by converting ^{14}C to benzene. In this way, a large sample can be used and the quench can be overcome. To obtain this, ^{14}C in CO$_2$ gas is reduced by lithium under heating to obtain lithium carbide (Li$_2$C$_2$), the hydrolysis of Li$_2$C$_2$ produces acetylene (C$_2$H$_2$), which is trimerised to benzene (C$_6$H$_6$) on vanadium catalyst [53]. This method has a much better detection limit for ^{14}C, and therefore can be

used for measurement of ^{14}C in low-level samples. However, the analytical procedure is very time consuming and therefore more expensive.

4.3 Measurement of tritium and ^{14}C using ionization chamber (on-line measurement)

The on-line monitoring of gaseous tritium and ^{14}C normally use ionization chambers as detectors. In this instrument, the gas sample passes through the chamber, the beta particles emitted from ^{14}C or tritium ionizes the surrounding gas in the ionization chamber, and produced ions are measured by the ionization current, which is proportional to the concentration of tritium or ^{14}C in the gaseous sample passing through the chamber. In general, this type of monitors could not discriminate between radionuclides, when used for specific radionuclides, i.e. tritium or [14]C. Therefore, ^{14}C or tritium has to be separated from each other and from other radionuclides before measurement. For ^{14}C, any gaseous forms such as [14]CO$_2$, [14]CO, [14]CH$_4$, and [14]C$_2$H$_6$ can be measured. While for tritium the monitoring works best for tritium gas such as HT (T$_2$). Although tritiated water vapor can also be measured, but the high risk of adsorption and deposition of tritiated water in the ionization chamber generates a high risk of contamination. Hence, a high memory effect, and the detector requires frequent decontamination. Most of ionization chambers are the flow through type, which requires pumping of the gas sample through the system. An open window type of ionization chamber is also used. These chambers employ a cover; air or gas penetrate through the window to the inside chamber for measurement. This type of instrument works without pump, and are often used to monitor rooms, hoods, glovebox, etc.

Because HTO can be easily uptake by humans through inhalation compared to HT (10,000 to 25,000 times greater), it is desirable to know the relative amounts of each species following a significant release. In the case of stack monitoring, discrete samples of the stack discharge should be taken using bubblers or desiccants with a catalyst for
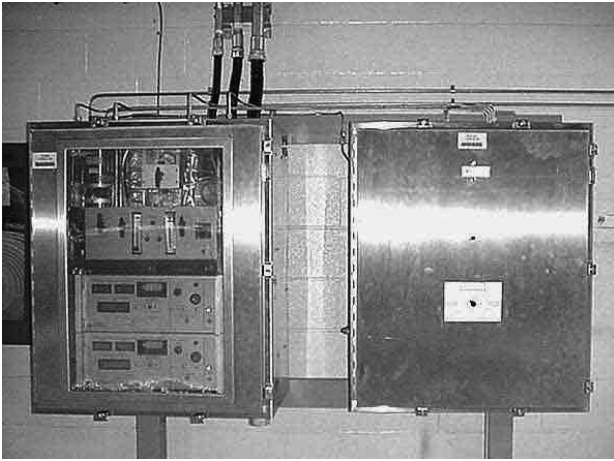
Fig. 9. A discriminating tritium monitor for total tritium and HT(T$_2$) [54].

oxidizing the HT. Fig. 9 shows a tritium monitor using ionization chamber as detector applied in nuclear power plant in Canada for monitoring tritium releases from stack [54]. This system is used to measure both total tritium and tritium gas (HT) by using two ionization chambers and a dryer between them. The gaseous sample passes through the first ionization chamber, in which the concentration of total tritium is measured, the off gas then passes through a desiccant to remove HTO vapor/moisture, leave the tritium gas (HT) which passes through the second ionization chamber to measure concentration of tritium gas (HT).

Another technique uses a semipermeable membrane tube bundle in the sampling line to remove the HTO (preferentially over the HT), which is directed to a HTO monitor. After removing the remaining HTO with another membrane dryer, the sampled air is directed to the HT monitor. Although this technique is slower than the one requiring a desiccant cartridge, it does not require a periodic cartridge replacement. Furthermore, it can be adapted to measure tritium in both species in the presence of noble gases or other radioactive gases by adding a catalyst after the HTO dryers, followed by additional membrane dryers for the HTO. However, because of its slow response, it is more suitable for discharge or stack monitoring than for room monitoring. Because significant releases into a room are quite rare, it is

easier to treat any such release as one of HTO than using complicated techniques for continuous differential monitoring [55].

4.4 Measurement of ^{14}C using AMS

The most sensitive measurement method for ^{14}C is AMS. In this method, the sample in CO$_2$ gas is reduced by H$_2$ in the presence of powdered iron or by Zn metal to elemental carbon (graphite). The carbon/graphite is deposited on the powdered iron or zinc and the mixture is pressed into a target for measurement by accelerator mass spectrometry. This method can analyze small sample of microgram carbon and very low level of ^{14}C down to μBq [56]. Because of high sensitivity, it is very often used to measure pre-nuclear samples for ^{14}C dating purpose. It is very seldom to be used for measurement of ^{14}C from nuclear facilities, because of high risk of contamination of laboratory by high level ^{14}C samples.

In summary, ionization chamber is the often used instrument for on-line monitoring of tritium or ^{14}C in gaseous form. This type of monitors could not discriminate between radionuclides. [14]C or tritium has to be separated from each other and from other radionuclides before measurement. Two ionization chambers and a dryer between them are used for monitoring of gaseous tritium in HT and HTO. The first chamber is used to measure both HT and HTO, while the second chamber measure only HT after HTO is removed by a dryer. In general, this type of monitor is used to measure tritium or ^{14}C in the stack with high concentration because of its low sensitivity. LSC is the most often used method for off-line measurement of tritium and [14]C. [14]C trapped in NaOH solution or pellet is normally converted to BaCO$_3$, which is suspended in scintillation cocktail for LSC measurement. Tritium in condensed water is directly measured using LSC after mixed with scintillation cocktail, while tritium trapped in dryer or molecular sieve has to be released and converted to water form for LSC measurement. The most sensitive method for tritium is noble gas mass spec-

trometry, which takes a long time for analysis because of ingrowth of [3]He from tritium. AMS is the most sensitive method for ^{14}C measurement; it can measure μBq level ^{14}C and just need a small sample. But the sample preparation is time consuming and measurement is high cost. Therefore, these two techniques are seldom used for monitoring tritium and ^{14}C in nuclear facilities.

5. Challenges, problems and methods in monitoring of tritium and [14]C

In the past decades, a numbers of methods for the monitoring of tritium and ^{14}C in air and liquid discharges has been developed and applied in the nuclear facilities including many nuclear power plants. The on-line monitor using ionization chamber is widely used for monitoring gaseous tritium in the nuclear facilities, especially heavy water reactors and reprocessing plants [29, 52]. While such an on-line monitoring system is still not well developed and widely used for monitoring gaseous ^{14}C in the nuclear facilities because of low activity concentration of ^{14}C compared to other radionuclides in the gas discharge. Separation and enrichment of ^{14}C from the discharge is required before measurement, therefore off-line measurement is often applied. Development of a rapid and on-line monitoring system will be helpful for rapid monitoring of the releases of gaseous ^{14}C, and therefore avoid accidental releases of elevated amounts of ^{14}C to the environment.

The collection of representative sample is one of the major challenges and sources of analytical uncertainty in monitoring gas releases and atmosphere. A robust sampling system is critical, whereby the sample is extracted at a homogeneous location within the point source. This requires an evaluation of the sample environment, transport mechanisms, and collection materials. The criterion for the homogeneous sampling location includes a determination of the angular or cyclonic flow, uniformity of the air velocity profile, gas concentration profile, etc. Modeling techniques

such as computational fluid dynamics may be used to validate a well-mixed location without the necessity of field tests conducted in the stack or vent [57].

A number of methods and instruments have been reported for separating different species of ^{14}C and tritium in the gaseous releases from the nuclear facilities [35, 52, 54, 58, 59]. While, many facilities still measure only [14]CO_2 and tritiated water in the gaseous releases, this might not be reasonable for PWRs, because of the high fraction of hydrocarbons in releases from PWRs. It is still a challenge to establish a reliable and easy operated system, which can be applied for monitoring different species of ^{14}C and tritium released from nuclear facilities.

Due to the major contribution of radiation dose to the public, ^{14}C monitoring in the environment surrounding the nuclear facilities becomes more important. Some countries have started to monitor the ^{14}C level in the atmosphere and environmental media such as grass and tree ring [49, 59, 60]. However, because of relative low concentration of ^{14}C in the atmosphere and environmental samples, its accurate determination is a challenge. A long sampling time or a big sample is needed to be able to measure the ^{14}C concentration in the environmental level. The present method for determination of ^{14}C in environmental samples is time consuming; normally take a few days to a week. It is a challenge to develop a more effective sampling instrument and rapid or on-line measurement instrument for prompt and accurate determination of ^{14}C level.

The concentration of tritium in the environment is also very low compared to the nuclear facilities. The monitoring of tritium level in the atmosphere and other environmental samples needs a long sampling time, especially for different species of tritium. The measurement is also often carried out in the laboratory after purification of the collected sample. It is still a challenge for on-line and rapid monitoring the tritium in the atmosphere.

Although dominant ^{14}C is released as gaseous discharge from the nuclear facilities, liquid discharges also contain various amount of ^{14}C depending on the sources of ^{14}C and

trapping technology used in the nuclear facilities. [14]C in the liquid discharges can be rapidly accumulated into food chain, causing a radiation exposure to the public. However, the monitoring of ^{14}C in the discharges and recipients is still limited in the surrounding area of nuclear facilities. It is still a challenge to develop a rapid analytical method to monitor ^{14}C in the environmental samples.

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