Radioactivity analysis of beta-emitting radionuclides of environmental samples in a nuclear or radiological emergency

RCA Regional Office

Contents

1. Introduction

1.1. Background

The International Atomic Energy Agency (IAEA) provides general guidelines for assessing the dose of critical groups and populations based on the monitoring of radioactive materials and the environment during nuclear or radiological emergencies in nuclear and radiation-related facilities[1-3]. The purpose of environmental radiation monitoring is to provide information that can aid effective decision-making, such as prompt judgment in emergency situations and initiation of protective actions to safeguard emergency workers and the public. Therefore, in the event of an accident at a nuclear or other facility, environmental sampling and subsequent measurements are performed to provide data on the levels, time dependence, and spatial distribution of radionuclides in various environmental media (such as air, soil, plants, food, etc.) in order to assess the doses to critical groups and populations and to support decisions on protective and mitigation actions[1-3].

The emergency environmental monitoring program involves determining the types of environmental samples, collection points, radionuclides to be monitored, and the frequency of analysis[4]. The program varies based on the characteristics of the nuclear or radiological facility, site characteristics of the environment, type and magnitude of the accident, and the timing of monitoring. Depending on the type of accident, it may be necessary to prioritize the measurement of environmental media and radionuclides that have a greater environmental impact or are of greater exposure assessment significance. For instance, in reactor facilities, radioactive noble gases and oxides; in nuclear fuel facilities, uranium or plutonium released by fire, explosion, or leakage; and in criticality accidents, fission products, neutrons, and gamma rays. Therefore, in order to evaluate the radiation impact from the facility to the environment and detect unexpected situations, each country that operates the facility establishes and implements a radiation environmental monitoring plan during normal operation of the facility, and prepares for abnormal emissions and accidents by establishing radiation disaster prevention measures and emergency monitoring plans.

Table 1 summarizes the IAEA guidelines, which should be considered as a simplified framework for emergency monitoring. A unique program should be established that is appropriate for the operational characteristics of the facility in a given country, taking into account the site characteristics, emission levels, and relevant radionuclides. The intensity and duration of the monitoring activities should be determined by the severity of the emergency, which may range from a few days to several years. As the situation evolves, a phased monitoring program should be established.

Table 1. Environmental Monitoring of Radionuclides to be Performed Following Emergencies (IAEA RG-S-1.8)[4]

Release	Monitored constituents	Frequency	Remarks
Airborne	Measurements during the passage of a cloud		
	External radiation Gamma dose rate Neutron dose rate (if neutron radiation is foreseen)	Continuous Continuous	Near and far field, external dose rate map Only near field, if neutrons are expected
	Air Air Rain	Continuous collection, measurement every 2 h Continuous collection, measurement every 2 h	Near and far field Near and far field
	Measurements after the passage of a cloud		In contaminated areas
	External radiation Gamma dose rate	Continuous	external dose rate map
	Deposition Soil	Once	Contamination map for relevant radionuclides
	Foodstuffs/ingestion Leafy vegetables Milk Other vegetables and fruits Grain Meat Drinking water and/or ground water	Daily Daily At harvest At harvest Representative samples Representative samples	Good indicator for plant food Good indicator for animal food
Liquid	After release		Affected areas and water bodies are limited
	Aquatic dispersion Surface water Sediment	Continuous sampling, daily measurement Weekly	
	Aquatic foodstuffs Fish Shellfish	Selected samples Selected samples	
	Aquatic indicators Seaweeds	Selected samples	

Table 2. Monitoring Quantities and Measurement Guidance (IAEA RG-S-1.8)[4]

Quantity to be measured	Sampling/measurement	Application
Source monitoring		
Gamma dose rate at the source	Stationary on-line equipment, continuous measurement	Practice, emergency
Gases in released air	Stationary on-line equipment, continuous measurement	Practice, emergency
Aerosols in released air [a]	On-line equipment and/or sampling; nuclide specific analysis, total alpha and total beta	Practice, emergency
Activity in released water [a]	On-line equipment and/or sampling; nuclide specific analysis, total alpha and total beta	Practice, emergency
Environmental monitoring		
Gamma dose rate over ground	Field measurements; mobile or stationary devices	Practice, emergency, chronic (prolonged) exposure
Aerosol activity in air	Filter sampling; nuclide specific analysis	Practice, emergency, chronic (prolonged) exposure
Radioiodine in air	Sampling specific to physical and chemical form; nuclide specific analysis	Practice, emergency
Activity in rain	Sampling in rain collector; nuclide specific analysis	Practice, emergency
Deposited activity	In situ gamma spectrometry; planchet sampling and nuclide specific analysis	Practice, emergency
Activity in soil	In situ gamma spectrometry; field sampling and nuclide specific analysis	Practice, emergency, chronic (prolonged) exposure
Activity in foodstuffs and feedstuffs, waters, sediment	Field sampling; nuclide specific analysis	Practice, emergency, chronic (prolonged) exposure

[a] If the discharge limits for a practice are given in terms of total alpha activity and/or total beta activity, and not for specific radionuclides, radionuclide specific measurements on a routine basis may not be necessary

1.2. Objective

The objective of this handbook is to aid ASEANTOM Member States in performing radioactivity analyses of beta-emitting radionuclides on environmental samples during radiological emergencies[5]. The handbook outlines the general process of radioactivity analysis of beta-emitting radionuclides with a focus on tritium, and ASEANTOM Member States are encouraged to develop their analytical procedures based on this guidance and tailored to their institutional needs.

2. Environmental samples

The summary below outlines the analysis of beta-emitting radionuclides (gross beta, ^{3}H, and ^{90}Sr), including sample collection, pretreatment, and instrumentation, that must be performed during an emergency. The target samples for each radionuclide are categorized by the physical type of the sample, such as air particulates and water samples.

2.1. Gross beta

The term "gross beta" refers to all beta-emitting radionuclides present in a sample, including natural radionuclides and beta-emitting artificial radionuclides such as ^{90}Sr. This measurement is typically used for naturally occurring radionuclides in water samples, such as surface, underground, and seawater, while also accounting for artificial radionuclides. The measurement of gross beta radionuclides is important for ensuring human safety in drinking water, with a recommended annual dose limit of 100 μSv per year set by the World Health Organization (WHO)[6]. This recommended dose excludes the dose received from ^{3}H, ^{40}K, ^{222}Rn, and ^{222}Rn daughter nuclides

and includes other alpha- and beta-emitting radionuclides. Gross beta measurement is a relatively simple and inexpensive screening method, but it does not provide specific radioactivity concentrations for individual beta-emitting radionuclides, which include ^{40}K, ^{228}Ra, ^{210}Pb, and their daughter nuclides. The WHO recommends a concentration limit of 1 Bq/L for all types of beta radiation in drinking water. If the concentration of gross beta radiation exceeds 1 Bq/L, further analysis is necessary to identify specific beta-emitting radionuclides. The analysis procedure is described in Appendix A.

Table 3. Gross beta radioactivity analysis

	Airborne particles	Water (precipitation, drinking water)
Sampling	GF/C filter Low volume-air sampler	Precipitation sampler for gross beta
Pretreatment	Dry	Evaporation to dryness
Preparation of sample	On a planchet	Evaporation to dryness on a planchet
Efficiency calibration	^{90}Sr disk source	Efficiency curve of calibration sources by KCl weight
Required reagent	-	Distilled water, HNO$_3$, KCl, Acetone
Measuring instrument	Gas flow proportional counter	

2.2. Tritium

^{3}H is a radioactive isotope of hydrogen with a physical half-life of 12.3 years and undergoes beta decay. Its maximum decay energy is 18.6 keV, and its average decay energy is 5.7 keV. It comprises one proton and two neutrons and shares physical and chemical properties with those of hydrogen.

^{3}H can combine with oxygen to form tritium water (HTO), and it also exists as a gas. Both HTO and HT gas can move freely in water and air. Naturally occurring ^{3}H is produced by cosmic rays when atmospheric gases such as nitrogen and oxygen react with them. The majority of naturally occurring ^{3}H is produced in the stratosphere and reaches the ground through rainfall, but its concentration is negligible. However, ^{3}H is released into the environment through nuclear reactions, atmospheric nuclear tests, nuclear power generation, and nuclear fuel reprocessing.

Exposure to tritium through skin contact is not significant because the beta particles emitted from airborne tritium cannot travel far due to their low energy. Nevertheless, ^{3}H is produced in large quantities in nuclear reactors, where heavy water is used for cooling and moderation. It is primarily distributed in the workplace as HTO, contributing to the workers' body exposure. Accordingly, it accounts for approximately 20%–30% of the workers' annual ^{3}H exposure dose. When ^{3}H is absorbed into the human body, its biological half-life varies depending on the age and season. The older the person, the longer the biological half-life, and it tends to be longer in winter than in summer.

Table 4. Tritium radioactivity analysis

	Water (precipitation)
Sampling	Precipitation sampler
Pretreatment	Direct distillation
Preparation of sample	Mixing with liquid scintillator
Efficiency calibration	Quench curve using standard ^{3}H sources with varying amounts of liquid scintillator
Required reagent	Distilled water, cocktail, ^{3}H source
Measuring instrument	Liquid Scintillation Counter (LSC)

2.3. ^{90}Sr

In the past, the analysis of ^{90}Sr was limited by the use of toxic fuming nitric acid and the need for a long standby period to equilibrate with ^{90}Sr/^{90}Y. Therefore, there has been a long-standing need for a rapid analysis method for emergencies. Recently, researchers have validated rapid analytical procedures for seawater and milk samples. However, an appropriate procedure for rapid response in emergency monitoring situations still needs to be developed for ^{90}Sr. The analysis procedure is described in Appendix B.

3. Detection system for beta-emitting radionuclides

3.1. Gas flow proportional counter

The gas flow proportional counter is an instrument used to measure the ionization of radiation, in which a thin wire is placed on the centerline of a cylindrical electrode as a collecting electrode. Other variations include the use of a box cathode or a collector electrode on a loop. The space between the electrodes is filled with an inert gas or methane (P-10 gas). This method measures the current generated by the ionization of radiation under the electric field applied to an instrument (gas flow proportional counter) in which the gas flows continuously. When a beta ray enters the counter, it ionizes the gas, and the ionized particles move to the electrode, generating an electrical signal (current). The electrical signal generated is proportional to the total number of ion pairs and is used to measure the gross beta radioactivity concentration. The gas flow proportional counter can also measure alpha radioactivity using the strength of the electrical signal. To measure low-level samples, the background level of the instrument is important. The instrument consists of a sample detector, a secondary detector, an amplifier, a

dynamic circuit, and software. An auxiliary detector is used to measure the background radiation from cosmic rays, and alpha- and beta-emitting radionuclides are separated in the kinetic circuit. The final measurement is obtained by subtracting the value of the secondary detector from that of the sample detector. Efficiency calibration is an essential part of the measurement process, and it involves calculating a correction for the spillover of alpha-emitting radionuclides into the beta-ray region and applying it to the final result.

Series 5 XLB   Series 6 LB

Figure 1. Low level alpha-beta counter

3.2. Liquid scintillation counter (LSC)

3.2.1. Liquid scintillator

Liquid scintillators have the advantage of being able to be placed in measuring containers of any size and shape. They can prevent the absorption of weakly transmissive alpha/beta particles through the windows and air layers by mixing the measurement sample directly with the scintillator. This makes them highly effective for measuring alpha- or low-energy beta-emitting radionuclides, such as ^{3}H and ^{14}C.

Typically, liquid scintillators are prepared by dissolving scintillation materials (first and second solutes) in a specific solvent, such as xylene or toluene. The first solute, PPO (2,5-Diphenyloxazole), and the second solute, POPOP (1,4-bis(5-phenyloxazol-2-yl) benzene), act as wavelength transducers. Adding them has the advantage of converting scintillation with a wavelength in the ultraviolet region into a form suitable for the sensitivity of a photomultiplier tube (PMT) by transferring it to the visible light region, thereby increasing counting efficiency.

Liquid scintillators may experience quenching, a phenomenon in which scintillation efficiency decreases based on the material composition and presence of impurities in the sample. This can lead to a reduction in the counting efficiency and an underestimation of the actual radioactivity of the sample. Instruments that use liquid scintillators are not suitable for measuring gamma rays, as the main components of liquid scintillators are carbon and hydrogen, and the interaction of gamma rays with low-atomic-number materials is dominated by the Compton effect rather than the photoelectric effect. This results in a Compton continuous spectrum instead of a photoelectric peak.

Figure 2 shows the principle of radioactivity measurement in liquid scintillation counting method. The solvent molecules are excited by absorbing the decay energy released from the radionuclide. Then, the excited solvent molecule transfer the absorbed energy back and forth with other solvent molecules until the energy is eventually transferred to a fluor molecule. Finally, the photon emissions are measured in a photomultiplier tube.
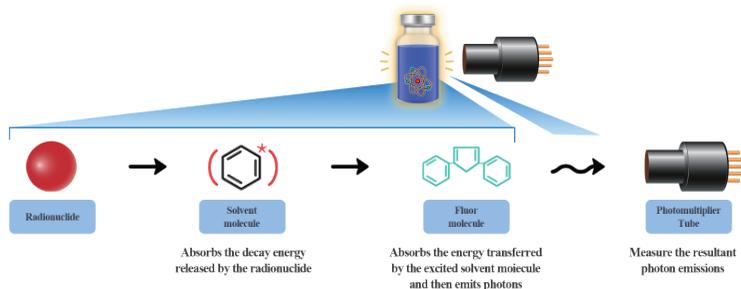
Figure 2. Principle of liquid scintillation counting method

3.2.2. Liquid scintillation counters

The sample mixed with the liquid scintillator emits scintillation based on the decay energy of the radiation, and the device that counts it is called a liquid scintillation counter. In a liquid scintillation counter, the sample is mixed with the liquid scintillator in a PMT, where the emitted scintillation signal is amplified and converted to radioactivity after counting . To improve sample counting efficiency, PMTs are placed on both sides of the sample to count simultaneous counting signals. Recently, liquid scintillation counters utilizing the triple-to-double coincidence ratio (TDCR) method by installing three PMTs to increase the counting efficiency have also been introduced. Depending on the measurement purpose, commercially available models include those for rapidly processing a large number of samples, such as urine samples from power plant workers, and liquid scintillation counters specialized for low-level radioactivity measurements, such as environmental samples. Liquid scintillation counters have a high counting efficiency of more than 60% for tritium and more than 95% for ^{14}C in unquenched samples.

Figure 3. Various liquid scintillation counters

3.2.3. Quenching effect

Liquid scintillation counting is advantageous for achieving high counting efficiency by directly mixing a liquid scintillator with a radioactive material, allowing for a highly efficient conversion of the decay energy emitted by a source into light. If the sample is perfectly pure and mixed with the liquid scintillator to achieve high energy-transfer efficiency, the counting efficiency would be 100%. However, achieving a perfect mix and purity is difficult, leading to quenching, which decreases the counting efficiency. Quenching can occur through chemical, color, or physical means, resulting in a decrease in the spectral area of the energy spectrum compared to an unquenched sample, as shown in Figure 4.
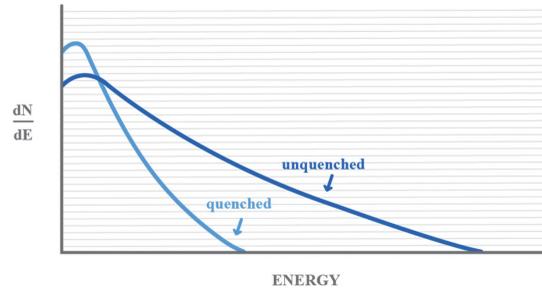
Figure 4. Comparison of the cumulative count per energy spectra of a quenched sample and an unquenched sample

3.2.3.1. Chemical quenching

Chemical quenching is caused by impurities in the scintillator or sample that results in a loss of a part of the scintillation as heat. Halogen elements such as chlorine, bromine, and iodine are the most common causes of chemical quenching in the analysis of drinking water tritium, as they attract beta particles when filling the outermost shell.

3.2.3.2. Color quenching

Color quenching refers to the absorption of scintillation by colored compounds in the sample.

3.2.3.3. Physical quenching

Physical quenching refers to the refraction of scintillation owing to the material of the sample container or dust on the surface of the sample container.

3.2.3.4. Correction for the quenching effect

Correcting the quenching effect is essential to obtain the desired radioactivity concentration in the original sample. Spectral correction and external gamma source correction are typically used to correct quenching.

3.2.3.5. Spectrum correction

The spectrum correction method corrects the quenching effect by comparing the spectra of quenched and unquenched samples. SQP(I) is one of quenching parameters, which corresponds to the channel number at the center of gravity of the radionuclide spectral distribution. The quenching correction is performed by comparing the SQP(I) values of the quenched and unquenched samples, as shown in Figure 5.
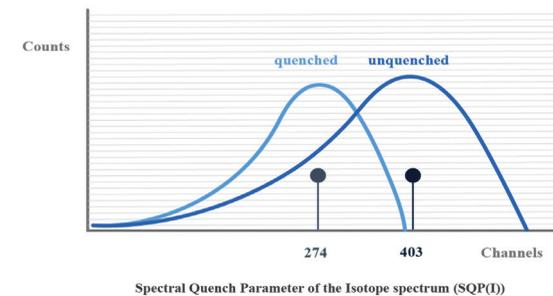

Figure 5. SQP(I) quenching parameter

3.2.3.6. External gamma source correction

The external gamma source correction method corrects the quenching effect by exposing the sample to a radioactive gamma source that is mounted inside a liquid scintillation counter, which generates a Compton spectrum. The level of quenching in the sample is assessed by comparing specific points in the Compton spectrum.
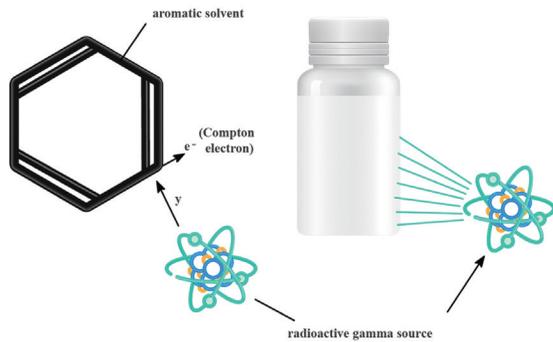
Figure 6. Quench monitoring using an external gamma source

SQP(E) is also one of quenching parameters and SQP(E) indicates the channel number corresponding to the 1% end of the Compton spectrum obtained by exposing the sample with external gamma source. Figure 7 shows how to determine the SQP(E) parameter.
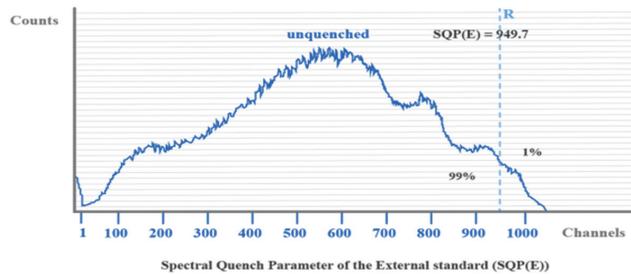

Figure 7. SQP(E) quenching parameter

3.2.4. Quench curve

Quench curve is a plot of the counting efficiency as a function of quenching parameter. The quench curve uses the relationship between counting efficiency and quenching parameter to calibrate the measured count in cpm to the radioactivity in dpm. The degree of quenching is directly proportional to the spectral effect, making it a useful tool for determining the counting efficiency of a sample.

To calculate the radioactivity of a sample, a quench curve is generated with proper quenching standards. To create quenching standards, a range of radioactivity levels is selected that matches the expected range of the sample to be measured, and equal amounts of the radionuclide standard are added to 8–10 sample containers. Subsequently, a scattering agent is added in increasing amounts to enhance the scattering phenomenon. Finally, the remaining space in the container is filled with liquid scintillator, mixed, and measured to generate a efficiency calibration curve. The counting efficiency formula that utilizes the quench curve is shown below, where ε is the coefficient efficiency and q represents the quenching parameter such as SQP(I) and SQP(E).

$$\varepsilon = aq^2 + bq + c$$

ε : counting efficiency
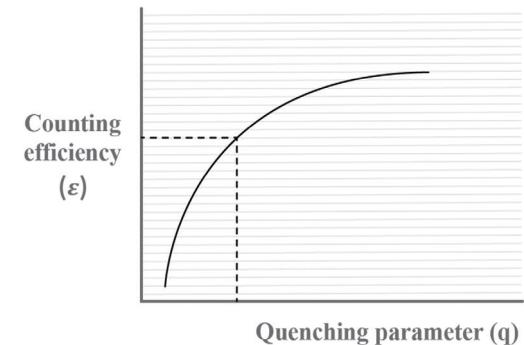q : quenching parameter
a, b, c : coefficients

Figure 8. Quench Curve

4. Calibration of liquid scintillation counter

4.1. Overview

In order to measure the sample using a liquid scintillation counter, it is essential to determine the degree of quenching of the sample, so the liquid scintillation counter must be calibrated using a standard solution depending on the sample. Therefore, it is necessary to create a set of quenching standards using a standard solution and measure them to generate a quench curve.

This handbook describes, as an example, how to calibrate a liquid scintillation counter for tritium analysis. Therefore, all reagents, equipment, and the procedure described in this section are specific to tritium analysis.

4.2. Reagents and instruments

• Counting vials

Counting vials

• Pipettes and pipette tips

Pipettes and pipette tips

• Laboratory balances

Laboratory Balances

• Scintillation cocktail

Scintillation cocktail

• Tritium standard solution (approximately 100–500 Bq/g)

³H Standard solution (approx. 100~500 Bq/g)

• Ultrapure water

Ultrapure water

• Liquid Scintillation Counter

Liquid scintillation counter
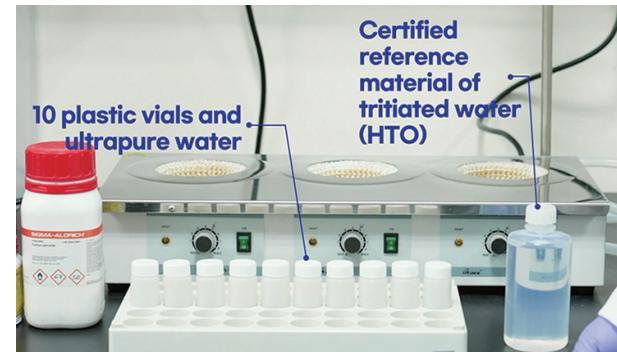
• Distillation unit

Distillation unit

4.3. Calibration procedure for tritium analysis

The procedure for generating the quench curve is as follows:

① Prepare ten plastic vials, ultrapure water, and ³H standard solution.

10 plastic vials and ultrapure water

Certified reference material of tritiated water (HTO)

② Add 0.5 g (approximately 50 Bq) of the standard solution to the ten prepared vials, and record the exact volume or mass.
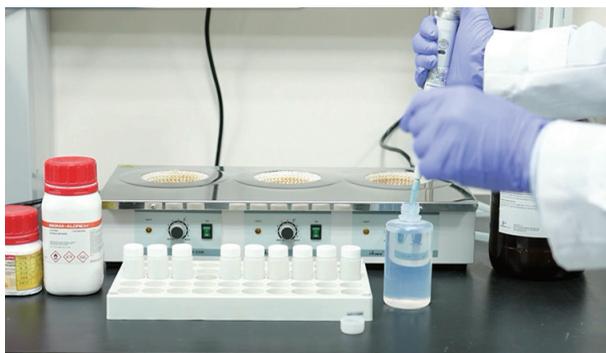
③ To each vial, add the scintillation cocktail and ultrapure water, as shown in Table 5, and mix thoroughly.

Table 5. Tritium quenching standards preparation

STD ID	Standard solution (mL or g)	Ultrapure water (mL or g)	Scintillation cocktail (mL or g)
STD 1	0.500	0.5	19
STD 2	0.500	1.5	18
STD 3	0.500	2.5	17
STD 4	0.500	3.5	16
STD 5	0.500	4.5	15
STD 6	0.500	5.5	14
STD 7	0.500	6.5	13
STD 8	0.500	7.5	12
STD 9	0.500	8.5	11
STD 10	0.500	9.5	10

④ In a separate vial, add 8 g of ultrapure water and 12 g of the scintillation cocktail, mix thoroughly, and use as blank samples.

⑤ Place the prepared blanks and standards for extinction correction inside a liquid scintillation counter for at least 12 h, and then select ^{3}H counting mode for 60 min per sample.

⑥ To calculate the measurement efficiency (%),first obtain the efficiency curve for the quenching parameters (e.g., SQP(I) and SQP(E)) of each standard solution for quenching correction and then fit the data with a polynomial equation.

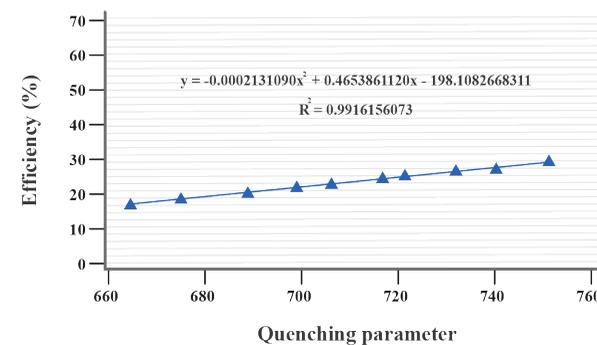$$\text{Counting efficiency } [\%] = \frac{\text{cpm}_{STD} - \text{cpm}_{BLK}}{\text{dpm}_{STD}} \times 100$$

$$y = -0.0002131090x^2 + 0.4653861120x - 198.1082668311$$
$$R^2 = 0.9916156073$$

Figure 9. Tritium counting efficiency curve

5. Measurement of tritium radioactivity

This procedure outlines the method for measuring ^3H in water and air samples using a liquid scintillation counter[7]. Water samples were distilled and analyzed using a liquid scintillation counter. Air samples were obtained by heating the water vapor collected in a molecular sieve for a specific duration and then analyzed using a liquid scintillation counter as well. It is important to note that this procedure cannot be used to determine organically bound tritium (OBT).

5.1. Water sample

For water samples, it is essential to check for the presence of gamma radionuclide contamination. If no gamma radionuclides are detected, a small aliquot of the sample is mixed with the scintillation cocktail (final volume 20 mL; for example, 2 g of sample + 18 g of scintillation cocktail) without any additional treatment, and stored in a cool, dark location for at least 12 h before being analyzed using a liquid scintillation counter. If the water samples are contaminated with gamma radionuclides, the sample must first be distilled and then undergo the same procedure as the uncontaminated samples.

Tritium Measurement Procedure

① Take a 100 mL aliquot from the collected sample and transfer it to a round flask.
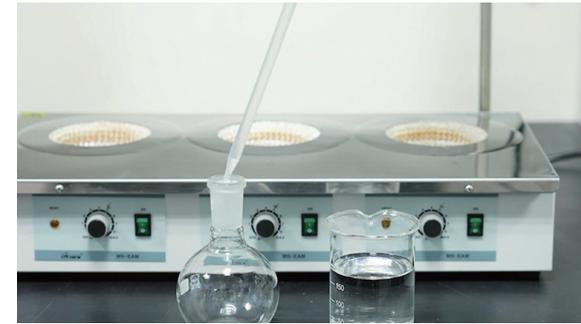
② Add approximately 0.1 g of potassium permanganate.

③ Add approximately 0.5 g of sodium hydroxide to the sample.

④ Thoroughly mix the sample to ensure the complete dissolution of the added reagents.

⑤ Mount a round flask on the heating mantle, and connect the cooling water line. Subsequently, heat the sample for distillation.

⑥ Extract the distillate in a beaker

⑦ Pipette an 8 mL aliquot of the extracted distillate into a counting vial.

⑧ Add 12 mL of liquid scintillator reagent to each sample

⑨ Prepare a blank sample by mixing ultrapure water and the scintillation cocktail in a ratio equivalent to that of the environmental sample

⑩ After mixing the sample and liquid scintillator well, observe whether there is any internal precipitation or turbidity

⑪ Assign a sample identification code, and write the code on the cap of the counting vial

⑫ Store the sample in a cold, dark room for at least 12 h to minimize chemical quenching inside the vial

⑬ Determine the measurement time by considering the sample. (Table 6)

⑭ Measure a sample for 60 min and repeat the measurement.

Table 6. Measurement time determination

Blank	1.15cpm												
Counting efficiency	22%												
Chemical recovery	100%												
Bq/kg or L	10 min	20 min	30 min	60 min	120 min	180 min	240 min	300 min	360 min	420 min	480 min	540 min	600 min
1 g/ml	139.99	94.74	75.81	52.19	36.20	29.30	25.24	22.49	20.48	18.92	17.67	16.64	15.76
2 g/ml	70.00	47.37	37.91	26.10	18.10	14.65	12.62	11.25	10.24	9.46	8.84	8.32	7.88
3 g/ml	46.66	31.58	25.27	17.40	12.07	9.77	8.41	7.50	6.83	6.31	5.89	5.55	5.25
4 g/ml	35.00	23.68	18.95	13.05	9.05	7.32	6.31	5.62	5.12	4.73	4.42	4.16	3.94
5 g/ml	28.00	18.95	15.16	10.44	7.24	5.86	5.05	4.50	4.10	3.78	3.53	3.33	3.15
6 g/ml	23.33	15.79	12.64	8.70	6.03	4.88	4.21	3.75	3.41	3.15	2.95	2.77	2.63
7 g/ml	20.00	13.53	10.83	7.46	5.17	4.19	3.61	3.21	2.93	2.70	2.52	2.38	2.25
8 g/ml	17.50	11.84	9.48	6.52	4.52	3.66	3.16	2.81	2.56	2.37	2.21	2.08	1.97
9 g/ml	15.55	10.53	8.42	5.80	4.02	3.26	2.80	2.50	2.28	2.10	1.96	1.85	1.75
10 g/ml	14.00	9.47	7.58	5.22	3.62	2.93	2.52	2.25	2.05	1.89	1.77	1.66	1.58
20 g/ml	7.00	4.74	3.79	2.61	1.81	1.46	1.26	1.12	1.02	0.95	0.88	0.83	0.79
30 g/ml	4.67	3.16	2.53	1.74	1.21	0.98	0.84	0.75	0.68	0.63	0.59	0.55	0.53
40 g/ml	3.50	2.37	1.90	1.30	0.90	0.73	0.63	0.56	0.51	0.47	0.44	0.42	0.39
50 g/ml	2.80	1.89	1.52	1.04	0.72	0.59	0.50	0.45	0.41	0.38	0.35	0.33	0.32
60 g/ml	2.33	1.58	1.26	0.87	0.60	0.49	0.42	0.37	0.34	0.32	0.29	0.28	0.26
70 g/ml	2.00	1.35	1.08	0.75	0.52	0.42	0.36	0.32	0.29	0.27	0.25	0.24	0.23
80 g/ml	1.75	1.18	0.95	0.65	0.45	0.37	0.32	0.28	0.26	0.24	0.22	0.21	0.20
90 g/ml	1.56	1.05	0.84	0.58	0.40	0.33	0.28	0.25	0.23	0.21	0.20	0.18	0.18
100 g/ml	1.40	0.95	0.76	0.52	0.36	0.29	0.25	0.22	0.20	0.19	0.18	0.17	0.16

5.2. Air sample

To collect moisture from the air, a Molecular Sieve (M/S) is used for a specific duration. The M/S column containing the captured moisture is heated to approximately 450 °C for more than 90 min, and the resulting moisture is collected in a collection bottle. The weight of the captured moisture is recorded, and 8 g of it is transferred to a plastic vial and mixed with 12 g of scintillation cocktail. The mixture is then stored in a cool, dark location for at least 12 h before being analyzed using a liquid scintillation counter. The analytical procedure for distilled water samples obtained from air samples is identical to that of the water samples described earlier.

6. Analysis of tritium radioactivity

6.1. Water sample

The tritium radioactivity concentration in the water sample can be calculated using the equation given below. The amount of water used in the measurement is substituted into the equation regardless of the initial distilled amount. Normally 8–10 mL of a water sample is used for the measurement; however, in the case of an emergency, the sample volume may vary depending on the minimum detectable activity.

$$A_{^3\mathrm{H}} \, [\mathrm{Bq/\,L\ or\ kg}] \;=\; \frac{\mathrm{cpm}_{Sample} - \mathrm{cpm}_{BLK}}{\varepsilon \times V(\mathrm{or}\ m) \times 60}$$

$A_{^3\mathrm{H}}$: Tritium radioactivity concentration $[\mathrm{Bq/L\ or\ kg}]$

ε : Measurement efficiency

$V(\mathrm{or}\ m)$: Volume [L] or mass [kg] collected water used in the measurement

6.2. Air sample

Although the manual does not cover air sample preparation, the analytical procedure is the same after collecting a distilled water sample from an air sample. For air samples, the tritium radioactivity concentration is calculated by converting the amount of water vapor captured by the M/S into the volume of the captured air sample. The tritium radioactivity concentration can be obtained by measuring the collected distilled water using the equation that considers the net count in cpm, the amount of collected water, and the volume of the air sample.

$$A_{^3\mathrm{H}} \, [\mathrm{Bq/\,m^3}] \;=\; \frac{\left(\mathrm{cpm}_{Sample} - \mathrm{cpm}_{BLK}\right) \times M}{\varepsilon \times m \times V \times 60}$$

$A_{^3\mathrm{H}}$: Tritium radioactivity concentration $[\mathrm{Bq/m^3}]$

M : Amount of collected water from M/S [g]

ε : Measurement efficiency

m : Amount of collected water used in measurement [g]

V : Volume of the captured air sampler $[\mathrm{m^3}]$

6.3. Minimum detectable activity

The minimum detectable activity (MDA) is an important parameter for radioactivity measurement performed using a liquid scintillation counter. It can be calculated by taking into account the background count, measurement time, sample volume, and measurement efficiency.

$$MDA = \frac{2.71 + 4.65\sqrt{B \times t}}{\varepsilon \times V \times t}$$

ε : Measurement efficiency

B : Background value [cps]

t : Measurement time [s]

V : Sample volume [kg or L]

7. Recording results

7.1. Recording information

7.1.1. Sampling information

- Worker's name
- Date of sample collection
- Sampling points
- Sample collection methods
- Sample preparation type
- Measurement labs

7.1.2. Calibration information

- Worker's name
- Liquid scintillation counter ID
- Counting efficiency
- Counting windows width
- Figure of merit
- Background counting rate
- Calibration date/time

7.1.3. Measurement

- Worker's name
- Sample ID
- Measurement date/time
- Measurement result

7.2. Notation of data

The measurement uncertainty is expressed as $(A \pm u(A))$ Bq/L or $(A \pm U(A))$ Bq/L, where the value of the coverage factor k, where U is the expanded uncertainty. The expanded uncertainty U is calculated by multiplying the standard uncertainty $u(A)$ with the coverage factor k.

Figure 10. Worksheet sample for tritium analysis[2]

8. References

[1] IAEA-TECDOC-955 "Generic assessment procedures for determining protective actions during a reactor accident", IAEA (1997)

[2] IAEA-TECDOC-1092 "Generic procedures for monitoring in a nuclear or radiological emergency", IAEA (1999)

[3] IAEA-GSG-2 "Criteria for Use in Preparedness and Response for a Nuclear or Radiological Emergency", IAEA (2011)

[4] IAEA RS-G-1.8 "Environmental and Source Monitoring for Purposes of Radiation Protection", IAEA (2005)

[5] KINS/HR-1670 "Development of training materials for beta emitting radionuclides in emergency situations", KINS (2018)

[6] WHO "Guidelines for drinking-water quality", 3rd ed. World Health Organization, Geneva, Switzerland (2006)

[7] Warwick, P. E., Croudace, I. W. & Howard, A. G. "Improved technique for the routine determination of tritiated water in aqueous samples." Analytica Chimica Acta 382 (1999) 225-231

[8] ISO 10704:2009 "Water quality — Measurement of gross alpha and gross beta activity in non-saline water — Thin source deposit method"

[9] IAEA/AQ/27 "Rapid Simultaneous Determination of ^{89}Sr and ^{90}Sr in Milk: A Procedure Using Cerenkov and Scintillation Counting.", IAEA (2013)

Appendix A. Gross beta analysis procedure

1. Overview

This procedure briefly described the measurement of gross beta particle activities in air and water samples using a gas flow proportional counter[8]. Air samples collected in the filter can be processed without further pretreatment, and water samples consist of two steps: the evaporation of the water to dryness and the measurement of the residue deposited on a planchet in a proportional detector. In this case of emergency, a small amount of water sample (10 mL) was used.

2. Reagents and instruments

- Counting container (stainless steel planchet)
- Air collected filter
- Pipettes and pipette tips
- Laboratory balances
- Infrared lamp
- Filtering unit
- 10 mL Syringe
- 0.45 μm syringe filter
- 65% HNO_3
- Ultrapure water
- ^{90}Sr standard solution (approximately 20 Bq/g)
- Gas flow proportional counter

3. Calibration procedure

The measuring instrument must be calibrated with a traceable standard solution before measuring the sample. The calibration procedure for gas flow proportional counter is as follows

① Prepare three filters each for water samples and air samples. Air sample filters used in the Air Collector and record the weight of the filter and the planchet using the laboratory balances

② Place the filter on the balance with the back of the filter not touching the planchet. Wet the filter uniformly with 0.5 g (approximately 10 Bq) of standard solution using a pipette and record the mass.

③ Prepare the calibration source by drying the solution in the filter using infrared lamp. (Keep the temperature below 85°C to prevent boiling of standard solution)

④ Measure the radioactive concentration of each standard source. The counting efficiency (%) is obtained using the formula below. Since there are three calibration sources, the final efficiency can be calculated by averaging three counting efficiencies.

$$\mathrm{Counting\ efficiency}\ [\%]\ =\ \frac{\mathrm{cpm}_{STD} - \mathrm{cpm}_{BLK}}{\mathrm{dpm}_{STD}}$$

When applying the above calibration method, consideration is alpha into beta spillover. This should be reviewed and evaluated by the user in accordance with the method described in the measuring equipment manual.

4. Measurement procedure

4.1. Air sample (filter)

The filter samples without pretreatment are measured in turn. And the background value is measured with a new filter under the same conditions.

4.2. Water sample

① Using a pipette, take 10 mL of the sample from the sample bottle. (In this case, be careful not to mix floating particles or impurities, and if necessary, remove floating particles beforehand.)

② Put the sample into a 10 mL syringe equipped with syringe filter and add 1–2 drops of nitric acid solution into the syringe.

③ Place a planchet under an infrared lamp and add the filtered water sample directly from the syringe into the planchet.

④ Maintain the planchet as horizontal as possible to ensure that the sample is evenly distributed over the bottom of the planchet and dried (Caution: do not heat the planchet rapidly, as this may cause the sample to boil and splash out or swell just before drying).

⑤ Measure the prepared planchet and measure the new planchet under the same conditions to obtain the background value.

5. Analysis of gross beta radioactivity

5.1. Air sample (filter)

For air samples, the gross beta radioactivity concentration can be calculated using this equation by converting to the volume of the air sample s collected through the air sampler.

$$A_{\mathrm{Gross\ beta}}\ [\mathrm{Bq/m^3}]\ =\ \frac{\mathrm{cpm}_{Sample} - \mathrm{cpm}_{BLK}}{\varepsilon \times V \times 60}$$

$A_{\mathrm{Gross\ beta}}$: Gross beta radioactivity concentration $[\mathrm{Bq/m^3}]$
ε : Measurement efficiency
V : Volume of the captured air sampler $[\mathrm{m^3}]$

5.2. Water sample

For water samples, the gross beta radioactivity concentration can be calculated using this equation as the amount of sample filtered through syringe and syringe filter.

$$A_{\text{Gross beta}} \ [\text{Bq}/\text{L or kg}] \ = \ \frac{\text{cpm}_{Sample} - \text{cpm}_{BLK}}{\varepsilon \times V(\text{or } m) \times 60}$$

$A_{\text{Gross beta}}$: Gross beta radioactivity concentration$[\text{Bq}/\text{L or kg}]$

ε \quad : Measurement efficiency

V (or m) : Volume [L] or mass [kg] used in the measurement

Figure A1. Worksheet sample for gross beta analysis[2]

Appendix B. ⁹⁰Sr analysis procedure

1. Overview

This procedure briefly described the measurement of ^{90}Sr in water samples using a liquid scintillation counter based on a radiochemical method described in IAEA/AQ/27 document[9].

2. Reagents and instruments

- Low background glass vial
- Filtering unit (Filter Dia. 23 mm)
- Vacuum pump
- Pipettes and pipette tips
- Laboratory balances
- Infrared lamp
- hot plate
- 100 mL Beaker
- pH paper
- ^{89}Sr standard solution (approximately 20 Bq/g)
- ^{90}Sr standard solution (approximately 20 Bq/g)
- Strontium carrier solution (10 mg Sr mL-1 in 1M HNO_3)
- Strontium resin (50–100 μm)
- Scintillation cocktail (ex. UltimaGold AB)
- 65% HNO_3
- 0.05M HNO_3
- ^{90}Sr-free $SrCO_3$
- 25% NH_4OH
- Ammonium carbonate
- Ethanol
- Ultrapure water
- Liquid Scintillation Counter

3. Calibration procedure

3.1. Preparation of ^{89}Sr calibration source

① Add a few µL of a known activity of ^{89}Sr standard solution (approximately 20 Bq/g) into a 20 mL glass vial.

② Gently evaporate the solution to dryness with an infrared lamp.

③ Add a few drops of 65% HNO_3 then evaporate to dryness to change the chemical form to a nitrate.

④ Add 8 mL of 0.05M HNO_3, 13 mg of ^{90}Sr-free $SrCO_3$ and an empty filter into the vial and gently shake to dissolve the $SrCO_3$ precipitate.

3.2. Preparation of mixed source of ^{90}Sr and ^{90}Y in secular equilibrium

① Add dozens of µL of a known activity of ^{90}Sr standard solution (approximately 20 Bq/g) in equilibrium with ^{90}Y to a 20 mL glass vial.

② Prepare the mixed source of ^{90}Sr and ^{90}Y in the same way as described for the preparation of the ^{89}Sr source.

③ Calculate the Cerenkov counting efficiency of ^{90}Sr by subtracting the counting efficiency of ^{90}Y from the total counting efficiency for the mixed source of ^{90}Sr and ^{90}Y.

3.3. Scintillation and Cerenkov counting efficiency of ^{89}Sr, ^{90}Sr and ^{90}Y

Sources are measured for 100 minutes (10 min for 10 cycles) in Cerenkov counting mode at the window (10-360 channels). After counting source in Cerenkov counting mode, sources are mixed with 12 mL UltimaGold AB cocktail, then measured for 100 minutes (10 min for 10 cycles) at the window (120-910 channels) in high energy mode of scintillation counting.

4. Measurement procedure

① Take 10 mL of well-mixed water sample in a 100 mL beaker.

② Add 1 mL of strontium carrier (10 mg/mL solution in 1M HNO_3) then mixed

③ Add approximately 12 mL of 65% HNO_3 to the sample and mix well so that the molarity of the sample solution is 8M. The final sample should be 22 mL of 8M HNO_3.

④ Load the solution on a strontium resin column (3 g strontium resin, inner diameter: 10 mm, length: 120 mm) preconditioned in advance with 50 mL of 8M HNO_3.

⑤ Pour the sample prepared in the pretreatment step into the column, rinse the beaker with 5 mL of 8M HNO_3, and pass the column.

⑥ Wash the column with 100 mL of 8M HNO_3 to remove interfering elements then record the time.

⑦ Elute strontium form the column with 30 mL of ultrapure water.

⑧ After adjusting the pH of the elute solution to about 7 with 25% NH_4OH, add 5 mL of saturated $(NH_4)_2CO_3$ to the solution while stirring to form a $SrCO_3$ precipitate

⑨ Heat the solution on a hot plate for a few minutes.

⑩ After cooling the solution, filter the precipitate through a pre-weighed filter paper (for example, Whatman 42, pore size: 2.5 µm,

diameter of filter: 23 mm).

⑪ Wash the precipitate with a few mL 80% ethanol then dry it at 65 °C for 30 minutes.

⑫ Determine the chemical recovery of Sr by a gravimetric method.

⑬ Transfer the $SrCO_3$ precipitate into a 20 mL glass vial together with the filter.

⑭ Add 8 mL of 0.05M HNO_3 to the vial to dissolve the precipitate and measure the sample immediately in Cerenkov counting mode of the liquid scintillation counter.

⑮ After counting in Cerenkov counting mode, add 12 mL of UltimaGold AB cocktail into the vial, and re-measure it in scintillation counting mode.

5. Analysis of ^{90}Sr radioactivity

Activities of ^{89}Sr and ^{90}Sr in water sample can be calculated from sequential measurement data of Cerenkov and scintillation counting. Net count rates for ^{89}Sr and ^{90}Sr in the 10–360 channels in Cerenkov and in the 120–910 channels in scintillation counting mode can be expressed by equations (1) and (2):

$$N_{t_1}^c = \varepsilon_c^{89Sr} \cdot A_{t_1}^{89Sr} + \varepsilon_c^{90Sr} \cdot A_{t_1}^{90Sr} + \varepsilon_c^{90Y} \cdot A_{t_0}^{90Sr} \cdot f_1 \tag{1}$$

$$N_{t_2}^s = \varepsilon_s^{89Sr} \cdot A_{t_2}^{89Sr} + \varepsilon_s^{90Sr} \cdot A_{t_2}^{90Sr} + \varepsilon_s^{90Sr} \cdot A_{t_0}^{90Sr} \cdot f_2 \tag{2}$$

If the time interval between t_0, t_1 and t_2 is much less than the half-life of 90Sr, $A_{t_0}^{90Sr} \cong A_{t_1}^{90Sr} \cong A_{t_2}^{90Sr}$, equation (1) and (2) can be expressed by (3) and (4):

$$N_{t_1}^c = \varepsilon_c^{89Sr} \cdot A_{t_1}^{89Sr} + \varepsilon_c^{90Sr} \cdot A_{t_1}^{90Sr} + \varepsilon_c^{90Y} \cdot A_{t_1}^{90Sr} \cdot f_1 \tag{3}$$

$$N_{t_2}^s = \varepsilon_s^{89Sr} \cdot A_{t_1}^{89Sr} \cdot f_3 + \varepsilon_s^{90Sr} \cdot A_{t_1}^{90Sr} + \varepsilon_s^{90Sr} \cdot A_{t_1}^{90Sr} \cdot f_2 \tag{4}$$

$A_{t_1}^{89sr}$ can be expressed as follow:

$$A_{t_1}^{89sr} = \frac{N_{t_1}^c - A_{t_1}^{90Sr} \cdot (\varepsilon_c^{90Sr} + \varepsilon_c^{90Y} \cdot f_1)}{\varepsilon_c^{89Sr}} \tag{5}$$

Inserting equation (5) to equation (4) and solving for $A_{t_1}^{90sr}$ we obtain:

$$A_{t_1}^{90sr} = \frac{N_{t_2}^s \cdot \varepsilon_c^{89Sr} - N_{t_1}^c \cdot \varepsilon_s^{89Sr} \cdot f_1}{\varepsilon_c^{89Sr} \cdot \varepsilon_s^{90Sr} + \varepsilon_c^{89Sr} \cdot \varepsilon_s^{90Y} \cdot f_2 - \varepsilon_s^{89Sr} \cdot \varepsilon_c^{90Sr} \cdot f_3 - \varepsilon_s^{89Sr} \cdot \varepsilon_c^{90Y} \cdot f_1 \cdot f_3} \tag{6}$$

The auxiliary parameter y can be defined and introduced :

$$y = \varepsilon_c^{89Sr} \cdot \varepsilon_s^{90Sr} + \varepsilon_c^{89Sr} \cdot \varepsilon_s^{90Y} \cdot f_2 - \varepsilon_s^{89Sr} \cdot \varepsilon_c^{90Sr} \cdot f_3 - \varepsilon_s^{89Sr} \cdot \varepsilon_c^{90Y} \cdot f_1 \cdot f_3 \tag{7}$$

Thus, the following equation is obtained for $A_{t_1}^{90sr}$:

$$A_{t_1}^{90sr} = \frac{N_{t_2}^s \cdot \varepsilon_c^{89Sr} - N_{t_1}^c \cdot \varepsilon_s^{89Sr} \cdot f_1}{y} \tag{8}$$

Substituting equation (8) into equation (5) we get the following expression:

$$A_{t_1}^{89sr} = \frac{N_{t_1}^c \cdot (y + \varepsilon_s^{89Sr} \cdot \varepsilon_c^{90Y} \cdot f_1 \cdot f_3 + \varepsilon_s^{89Sr} \cdot \varepsilon_c^{90Sr} \cdot f_3) - N_{t_2}^2 \cdot (\varepsilon_c^{89Sr} \cdot \varepsilon_c^{90Sr} + \varepsilon_c^{89Sr} \cdot \varepsilon_c^{90Y} \cdot f_1)}{\varepsilon_c^{89Sr} \cdot y} \tag{9}$$

where:

$$f_1 = 1 - \exp\left(-\lambda_{90Y} \cdot (t_1 - t_0)\right)$$

$$f_2 = 1 - \exp\left(-\lambda_{90Y} \cdot (t_2 - t_0)\right)$$

$$f_3 = \exp\left(-\lambda_{89Sr} \cdot (t_2 - t_1)\right)$$

The radioactivity concentration of ^{89}Sr and ^{90}Sr on the target date can be calculated as follows:

$$A_t^{89Sr} = \frac{A_{t_1}^{89Sr}}{r \cdot V} \cdot e^{\lambda_{89Sr} \cdot (t_1 - t)} \tag{10}$$

$$A_t^{90Sr} = \frac{A_{t_1}^{90Sr}}{r \cdot V} \cdot e^{\lambda_{90Sr} \cdot (t_1 - t)} \tag{11}$$

Completed by :	WORKSHEET E2	No. _____
	STRONTIUM ANALYSIS RESULTS	

Prepared by: _____   Date: _____
                         (Full name)
Provide to: ☐ Sample Analyst   Time: _____

Liquid scintillation counter

Instrument type: _____   Model: _____   Serial no.: _____

Calibration performed by: _____   Date: _____
                                            (Full name)
LSC counting efficiency for ^{89}Sr: _____
LSC counting efficiency for ^{90}Sr: _____
LSC counting efficiency for ^{90}Y: _____

Background counting rate: _____[cps] Date: _____

Sample preparation

Sample prepared by: _____   Date: _____
                                     (Full name)

Analysis

Measured and evaluated by: _____   Date: _____
                                           (Full name)

MEASUREMENT RESULTS

Sample identification code	Sample type	Strontium concentration [Bq/]		File name
		^{89}Sr	^{90}Sr	

REMARKS:

Signature: _____

Figure B1. Worksheet sample for ^{90}Sr analysis[2]