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Measurement of the radioactivity in the environment — Air: tritium — Test method using bubbler sampling

Mesurage de la radioactivité dans l'environnement — Air : tritium — Méthode d'essai à l'aide d'un prélèvement par barbotage

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, SC 2, *Radiological protection*.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Everyone is exposed to natural radiation. The natural sources of radiation include cosmic rays and naturally occurring radioactive substances which exist on Earth such as flora, fauna or the human body. Human activities involving the use of radiation and radioactive substances add to the radiation exposure from this natural exposure. Some of those activities, such as the mining and use of ores containing naturally-occurring radioactive materials (NORM) and the production of energy by burning coal that contains such substances, simply enhance the exposure from natural radiation sources. Nuclear power plants and other nuclear installations use radioactive materials and produce radioactive effluents and waste during operation and decommissioning. The use of radioactive materials in industry, medicine, agriculture and research is expanding around the globe.

All these human activities give rise to radiation exposures that are only a small fraction of the global average level of natural exposure. The medical use of radiation is the largest and a growing man-made source of radiation exposure in developed countries. It includes diagnostic radiology, radiotherapy, nuclear medicine and interventional radiology.

Radiation exposure also occurs as a result of occupational activities. It is incurred by workers in industry, medicine and research using radiation or radioactive substances, as well as by passengers and crew during air travel. The average level of occupational exposures is generally below the global average level of natural radiation exposure (see Reference [2]).

As uses of radiation increase, so do the potential health risk and the public's concerns. Thus, all these exposures are regularly assessed in order to

a) improve the understanding of global levels and temporal trends of public and worker exposure,

b) evaluate the components of exposure so as to provide a measure of their relative impact, and

c) identify emerging issues that may warrant more attention and study. While doses to workers are mostly directly measured, doses to the public are usually assessed by indirect methods using the results of radioactivity measurements of waste, liquid and/or gaseous effluents and/or environmental samples.

Radioactivity from several naturally-occurring and anthropogenic sources is present throughout the environment. Thus, atmosphere can contain radionuclides of natural, human-made, or both origins.

— Natural radionuclides including ^{40}K, ^{3}H, ^{14}C and those originating from the thorium and uranium decay series, in particular ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U and ^{210}Pb which can be found in materials from natural sources or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizer production and use).

— Human-made radionuclides, such as transuranic elements (americium, plutonium, neptunium, and curium), ^{3}H, ^{14}C, ^{90}Sr and gamma-ray emitting radionuclides can also be found gaseous effluent discharges, in environmental matrices (water, air, soil and biota), in food and in animal feed as a result of authorized releases into the environment, fallout from the explosion in the atmosphere of nuclear devices and radionuclides releases from accidents of nuclear reactors, such as those that occurred in Chernobyl and Fukushima.

To ensure that the data obtained from radioactivity monitoring programs support their intended use, it is essential that the stakeholders (for example nuclear site operators, regulatory and local authorities) agree on appropriate methods and procedures for obtaining representative samples and for sampling, handling, storing, preparing and measuring the test samples. An assessment of the overall measurement uncertainty also needs to be carried out systematically. As reliable, comparable and 'fit for purpose' data are an essential requirement for any public health decision based on radioactivity measurements, international standards of tested and validated radionuclide test methods are an important tool for the production of such measurement results. The application of standards serves also to guarantee comparability of the test results over time and between different testing laboratories. Laboratories

apply them to demonstrate their technical competencies and to complete proficiency tests successfully during interlaboratory comparisons, two prerequisites for obtaining national accreditation.

Today, over a hundred International standards, prepared by Technical Committees of the International Organization for Standardization, including those produced by ISO/TC 85, and the International Electrotechnical Commission (IEC), are available to testing laboratories for measuring radionuclides in different matrices.

Tritium (^3H) is a radioactive isotope of hydrogen. It is a pure beta emitting radionuclide, with a maximum energy equal to 18,591 ± 1 keV and a radiological half-life equal to 12,312 (0,025) years (see Reference [3]). It is naturally occurring and continuously produced in the upper atmosphere by interaction of cosmic rays with nitrogen and oxygen nuclei (see Reference [4]).

Two main chemical species of both natural and anthropogenic tritium are present in the environment. The most abundant chemical form is tritiated water (HTO) (see Reference [5]). Tritium can also be present in the form of tritiated gas (HT or T_2) usually present in the vicinity of tritium-emitting facilities (see Reference [6]), tritiated methane (CH_3T), or in other various organic forms of tritium commonly observed in terrestrial, aquatic continental, and marine ecosystems (see References [7], [8] and [9]).

Anthropogenic tritium compounds come from radioactive releases of nuclear facilities i.e., nuclear power plants, irradiated fuel reprocessing and recycling plants, military defence, medical research applications, and past atmospheric testing of nuclear devices (see Annex A).

This document describes the method to assess the activity concentration of atmospheric tritium via air sampling by bubbler devices which trap tritiated water vapour and tritiated gas in a water solution. The method can be used for any type of environmental study or monitoring.

The test method is used in the context of a quality assurance management system (ISO/IEC 17025). It can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the test results of the atmospheric tritium activity concentrations can be verified to be below guidance levels required by a national authority for either planned or existing situations or for an emergency situation.

Measurement of the radioactivity in the environment — Air: tritium — Test method using bubbler sampling

1 Scope

This document describes a test method to determine the activity concentration of atmospheric tritium by trapping tritium in air by bubbling through a water solution. Atmospheric tritium activity concentration levels are expressed in becquerel per cubic metre ($Bq \cdot m^{-3}$).

The formulae are given for a sampling system with four bubblers. They can also be applied to trapping systems with only one trapping module consisting of two bubblers if only HTO is in the atmosphere to be sampled.

This document does not cover laboratory test sample results, in becquerel per litre of trapping solution, according to ISO 9698 or ISO 13168.

The test method detection limit result is between 0,2 $Bq \cdot m^{-3}$ and 0,5 $Bq \cdot m^{-3}$ when the sampling duration is about one week.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 4788, *Laboratory glassware — Graduated measuring cylinders*

ISO 9698, *Water quality — Tritium — Test method using liquid scintillation counting*

ISO 13168, *Water quality — Simultaneous determination of tritium and carbon 14 activities — Test method using liquid scintillation counting*

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 80000-10, *Quantities and units — Part 10: Atomic and nuclear physics*

3 Terms, definitions and symbols

For the purposes of this document, the definitions, symbols and abbreviations given in, ISO/IEC Guide 98-3, ISO/IEC Guide 99, ISO 80000-10 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1 Terms and definitions

3.1.1
aerosol
dispersion of very fine solid particles or liquid droplets in air or gases

3.1.2
air sample
representative part of the atmosphere sampled routinely, intermittently or continuously to examine its various characteristics

3.1.3
bubbler
glass container that holds the *trapping water solution* (3.1.11)

3.1.4
bubbler sample
bubbler (3.1.3) which an *air sample* (3.1.2) bubbled through

3.1.5
oxidizing efficiency
ratio of atmospheric tritium gas compounds converted into *tritiated water vapour* (3.1.13), oxidized with a catalytic converter furnace, to tritium gas compounds in the atmosphere during the sampling period

3.1.6
sampling module
module composed of two *bubblers* (3.1.3) connected in series to trap tritium species *HTO* (3.1.13) or *no-HTO* (3.1.12)

3.1.7
sampling system
device for sampling atmospheric tritium by bubbling through a water solution that consists of a sampling head which is the air inlet, a transport line, collector, and flow conditioning system

Note 1 to entry: Recorded samples are analysed off-line in a testing laboratory.

3.1.8
standard conditions
temperature of 273,13 K (0 °C) and a pressure of 101 325 Pa

Note 1 to entry: Used to convert air densities into a common basis. Other temperature and pressure conditions may be used and should be applied consistently.

3.1.9
test sample
representative volume taken from the *bubbler sample* (3.1.4) to analyse the tritium activity concentration by a testing laboratory

3.1.10
trapping efficiency
ratio of *tritiated water vapour* (3.1.13) activity concentration collected, during the sampling period, to atmospheric *tritiated water vapour* (3.1.13) activity concentration

3.1.11
trapping water solution
any types of colourless water with no apparent biological activities to trap atmospheric tritium by molecular and/or isotopic exchange between the tritium atoms in water vapour of the air and the hydrogen atoms of the water molecules in solution

3.1.12
tritiated gas
no-HTO
tritium gas compounds where HT and CH_3T molecules are predominant chemical gas species in atmosphere

3.1.13
tritiated water vapour
HTO
water vapour where one hydrogen atom of a water molecule is substituted by one tritium atom

3.2 Symbols, definitions and units

Table 1 — Symbols, definitions and units

Symbol	Definition and unit
A_i	tritium activity of the bubbler sample, B_i, in becquerel (Bq) where i =1, 2, 3 or 4
A_{ref}	reference tritium activity of tritiated water vapour (HTO) in the atmosphere in becquerel (Bq)
c_i	tritium activity concentration of the test sample, i, in becquerel per litre ($Bq \cdot l^{-1}$)
c_i^*	decision threshold of the tritium activity concentration of the test sample, i, in becquerel per litre ($Bq \cdot l^{-1}$)
$c_i^\#$	detection limit of the tritium activity concentration of the test sample, i, in becquerel per litre ($Bq \cdot l^{-1}$)
c_{ref}	reference tritium activity concentration of tritiated water vapour (HTO) in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
c_w	tritium activity concentration of tritiated water vapour (HTO) in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
c_g	tritium activity concentration of tritiated gas compounds (no-HTO) in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
c_w^* and c_g^*	decision threshold of the tritium activity concentration of HTO and no-HTO respectively in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
$c_w^\#$ and $c_g^\#$	detection limit of the tritium activity concentration of HTO and no-HTO respectively in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
$c_w^\triangleleft, c_w^\triangleright$ and $c_g^\triangleleft, c_g^\triangleright$	lower and upper limits of the probabilistically symmetric coverage interval of HTO and no-HTO respectively in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
$c_w^<, c_w^>$ and $c_g^<, c_g^>$	lower and upper limits of the shortest coverage interval of HTO and no-HTO respectively in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions
ε_{Bi}	trapping efficiency of each bubbler sample, i
ε_F	oxidizing efficiency of the catalytic converter furnace
k	coverage factor with k = 1, 2, 3, ...
q_p	air flow rate of sampling system in cubic metre per hour ($m^3 \cdot h^{-1}$) at standard conditions
t_i	counting duration of the test sample, i, in seconds (s)
t_p	sampling duration in hour (h)
$u(c_i)$	standard uncertainty of the tritium activity concentration of the test sample, i, in becquerel per litre ($Bq \cdot l^{-1}$)
$u(y)$	standard uncertainty associated with parameter, y, result (k = 1)
$U(y)$	expanded uncertainty calculated by $U(y) = k \cdot u(y)$ with $k > 1$

Table 1 *(continued)*

Symbol	Definition and unit
$u_{\mathrm{rel}}(y)$	relative standard uncertainty associated with parameter, y, result calculated by $u_{\mathrm{rel}}(y) = u(y) \cdot y^{-1}$
$U_{\mathrm{rel}}(y)$	relative expanded uncertainty calculated by $U_{\mathrm{rel}}(y) = k \cdot u_{\mathrm{rel}}(y)$ with $k > 1$
V	sampled air volume in cubic metre (m^3) at standard conditions where $V = q_{\mathrm{p}} \cdot t_{\mathrm{p}}$
$V_{\mathrm{B}i}$	water volume of bubbler sample, B_i, at the end of sampling duration in litre (l)
V_{Bref}	initial same volume of water in each bubbler, B_i, in litre (l)
w_i	correction factor for the tritium activity concentration of the test sample, i, in per litre (l^{-1})

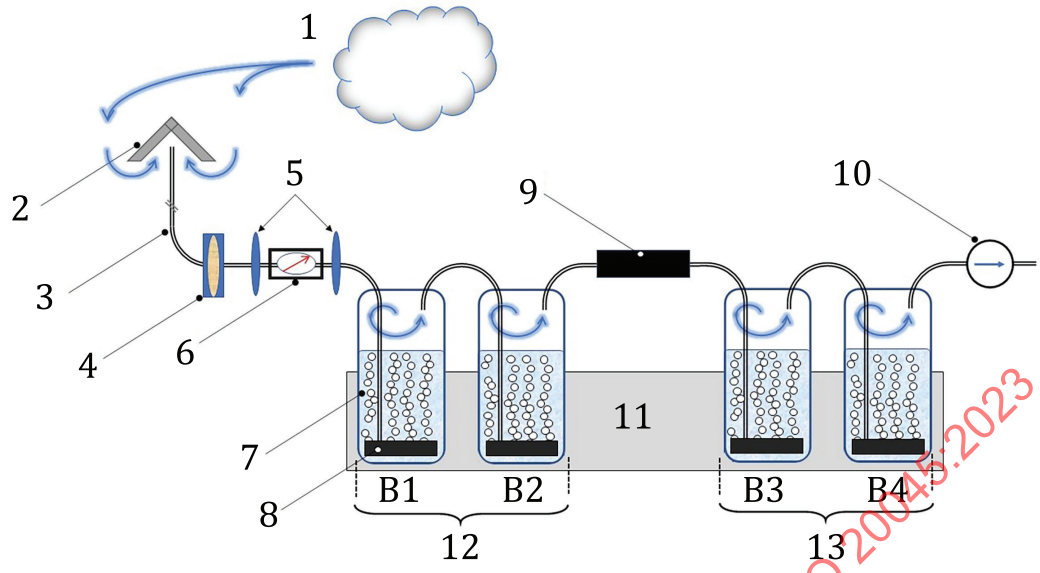
4 Principle

The bubbler sampling method consists of trapping airborne tritium compounds in water solution. The sampled air is continuously pumped through a series of bubblers containing trapping water and transformed as micro-bubbles in the water. The micro bubbles allow for the efficient capture of airborne tritium water vapour in the trapping solution by molecular and isotopic exchanges.

After filtering of solid aerosol particles by the dust filter, the sampled air passes through a first sampling module of two bubblers. This unit collects tritiated water vapour from the air. A second module, specifically for no-HTO compounds, can also be connected in series. In this case, the sampled air shall pass through a catalytic converter furnace which converts no-HTO compounds into HTO. This second module collects residual HTO not trapped by the first module and no-HTO compounds that have been converted into HTO.

The flow of air through the sampling system is controlled by a mass flow metre.

The Figure 1 shows a diagram of an example of a sample system. Other air flow control and injection configurations can be used.



Key

1 atmospheric air to monitor at temperature, *T*, and relative humidity RH in %
2 sampling head
3 connection pipe
4 anti-dust filter
5 hydrophobic filter
6 mass flow meter
7 bubbler with trapping water solution
8 micro-bubbles generator
9 catalytic converter furnace
10 pump
11 cooling module
12 first module for HTO trapping (bubblers B1 and B2)
13 second module for no-HTO and residual HTO trapping (bubblers B3 and B4)

Figure 1 — Example of an atmospheric air sampling system diagram with two sampling modules

At the end of the sampling period, trapping solutions shall be collected separately and transported as soon as possible to the testing laboratory.

Tritium activity concentration of water from each bubbler sample, in becquerel per litre of bubbler sample, shall be estimated by liquid scintillation in accordance with ISO 9698 or ISO 13168.

Activity concentrations of atmospheric tritium shall be calculated taking into account:

— air volume sampled;

— water volume of each bubbler sample at the start and end of sampling period;

— activity concentration of each bubbler sample;

— HTO trapping efficiency and if required;

— oxidizing efficiency of the catalytic converter furnace.

5 Influence quantities

Numerous parameters can affect the sampling of atmospheric air. These influencing quantities may be categorized as controllable or uncontrollable parameters. Controllable parameters can be monitored by applying the requirements of this document. Uncontrollable parameters are closely linked with environmental conditions such as atmospheric air temperature and humidity or ambient temperature at the sampling location.

Controllable quantities are:

— air flow rate;

— height of trapping solution into each bubbler;

— micro-bubbling into each bubbler;

— temperature of the bubbler sample during sampling;

— oxidizing efficiency of the catalytic converter furnace during heating;

— hermetically sealing of sampling system;

— conditions of sampling and filtration of atmospheric air upstream of sampling device.

6 Equipment

6.1 Description and requirements of the sampling system

The sampling system shall include:

— a sampling head equipped with protection against direct rainfall or splashing;

— a connection pipe as short as possible, between the sampling head and the sampling system, watertight, airtight and dustproof. The composition of the connection line shall reduce the retention of water vapour and isotopic exchanges with hydrogen. The connection pipe shall be protected from condensation and frost in the winter season;

— a dust filter upstream of the first module to limit chemical luminescence and quenching during sample analysis via liquid scintillation counting. The dust filter shall be periodically changed to protect it from clogging-up;

— a mass flow meter, associated with a pump flow rate control, protected by hydrophobic filters located upstream and downstream of the mass flow meter. The mass flow meter shall be periodically calibrated to ensure their accuracy;

— a minimum of one sampling module consisting of two bubblers connected in series each with a micro-bubble generator to improve exchanges between atmospheric tritiated water vapour and trapping water. It is recommended to use glass bubblers to reduce the risk of cross contamination after use, washing and drying;

— if required, to collect no-HTO and residual HTO not trapped by the first module;

  — a catalytic converter furnace to convert no-HTO tritium compounds to HTO by oxidizing;

  — a second module of two bubblers connected in series each with a micro-bubble generator to improve the exchange between HTO, converted by the catalytic converter furnace, and trapping water. The oxidizing efficiency shall be known (see Table B.1). Efficiency of the conversion catalyst depends of furnace temperature and material type used as catalyst to convert tritium species of interest see References [12], [13], [14], [15] and [16].

— a pump located downstream of sampling module(s);

— a cooling system to reduce evaporation of water into bubblers and to ensure a temperature range between 2 °C and 15 °C.

6.2 Location of sampling head

Sampling head shall be located in accordance with aeraulic conditions at the sampling point (cleared area, dominant wind, etc.). To limit clogging-up of dust filter and rain splashing, the sampling head shall be located at one metre above the sampling zone (roof or other).

6.3 Air flow rate, sampling duration and air volume sampling

The air flow rate shall be known, continuous and constant to ensure the representativeness of sampling. The air volume sampled is calculated from the mass flow meter and the sampling duration data. The result of this volume is expressed in cubic metre (m^3) in standard conditions. The mass flow meter shall be calibrated at standard conditions, i.e. temperature of 273,13 K (0 °C) and a pressure of 101 325 Pa.

A periodically verification of flow meter calibration according to the international system shall ensure the accuracy and uncertainty of sampling volume measurements.

6.4 Trapping water solution

Any type of water acceptable to the measurement by the test laboratory (e.g. deionized water, mineral water or deep aquifer water) that does not generate unacceptable chemical luminescence or quenching phenomena may be used. The tritium activity of the trapping solution shall be negligible related to the tritium activities to be monitored. Tritium activity of the trapping water solution shall be monitored with appropriate performances before use as trapping water solution to ensure that the decision threshold or the detection limit are in accordance with customer request.

If the sampling system operates under ambient temperatures less than 0 °C, it may be necessary to add antifreeze into trapping solution. This addition can generate chemical luminescence and quenching phenomena influencing the detection efficiency of the liquid scintillation measurement. The user shall ensure that the corresponding test sample is acceptable to the measurement by the test laboratory.

Before the start of sampling and at the end of the sampling period, the volume or the mass of the trapping solution in each bubbler shall be measured with a known accuracy, by graduated cylinder in accordance with ISO 4788 requirements or by mass.

6.5 Specifications for use

Specifications for use shall be defined and shall take into account:

— an unambiguous identification of bubblers;

— a hermetically sealed sampling system;

— a sufficient volume of trapping water to ensure a minimum vertical path of bubbles;

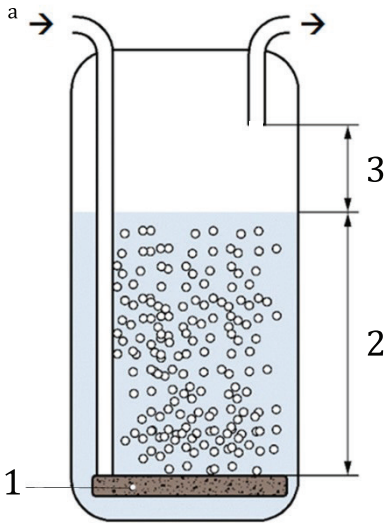
— a sufficient clearing height above the air-water interface to limit mechanical transfers of water from one bubbler to the next one;

— an air flow rate in accordance with a good exchange of HTO between bubbles and trapping water.

NOTE 1 The clearing height above the air-water interface and the vertical path of bubbles depend on the design of the bubbling system. They shall be optimized by the manufacturer.

NOTE 2 For example, air flow rate at standard conditions can range from 10 $l \cdot h^{-1}$ to 50 $l \cdot h^{-1}$ for a sampling period ranging from few hours to a week.

Figure 2 gives an example of a bubbler diagram.



Key

1 micro-bubbles generator
2 vertical path of bubbles
3 clearing height
a Air input.

Figure 2 — Example of bubbler diagram

Precautions shall be taken to avoid equipment cross-contamination. For example, the following precautions may be used:

— a systematic cleaning of the sample container (e.g. dishwasher and drying);

— a systematic cleaning of the micro-bubble generators (e.g. absorbent paper);

— a control of "absence" of contamination of the sampling system (e.g. by sampling an atmospheric air with a low-level tritium activity concentration during maintenance operations or after the sampling system is replaced). It is also advisable to check for the "absence" of contamination when the sampling system has been subjected to unusual tritium atmospheric activity concentration.

7 Procedure

7.1 Sampling

The purpose of the sampling is to collect atmospheric tritium of various forms for a quantitative analysis by a testing laboratory.

Bubbler samples shall be representative of the monitored or studied site. Consequently, the sampling system shall be located taking into account environmental characteristics such as local landscapes, barriers or dominant winds.

The sampling shall be done uninterrupted and with a constant air flow rate.

Air flow rate and sampling duration shall be adjusted to achieve appropriate performances; a sampled volume of 5 m^3 corresponding to an air flow rate about 30 $l \cdot h^{-1}$ and a sampling duration of one week, allows to reach an HTO detection limit of 0,2 $Bq \cdot m^{-3}$.

Atmospheric sampling for monitoring or studying operations, often, take place outside directly in the environment. Generally, in controlled conditions of use, recommended controllable parameters values

are sufficient to neglect humidity and temperature parameters. However, extreme climatic conditions may affect the sampling system and can disrupt the air sampling (e.g. a warm moist atmospheric air or a dry cold atmospheric air causes strong variations of relative humidity). These variations may have a significant impact on the final water volume collected at the end of sampling duration in the first bubbler sample (see References [10] and [11]).

7.2 Sample collection and transportation

At the end of the sampling period bubbler samples are disconnected from the sampling system and hermetically sealed as soon as possible. Optionally, a volume of bubbler samples' trapping solution can be removed and stored into an acceptable container. The container shall be, as soon as possible, hermetically sealed and unambiguously identified. Moreover, it is recommended to fill the container completely, leaving no headspace to minimize tritium exchange with atmospheric moisture.

Samples and associated information are given to the testing laboratory (see Annex D). Transport and conservation shall be carried out in accordance with testing laboratory recommendations (see Annex C).

7.3 Receipt

Bubbler samples shall be delivered to the testing laboratory as soon as possible after sampling. The laboratory shall check the completeness of samples received such as the number of samples, their integrity, identification or other useful information.

The laboratory should have procedures in place to handle these types of samples and prevent cross-contamination during handling or test sample preparation.

7.4 Conservation

Analysis of samples are achieved as soon as possible after receipt.

Given the specific nature of samples (filtered air and sample medium without apparent biological activities), it is possible to keep them at room temperature of the laboratory, i.e. without refrigerated and without protection from the laboratory light, without degradation of tritium activity concentration up to two months in sealed bubbler samples or in a hermetically sealed container (see Annex C).

7.5 Tritium activity concentration measurement

The testing laboratory shall count test samples from bubbler samples by liquid scintillation in accordance with ISO 9698 or ISO 13168.

The volume of bubbler samples shall be assessed by a graduated measuring cylinder in accordance with ISO 4788 or by mass. In this case, it is allowed that one litre of trapping water is equal to one kilogram exactly.

8 Expression of results

8.1 General

Generally, tritium activity concentration values c_2, and c_4 are respectively less than tritium activity concentration values c_1, and c_3 or less than or equal to the decision threshold level. Otherwise, a failure of sampling, an ambiguous identification of bubbler samples, unsealed cap increasing atmospheric exchanges, or switching of testing samples shall be suspected.

Only c_1 and, c_3 are used to estimate atmospheric air tritium activities given in becquerel per cubic metre at standard condition. Tritium activity concentration of bubbler samples B2 and B4 can be used as quality control of the sampling.

To quantify sampling uncertainty, trapping efficiency and oxidizing efficiency shall be taken into account with their associated uncertainty. Table B.1 gives typical trapping and oxidizing efficiency values under typical conditions of use.

Tritium activity concentrations, c_i, tritium decision thresholds, c_i^*, detection limits, $c_i^\#$ are determined according to ISO 9698 or ISO 13168.

To calculate characteristic limits of decision thresholds and detection limits, $\alpha = \beta = 0{,}05$ and $k_{1-\alpha} = k_{1-\beta} = k = 1{,}65$ are often chosen.

Other symbols used are defined in Clause 3.

8.2 Calculations for tritiated water vapour

8.2.1 Activity concentration

The tritium activity concentration of tritiated water vapour (HTO) in the atmosphere c_w is calculated using Formula (1):

$$c_w = c_1 \cdot \frac{V_{B1}}{V \cdot \varepsilon_{B1}} \tag{1}$$

The combined relative uncertainty is calculated using Formula (2):

$$u_{rel}(c_w) = \sqrt{u_{rel}^2(c_1) + u_{rel}^2(V_{B1}) + u_{rel}^2(V) + u_{rel}^2(\varepsilon_{B1})} \tag{2}$$

NOTE A method to assess the trapping efficiency ε_{B1} is given in Annex B.

For a sampling duration of 168 h and an air flow rate of 30 l·h^{-1} at standard conditions, the following values of bubbler sample B1 trapping efficiency and its associated standard uncertainty can be used by default: $\varepsilon_{B1} = 0{,}856$ and $u_{rel}(\varepsilon_{B1}) = 0{,}078$ (see Table B.1).

8.2.2 Decision threshold

The decision threshold of the tritium activity concentration of HTO in the atmosphere c_w^* is calculated using Formula (3):

$$c_w^* = c_1^* \cdot \frac{V_{B1}}{V \cdot \varepsilon_{B1}} \tag{3}$$

8.2.3 Detection limit

The detection limit of the tritium activity concentration of HTO in the atmosphere $c_w^{\#}$ of test sample 1 is calculated using Formula (4):

$$c_w{}^{\#} = \frac{2 \cdot c_w{}^{*} + k^2 \cdot \frac{w_1}{t_1} \cdot \frac{V_{B1}}{V \cdot \varepsilon_{B1}}}{1 - k^2 \cdot \left[u_{rel}^2(w_1) + u_{rel}^2(V_{B1}) + u_{rel}^2(V) + u_{rel}^2(\varepsilon_{B1}) \right]} \tag{4}$$

This detection limit can also be calculated using Formula (5):

$$c_w{}^{\#} = \frac{1 - k^2 \cdot u_{rel}^2(w_1)}{1 - k^2 \cdot \left[u_{rel}^2(w_1) + u_{rel}^2(V_{B1}) + u_{rel}^2(V) + u_{rel}^2(\varepsilon_{B1}) \right]} \cdot \frac{c_1{}^{\#}}{c_1{}^{*}} \cdot c_w{}^{*} \tag{5}$$

where w_1 is the correction factor of the tritium activity concentration of the test sample from bubbler sample B1.

To calculate the detection limit of the tritium activity concentration of HTO in the atmosphere from Formula (4), w_1 correction factor, its relative uncertainty $u_{rel}^2(w_1)$ and the counting duration t_1 of test sample 1 shall be given by the testing laboratory.

To calculate the detection limit of the tritium activity concentration of HTO in the atmosphere from Formula (5), relative uncertainty $u_{rel}^2(w_1)$, decision threshold $c_1{}^{*}$ and detection limit $c_1{}^{\#}$ shall be given by the testing laboratory.

8.2.4 Coverage intervals limits

8.2.4.1 Probabilistically symmetric coverage interval

The lower $c_w^{\triangleleft}$ and upper $c_w^{\triangleright}$ coverage interval limits are calculated using Formulae (6) and (7) (see ISO 11929-1):

$$c_w^{\triangleleft} = c_w \cdot \left[1 - k_p \cdot u_{rel}(c_w) \right]; p = \omega \cdot (1 - \gamma/2) \tag{6}$$

$$c_w^{\triangleright} = c_w \cdot \left[1 + k_q \cdot u_{rel}(c_w) \right]; q = 1 - \omega \cdot \gamma/2 \tag{7}$$

where

$\omega = \phi\left[\frac{c_w}{u(c_w)}\right]$, ϕ being the distribution function of the standardized normal distribution;

$(1-\gamma/2)$ is the probability for the coverage interval of the measurand;

$\omega = 1$ may be set if $c_w \geq 4 \cdot u(c_w)$.

In this case, the probabilistic coverage interval is symmetric and given by Formula (8):

$$c_w^{\triangleleft}, c_w^{\triangleright} = c_w \cdot \left[1 \pm k_{1-\gamma/2} \cdot u_{rel}(c_w) \right] \tag{8}$$

$\gamma = 0{,}05$ and then $k_{1-\gamma/2} = 1{,}96$ is often chosen by default.

8.2.4.2 Shortest coverage interval

The lower limit of the shortest coverage interval, $c_w^<$, and the upper limit of the shortest coverage interval, $c_w^>$, calculated from a primary measurement result, c_w, of the measurand and the standard uncertainty, $u(c_w)$, associated with c_w, are given by Formulae (9) or (10) (see ISO 11929-1):

$$c_w^<, c_w^> = c_w \cdot \left[1 \pm k_p \cdot u_{rel}(c_w)\right]; p = [1 + \omega \cdot (1 - \gamma)]/2 \quad (9)$$

Or if $c_w^< < 0$, then $c_w^< = 0$ and

$$c_w^> = c_w \cdot \left[1 \pm k_q \cdot u_{rel}(c_w)\right]; \quad (10)$$

where

$$q = 1 - \omega \cdot \gamma$$

$$\omega = \phi\left[\frac{C_w}{u(C_w)}\right], \quad \phi \text{ being the distribution function of the standardized normal distribution.}$$

The relation $0 \leq c_w^< < c_w^>$ apply and the approximation of Formula (8) is valid.

8.2.5 Conditions of use

Conditions to calculate tritium activity concentration of HTO in the atmosphere are given from four possible cases in Table 2.

An example to calculate the tritium activity concentrations of HTO in the atmosphere for an initial water volume of 0,160 l and an air flow rate of 30 $l \cdot h^{-1}$ in standard sampling conditions during one week is given in Annex E.

Table 2 — Four cases of possible results from bubbler samples B1 and B2

Case	B1	B2	c_w calculation
1	$c_1 \pm u(c_1)$	$c_2 \pm u(c_2)$	c_w calculated from Formula (1) $u_{rel}(c_w)$ calculated from Formula (2)
2	$c_1 \pm u(c_1)$	$\leq c_2^*$	
3	$\leq c_1^*$	$\leq c_2^*$	c_w calculated from Formula (3)
4	$\leq c_1^*$	$c_2 \pm u(c_2)$	Measurement result shall be confirmed because c_2 cannot be significantly greater than c_1^*

If the case 4 is confirmed and if the relative expanded uncertainty $U_{rel}(c_2)$ is greater than or equal to 60 % (expanded factor $k = 2$), case 3 is assumed to calculate the result of the tritium activity concentration of HTO in the atmosphere. Otherwise, further investigations are needed to determine the potential causes of this anomaly such as ambiguous identification of bubbler samples, unsealed cap increasing atmospheric exchanges or a test samples switch.

8.3 Calculation for tritiated gas compounds

Generally, tritium gas is not significantly measurable outside areas near specific tritium production or use facilities. However, when tritium gas compounds are to be measured in the presence of a significant HTO level, the part of HTO shall be subtracted of the primary result of the tritium activity concentration from bubbler sample B3. It therefore has two ways to calculate tritium gas compounds with or without a significant presence of HTO, i.e. when the activity concentration of HTO in atmosphere is greater or

lower than the decision threshold from bubbler B2. Corresponding quantities are noted $c_{g\left(c_2 \le c_2^*\right)}$ when the tritium activity concentration of HTO in atmosphere is not significant and $c_{g\left(c_2 > c_2^*\right)}$ otherwise.

8.3.1 Tritiated gas without significant HTO level

8.3.1.1 Activity concentration

The tritium activity concentration of tritiated gas (no-HTO) in the atmosphere $c_{g\left(c_2 \le c_2^*\right)}$ is calculated using Formula (11):

$$c_{g\left(c_2 \le c_2^*\right)} = c_3 \cdot \frac{V_{B3}}{V \cdot \varepsilon_{B3} \cdot \varepsilon_F} \tag{11}$$

The combined relative uncertainty is calculated using Formula (12):

$$u_{rel}\left(c_{g\left(c_2 \le c_2^*\right)}\right) = \sqrt{u_{rel}^2(c_3) + u_{rel}^2(V_{B3}) + u_{rel}^2(V) + u_{rel}^2(\varepsilon_B) + u_{rel}^2(\varepsilon_F)} \tag{12}$$

For a sampling duration of 168 h and an air flow rate of 30 l·h^{-1} at normal conditions the following values of bubbler sample B3 trapping efficiency, and oxidizing efficiency of the catalytic converter furnace and their associated standard uncertainty can be used by default: $(\varepsilon_{B3} = 0{,}856;\ u_{rel}(\varepsilon_{B3}) = 0{,}078)$; $(\varepsilon_F = 0{,}999;\ u_{rel}(\varepsilon_{B3}) = 0{,}033)$ (see Table B.1).

8.3.1.2 Decision threshold

The decision threshold of the tritium activity concentration of tritiated gas (no-HTO) in the atmosphere $c^*_{g\left(c_2 \le c_2^*\right)}$ is calculated using Formula (13):

$$c^*_{g\left(c_2 \le c_2^*\right)} = c_3^* \cdot \frac{V_{B3}}{V \cdot \varepsilon_{B3} \cdot \varepsilon_F} \tag{13}$$

8.3.1.3 Detection limit

The detection limit of the tritium activity concentration of tritiated gas (no-HTO) in the atmosphere $c^{\#}_{g\left(c_2 \le c_2^*\right)}$ is calculated using Formula (14):

$$c^{\#}_{g\left(c_2 \le c_2^*\right)} = \frac{2 \cdot c^*_{g\left(c_2 \le c_2^*\right)} + k^2 \cdot \frac{w_3}{t_3} \cdot \frac{V_{B3}}{V \cdot \varepsilon_{B3} \cdot \varepsilon_F}}{1 - k^2 \cdot \left[u_{rel}^2(w_3) + u_{rel}^2(V_{B3}) + u_{rel}^2(V) + u_{rel}^2(\varepsilon_{B3}) + u_{rel}^2(\varepsilon_F)\right]} \tag{14}$$

The detection limit can also be calculated using Formula (15):

$$c^{\#}_{g\left(c_2 \le c_2^*\right)} = \frac{1 - k^2 \cdot u_{rel}^2(w_3)}{1 - k^2 \cdot \left[u_{rel}^2(w_3) + u_{rel}^2(V_{B3}) + u_{rel}^2(V) + u_{rel}^2(\varepsilon_{B3}) + u_{rel}^2(\varepsilon_F)\right]} \cdot \frac{c_3^{\#}}{c_3^*} \cdot c^*_{g\left(c_2 \le c_2^*\right)} \tag{15}$$

where w_3 is the correction factor of the tritium activity concentration of the test sample 3.

To calculate the detection limit of the tritium activity concentration of no-HTO in the atmosphere from Formula (14), w_3 correction factor, its relative uncertainty $u_{rel}^2(w_3)$ and the counting duration t_3 of test sample 3 shall be given by the testing laboratory.

To calculate the detection limit of the tritium activity concentration of no-HTO in the atmosphere from Formula (15), relative uncertainty $u^2_{\text{rel}}(w_3)$, decision threshold $c_3{}^*$ and detection limit $c_3{}^\#$ shall be given by the testing laboratory.

8.3.2 Tritiated gas compounds with significant HTO level

8.3.2.1 Activity concentration

The tritium activity concentration of no-HTO in the atmosphere $c_{g\left(c_2>c_2{}^*\right)}$ is calculated using Formula (16):

$$c_{g\left(c_2>c_2{}^*\right)} = \frac{A_3 - (1-\varepsilon_{B3})\cdot A_2}{V\cdot\varepsilon_F\cdot\varepsilon_{B3}} \tag{16}$$

The combined relative uncertainty is calculated using Formula (17):

$$u_{\text{rel}}\left[c_{g\left(c_2>c_2{}^*\right)}\right] = \sqrt{\frac{A_3^2\cdot u^2_{\text{rel}}(A_3)+\left[(1-\varepsilon_{B3})\cdot A_2\right]^2\cdot u^2_{\text{rel}}(A_2)+(A_2-A_3)^2\cdot u^2_{\text{rel}}(\varepsilon_{B3})}{c_{g\left(c_2>c_2{}^*\right)}\cdot V\cdot\varepsilon_F\cdot\varepsilon_{B3}}+u^2_{\text{rel}}} \tag{17}$$

where

$$u^2_{\text{rel}} = u^2_{\text{rel}}(\varepsilon_F)+u^2_{\text{rel}}(V) \tag{18}$$

$$A_2 = c_2\cdot V_{B2} \tag{19}$$

$$A_3 = c_3\cdot V_{B3} \tag{20}$$

$$u^2_{\text{rel}}(A_2) = u^2_{\text{rel}}(c_2)+u^2_{\text{rel}}(V_{B2}) \tag{21}$$

$$u^2_{\text{rel}}(A_3) = u^2_{\text{rel}}(c_3)+u^2_{\text{rel}}(V_{B3}) \tag{22}$$

$$c_{g\left(c_2>c_2{}^*\right)}\cdot V\cdot\varepsilon_F\cdot\varepsilon_{B3} = c_3\cdot V_{B3}-(1-\varepsilon_{B3})\cdot c_2\cdot V_{B2} \tag{23}$$

For a sampling duration of 168 h and an air flow rate of 30 l·h^{-1} at normal conditions, the following values of bubbler sample B3 trapping efficiency, and oxidizing efficiency of the catalytic converter furnace and their associated standard uncertainty can be used by default: $(\varepsilon_{B3}=0{,}856;\ u_{\text{rel}}(\varepsilon_{B3})=0{,}078)$; $(\varepsilon_F=0{,}999;\ u_{\text{rel}}(\varepsilon_{B3})=0{,}033)$ (see Table B.1).

8.3.2.2 Decision threshold

The decision threshold of the tritium activity concentration of no-HTO in the atmosphere $c^{*}_{g\left(c_2>c_2^{*}\right)}$ is calculated using Formulae (24) and (25):

$$c^{*}_{g\left(c_2>c_2^{*}\right)}=\sqrt{k^2\cdot D+c^{*}_{g\left(c_2\le c_2^{*}\right)}{}^2} \tag{24}$$

where

$$\mathrm{D}=\frac{A_2^2}{V^2\cdot\varepsilon_{\mathrm{F}}^2}\cdot\left\{\frac{(1-\varepsilon_{\mathrm{B3}})^2}{\varepsilon_{\mathrm{B3}}^2}\cdot\left[u_{\mathrm{rel}}^2(c_2)+u_{\mathrm{rel}}^2(V_{\mathrm{B2}})+u_{\mathrm{rel}}^2(V_{\mathrm{B3}})+u_{\mathrm{rel}}^2(w_3)\right]+u_{\mathrm{rel}}^2(\varepsilon_{\mathrm{B3}})\right\}+\left(\frac{V_{\mathrm{B3}}\cdot A_2\cdot(1-\varepsilon_{\mathrm{B3}})\cdot\left\{c_3{}^{\#}\cdot\left[1-\mathrm{k}^2\cdot u_{\mathrm{rel}}^2(w_3)\right]-2\cdot c_3{}^{*}\right\}}{\mathrm{k}^2\cdot V^2\cdot\varepsilon_{\mathrm{F}}^2\cdot\varepsilon_{\mathrm{B3}}^2}\right) \tag{25}$$

where

$c^{*}_{g\left(c_2\le c_2^{*}\right)}$ is calculated using Formula (13);

A_2 is calculated using Formula (19).

To calculate the decision threshold of the tritium activity concentration of no-HTO in the atmosphere, with significant level of HTO into the bubbler sample B2, from Formulae (24) and (25), the relative uncertainty $u_{\mathrm{rel}}^2(w_3)$, the decision threshold $c_3{}^{*}$ and the detection limit $c_3{}^{\#}$, calculated from bubbler sample B3 data shall be given by the testing laboratory.

8.3.2.3 Detection limit

The detection limit of the tritium activity concentration of no-HTO in the atmosphere $c^{\#}_{g\left(c_2>c_2^{*}\right)}$ is calculated using Formula (26):

$$c_{\mathrm{g}}^{\#}\left(c_2>c_2^{*}\right)=c^{\#}_{g(c_2\le c_2{}^{*})}+2\cdot\frac{c^{*}_{g(c_2>c_2{}^{*})}-c^{*}_{g(c_2\le c_2{}^{*})}-k^2\cdot\frac{A_2}{V\cdot\varepsilon_{\mathrm{F}}}\cdot\left\{u_{\mathrm{rel}}^2(\varepsilon_{\mathrm{B3}})-\frac{1-\varepsilon_{\mathrm{B3}}}{\varepsilon_{\mathrm{B3}}}\cdot\left[u_{\mathrm{rel}}^2(w_3)+u_{\mathrm{rel}}^2(V_{\mathrm{B3}})\right]\right\}}{1-k^2\cdot\left[u_{\mathrm{rel}}^2(w_3)+u_{\mathrm{rel}}^2(V_{\mathrm{B3}})+u_{\mathrm{rel}}^2(V)+u_{\mathrm{rel}}^2(\varepsilon_{\mathrm{B3}})+u_{\mathrm{rel}}^2(\varepsilon_{\mathrm{F}})\right]} \tag{26}$$

where

$c^{*}_{g\left(c_2\le c_2^{*}\right)}$ is calculated using Formula (13);

$c^{\#}_{g\left(c_2\le c_2^{*}\right)}$ is calculated using Formula (14);

A_2 is calculated using Formula (19);

$c^{*}_{g\left(c_2>c_2^{*}\right)}$ is calculated using Formula (24).

To calculate the detection limit of the tritium activity concentration of no-HTO, with significant level of HTO into the bubbler sample B2, from Formula (26), relative uncertainty $u_{\mathrm{rel}}^2(w_3)$ shall be given by the testing laboratory.

8.3.3 Coverage intervals limits

8.3.3.1 Probabilistically symmetric coverage interval

The lower $c_g^{\triangleleft}$ and upper $c_g^{\triangleright}$ coverage interval limits are calculated using Formulae (27) and (28) (see ISO 11929-1):

$$c_g^{\triangleleft} = c_g\left[1 - k_p \cdot u_{rel}\left(c_g\right)\right]; p = \omega \cdot (1 - \gamma/2) \tag{27}$$

$$c_g^{\triangleright} = c_g\left[1 + k_q \cdot u_{rel}\left(c_g\right)\right]; q = 1 - \omega \cdot \gamma/2 \tag{28}$$

where

$\omega = \phi\left[\frac{c_w}{u(c_w)}\right]$, ϕ being the distribution function of the standardized normal distribution;

$(1-\gamma/2)$ is the probability for the coverage interval of the measurand;

$\omega = 1$ may be set if $c_w \geq 4 \cdot u(c_w)$.

In this case, the probabilistic coverage interval is symmetric and given by Formula (29):

$$c_g^{\triangleleft}, c_g^{\triangleright} = c_g \cdot \left[1 \pm k_{1-\gamma/2} \cdot u_{rel}\left(c_g\right)\right] \tag{29}$$

$\gamma = 0{,}05$ and then $k_{1-\gamma/2} = 1{,}96$ is often chosen by default.

8.3.3.2 Shortest coverage interval

The lower limit of the shortest coverage interval, $c_g^{<}$, and the upper limit of the shortest coverage interval, $c_g^{>}$, are calculated from a primary measurement result, c_g, of the measurand and the standard uncertainty, $u(c_g)$, associated with c_g, given by Formulae (30) or (31) (see ISO 11929-1):

$$c_g^{<}, c_g^{>} = c_g \cdot \left[1 \pm k_p \cdot u_{rel}\left(c_g\right)\right]; p = [1 + \omega \cdot (1 - \gamma)]/2 \tag{30}$$

Or if $c_g^{<} < 0$, then $c_g^{<} = 0$ and

$$c_g^{>} = c_g \cdot \left[1 \pm k_q \cdot u_{rel}\left(c_g\right)\right]; q = 1 - \omega \cdot \gamma \tag{31}$$

$\omega = \phi\left[\frac{c_g}{u(c_g)}\right]$ ϕ being the distribution function of the standardized normal distribution;

The relation $0 \leq c_g^{<} < c_g^{>}$ apply and the approximation of Formula (29) is valid.

8.3.4 Conditions of use

Conditions to calculate tritium activity concentration of no-HTO in the atmosphere are given from eight possible cases in the following Table 3.

An example to calculate the tritium activity concentrations of no-HTO for an initial water volume of 0,160 l and an air flow rate of 30 $l \cdot h^{-1}$ at standard conditions of sampling during one week is given in Annex E.

Table 3 — Eight cases of possible results from bubbler samples B2, B3 and B4

Case	B2	B3	B4	c_g calculation
1	$\leq c_2^*$	$c_3 \pm u(c_3)$	$c_4 \pm u(c_4)$	$c_{g(c_2 \leq c_2^*)}$ calculated from Formula (11)
2	$\leq c_2^*$	$c_3 \pm u(c_3)$	$\leq c_4^*$	$u_{rel}\left[c_{g(c_2 \leq c_2^*)}\right]$ calculated from Formula (12)
3	$\leq c_2^*$	$\leq c_3^*$	$\leq c_4^*$	$c^*_{g(c_2 \leq c_2^*)}$ calculated from Formula (13)
4	$\leq c_2^*$	$\leq c_3^*$	$c_4 \pm u(c_4)$	Measurement result shall be confirmed because c_4 cannot be significantly greater than c_3^*
5	$c_2 \pm u(c_2)$	$\leq c_3^*$	$c_4 \pm u(c_4)$	
6	$c_2 \pm u(c_2)$	$c_3 \pm u(c_3)$	$c_4 \pm u(c_4)$	$c_{g(c_2 > c_2^*)}$ calculated from Formula (16)
7	$c_2 \pm u(c_2)$	$c_3 \pm u(c_3)$	$\leq c_4^*$	$u_{rel}\left[c_{g(c_2 > c_2^*)}\right]$ calculated from Formula (17)
8	$c_2 \pm u(c_2)$	$\leq c_3^*$	$\leq c_4^*$	$c^*_{g(c_2 > c_2^*)}$ calculated from Formulae (24) and (25)

If cases 4 or 5 are confirmed and if the relative expanded uncertainty $U_{rel}(c_4)$ is greater than or equal to 60 % (expanded factor $k=2$), respectively cases 3 or 8 are assumed to calculate the result of the tritium activity concentration of no-HTO in the atmosphere. Otherwise, further investigations are needed to determine the potential causes of this anomaly such as ambiguous identification of bubble samples, unsealed cap increasing atmospheric exchanges or a testing samples switch.

In cases 1 to 4, assuming $c_{g(c_2 \leq c_2^*)} \leq c_w^*$ and, $c_{g(c_2 \leq c_2^*)} \leq c^*_{g(c_2 \leq c_2^*)}$ then $c^*_{g(c_2 \leq c_2^*)} = \frac{C_w^*}{\varepsilon_F}$

9 Test report

The test report shall conform to ISO/IEC 17025 requirements. It shall contain the following information:

a) reference to this document, i.e. (ISO 20045:2023);

b) identification of all samples;

c) units in which the results are expressed;

d) values of temperature and atmospheric pressure at standard conditions;

e) test result:

1) when the activity concentration of tritiated tritium vapour, c_w, or when the activity concentration of tritiated gas compounds, c_g, are compared with the respectively decision thresholds (see ISO 11929 series);

— if the result is less than the decision threshold, the result of the measurement is expressed as c_w^* or as c_g^*,

— if the result is greater than the decision threshold, the result of the measurement is expressed as:

$c_w \pm u(c_w)$ or $c_w \pm U(c_w)$ with the associated k value or as,

$c_g \pm u(c_g)$ or $c_g \pm U(c_g)$ with the associated k value,

2) when the activity concentration of tritiated tritium vapour, c_w, or when the activity concentration of tritiated gas compounds, c_g, are compared with their respectively detection limit,

   — if the result is less than the detection limit, the result of the measurement is expressed as $c_w^{\#}$ or as $c_g^{\#}$,

   — if the result is greater than the detection limit, the result of the measurement is expressed as:

   $c_w \pm u(c_w)$ or $c_w \pm U(c_w)$ with the associated k value or as,

   $c_g \pm u(c_g)$ or $c_g \pm U(c_g)$ with the associated k value.

Complementary information can be provided such as:

f) the uncertainty can also be expressed as the limits of the probabilistically symmetric coverage interval and/or the limits of the shortest coverage interval;

g) probabilities α, β and $(1-\gamma/2)$;

h) decision thresholds and the detection limits;

i) if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

j) mention of any relevant information likely to affect and/or to explain the results;

NOTE Occasionally, it is requested by the customer or regulator to compare the primary measurement results, c_w or c_g, with the respectively detection limit, $c_w^{\#}$ or $c_g^{\#}$, in order to decide whether the physical effect is recognized or not. Such stipulations are not in accordance with this document. They have the consequence that it is decided too frequently that the physical effect is absent when in fact it is not absent.

Annex A
(informative)

Technical data for tritium

Tritium (^3H) is a radioactive isotope of hydrogen. Tritium transforms by beta minus emission to the ground state of helium 3. Its half-life is about 12,3 years and its maximum beta energy is 18,6 keV (energies average 5,7 keV).

The tritium present in the environment has two origins, natural and artificial:

a) Tritium is continuously produced naturally by nuclear reactions in the upper atmosphere between high-energy cosmic rays and atmospheric nitrogen, oxygen and argon atoms. Overall, 99 % of naturally produced tritium is incorporated into the water cycle from the upper atmosphere to the ocean. UNSCEAR 2000 estimates than terrestrial natural stock of tritium is approximately $1{,}3 \cdot 10^{18}$ Bq (about 3,5 kg), corresponding at an absorbed dose about 0,01 µGy·a^{-1}, with annually production of $5 \cdot 10^{16}$ Bq·a^{-1} to $6 \cdot 10^{16}$ Bq·a^{-1} (0,150 kg to 0,200 kg).

b) Man-made tritium comes from historical atmospheric tests of nuclear weapons, radioactive releases of nuclear facilities including: pressurized water reactors, irradiated fuel reprocessing and recycling plants, military defence, medical and research applications.

   — Up to 1970, atmospheric tests of nuclear weapons released a quantity of tritium estimated at $2{,}4 \cdot 10^{20}$ Bq. The oceans inventory of tritium in 1972 reached $6{,}3 \cdot 10^{19}$ Bq. Currently, its accumulation in the environment (mainly in the oceans) is estimated at about $4{,}3 \cdot 10^{19}$ Bq.

   — In nuclear reactors, tritium is formed as a product of the ternary fission of certain isotopes of uranium and plutonium and by neutron reactions on light elements of the primary circuit, mainly boron, ${}^{10}_{5}\mathrm{B}(n,2\alpha)\,{}^{3}_{1}\mathrm{T}$, and in a lower proportion of lithium. In light water reactors, the tritium created by the fission reactions remains largely in the fuel itself (about 87 %), as well as in the zircaloy sheaths of the fuel-element pencils where it is under zirconium hydride form (about 13 %). The release of tritium into the water of the primary circuit is minimal or even negligible. It occurs only in the case of defects in zircaloy sheaths (which is infrequent), so that the release of fission tritium during reactor operation is limited to 0,1 % to 1 % of the tritium produced. Globally, all global nuclear reactors annually dissolve $1{,}2 \cdot 10^{16}$ Bq (0,035 kg) of tritium, mainly in liquid tritiated water form, and $6{,}0 \cdot 10^{15}$ Bq (0,018 kg) in gas form.

   — Fission tritium is released for the most part during spent fuel reprocessing operations. From 1985 to 1989, during the reprocessing of 4 % of global nuclear fuel, nuclear fuel reprocessing plants rejected $2{,}6 \cdot 10^{14}$ Bq per year of gaseous tritium in the atmosphere and mainly $4{,}4 \cdot 10^{15}$ Bq per year of tritiated water in the marine environment. In 2012, the French nuclear fuel reprocessing plant, La Hague, released $5{,}5 \cdot 10^{13}$ Bq of gaseous tritium and $1{,}16 \cdot 10^{16}$ Bq by liquid releases.

   — Medical centers are also producers of tritium; for example, the laboratory of the labelled molecules of the CEA center of Saclay rejects each year in the order of $2 \cdot 10^{13}$ Bq (see Reference [6]).

The fundamental characteristic of tritium (^3H) is its extreme propensity to exchange with its stable isotope (^1H) and reciprocally. In fact, it follows the water cycle and it is incorporated into the water and organic matter of all living organisms. Its biological period is about 12 days.

The atmosphere contains mainly tritium in the form of tritiated water (HTO) or tritiated hydrogen gas (HT and T_2) and in a lesser proportion tritiated methane (CH_3T). These last two forms, not directly incorporated by living organisms, have almost no influence on their tritium concentrations.

At the beginning of the 20th century atmospheric tritium activity concentration was $6 \cdot 10^{-3}$ Bq·m^{-3} of air in HTO form and $0{,}2 \cdot 10^{-3}$ Bq·m^{-3} in HT form. Following the atmospheric testing of nuclear weapons,

this activity concentration reached a maximum in the Sixties. In 1987, it was 0,02 $Bq \cdot m^{-3}$ in HTO form, 0,036 $Bq \cdot m^{-3}$ in HT form, and 0,012 $Bq \cdot m^{-3}$ in CH_3T form. In the year 2010, the average activity levels in HTO measured in air in France were between 0,01 $Bq \cdot m^{-3}$ and 0,02 $Bq \cdot m^{-3}$ of air. Activity concentrations greater than 1 $Bq \cdot m^{-3}$ can be measured in the immediate vicinity of the facility which releases tritium by atmospheric means.

Annex B
(informative)

Determination of trapping efficiency

B.1 Measurement principle

The trapping of atmospheric air tritium by bubbling in water is done by molecular and/or isotopic exchanges between the tritium atoms of water vapour in the air and the hydrogen atoms of the water molecules in solution. These exchanges induce activity losses by transferring part of the tritium activity integrated into the bubbler B1 during the sampling period to the other bubblers B2 (see Figure B.1) and in a lesser extent to the other bubblers. These activity losses are corrected by determining the trapping efficiency.

The trapping efficiency value can vary according to several parameters such as:

— the speed of bubbles i.e., live time of bubbles through in the liquid;

— the number of gas bubbles and their exchange area with the liquid;

— the sampling period, depending on the selected air flow rate, represents the volume of air sampled;

— the relative humidity and the temperature of the atmospheric air sampled;

— etc.

Trapping efficiency can not be defined solely by a constant function of time when the duration of sampling is long (several days) in an atmosphere where tritium activity concentration is not continuous. It is therefore necessary to determine analytically the value of the trapping efficiency of each sample, when the results of measurements permit, or if not, to estimate the mean value by a prior determination.

Information on methods to estimate trapping efficiency and oxidizing efficiency of tritiated gas compounds in a catalytic converter furnace with palladium-based catalyst is available from the scientific literature (see References [11], [12], [13], [14], [15] and [16]).

B.2 Trapping efficiency of first bubbler sample

The trapping efficiency of bubbler sample B1 ε_{B1} by bubbling of atmospheric water vapour tritium in a water solution corresponds to the ratio of the activity A_1 contained in the bubbler sample at the end of the sampling duration to the activity A_{ref} passed through the water solution.

Trapping efficiency $\varepsilon_{\mathrm{B1}}$ is calculated using Formula (B.1):

$$\varepsilon_{\mathrm{B1}} = \frac{A_1}{A_{\mathrm{ref}}} \tag{B.1}$$

where

$$A_1 = c_1 \cdot V_{\mathrm{B1}} \tag{B.2}$$

$$A_{\mathrm{ref}} = c_{\mathrm{ref}} \cdot V \tag{B.3}$$

$$V = \mathrm{q_p} \cdot t_{\mathrm{p}} \tag{B.4}$$

— A_{ref} is the reference tritium activity of tritiated water vapour (HTO) in the atmosphere in becquerel (Bq);

— c_{ref} is the reference tritium activity concentration of tritiated water vapour (HTO) in the atmosphere in becquerel per cubic metre ($Bq \cdot m^{-3}$) at standard conditions;

— V is the sampled air volume during calibration process in cubic metre (m^3) at standard conditions;

— q_p is the air flow rate of sampling system during calibration process in cubic metre per hour ($m^3 \cdot h^{-1}$) at standard conditions and

— t_p is the air sampling duration in hour (h) applied for calibration.

To ideally determine the trapping efficiency of the first bubbler, several other bubbler samples shall be connected in series. Under these conditions, the trapping efficiency can be calculated using Formula B.5 (Reference [10]):

$$\varepsilon_{B1} = \frac{c_1 \cdot V_{B1}}{\sum_{i=1}^{n} c_i \cdot V_{Bi}} \tag{B.5}$$

where $i = 1, 2, \ldots, n$

In practice, sampling devices for tritiated water vapour (HTO) have two or three bubbler samples connected in series. At the end of the sampling duration, if the height level of water in two first bubblers is equal and corresponds to the height vertical path of bubbles recommended by the manufacturer, the trapping efficiency is calculated using Formula (B.6):

$$\varepsilon_{B1} = 1 - \frac{c_2 \cdot V_{B2}}{c_1 \cdot V_{B1}} \tag{B.6}$$

The combined relative uncertainty is calculated using Formula (B.7):

$$u_{rel}(\varepsilon_{B1}) = \frac{c_2 \cdot V_{B2}}{c_1 \cdot V_{B1} - c_2 \cdot V_{B2}} \cdot \sqrt{u_{rel}^2(c_1) + u_{rel}^2(V_{B1}) + u_{rel}^2(c_2) + u_{rel}^2(V_{B2})} \tag{B.7}$$

where

$$\frac{c_2 \cdot V_{B2}}{c_1 \cdot V_{B1} - c_2 \cdot V_{B2}} = \frac{1 - \varepsilon_{B1}}{\varepsilon_{B1}} \tag{B.8}$$

NOTE This formula is correct if the height value of water at the end of the sampling duration is around of the initial value of height water.

In the other cases, when water heights of bubbler sample B1 at the beginning and at the end of sampling duration are different and/or, when the activity in the bubbler sample B2 is less than the decision threshold, the Formula B.5 shows that is impossible to determine the trapping efficiency ε_{B1}.

For a sampling duration t_p given ε_{B1} can be estimated as a function of the volume of water within range of variations of the first bubbler from the Formula B.9:

$$\varepsilon_{B1}\left(t_p, \frac{\Delta V_{B1}}{V_{Bref}}\right) = a \cdot e^{-b \cdot t_p} + c \cdot \left(1 - e^{-d \cdot \frac{\Delta V_{B1}}{V_{Bref}}}\right) \tag{B.9}$$

where V_{Bref} is the same initial volume of water in each bubbler B1, B2, B3, and B4 at the beginning of sampling duration.

The coefficient parameters a, b, c, d, and their associated uncertainty can be determined from experimental trapping efficiency values ε_j from bubbler sample B1 by a least squares method. Each ε_j is calculated using Formula (B.10):

$$\varepsilon_{\mathrm{j}} = \frac{1}{1+\frac{c_{2\mathrm{j}}}{c_{1\mathrm{j}}}\cdot\frac{1}{1-\frac{c_{4j}}{c_{3j}}}} \tag{B.10}$$

B.3 Typical values

Under typical conditions of use i.e., air flow rate of 30 l·h^{-1}, final height trapping water solution of 7 cm corresponding to 0,160 l, furnace temperature of 450 °C (catalyst Pd/Al_2O_3), the values of tritium trapping and oxidizing efficiencies, given in the Table B.1, should be used by default:

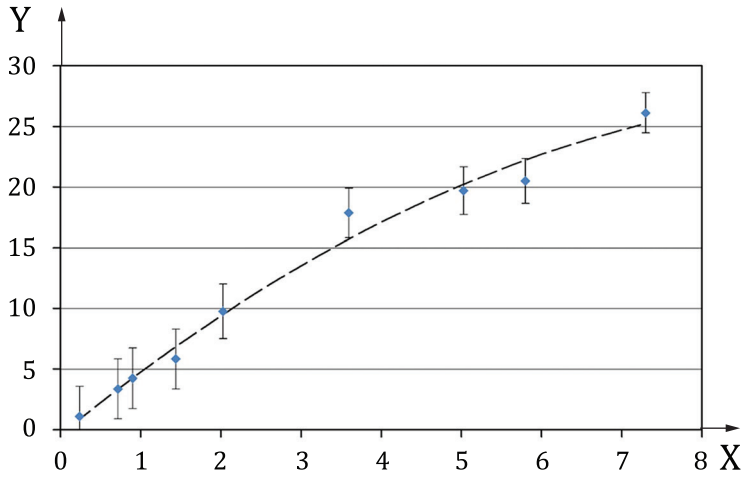
Table B.1 — Typical values of tritium trapping and oxidizing efficiencies

Typical conditions		Trapping efficiencies and associated standard uncertainties	Oxidizing efficiency and associated standard uncertainty
Air flow rate	30 l·h^{-1}		
Water volume	0,160 l		
Sampling period	168 h	$\varepsilon_{B1} = \varepsilon_{B3} = 0,856 \pm 0,067$	$\varepsilon_F = 0,989 \pm 0,033$
	336 h	$\varepsilon_{B1} = \varepsilon_{B3} = 0,747 \pm 0,067$	

Trapping efficiency values given in the Table B.1 are calculated from Formula B.9 where coefficient parameters a, b, c, d, and their associated uncertainty come from Reference [11] with $\Delta V_{B1} / V_{Bref} = 0$ % exactly. It showed that water volume of bubbler sample B1 at the end of sampling duration depends on weather conditions principally due to atmospheric water concentration of sampled air. Under these conditions, the values of bubbler B1 trapping efficiencies, calculated from Formula B.9, and their associated uncertainty are between (0,820 ± 0,070) and (0,87 ± 0,065) after 7 days of sampling duration when the $\Delta V_{B1} / V_{Bref}$ range is respectively between −0,22 and + 0,18. After 14 days of sampling duration and a $\Delta V_{B1} / V_{Bref}$ range between −0,32 and + 0,28, these values of trapping efficiencies are respectively (0,67 ± 0,070) and (0,76 ± 0,065).

For other species of tritium compounds (e.g. CH_3T) collected in same conditions, oxidizing efficiency given in the Table B.1 can be used.

Figure B.1 shows an example of study of transfer rate of the HTO form from B1 bubbler sample to B2 bubbler sample where bubblers B1 and B2 contain 0,160 l of a reference ground water with a low level of tritium activity concentration (Abatilles deep aquifer water). Bubbler sample B1 is spiked with a known tritium activity. At the end of each tritium transfer cycle, 10 ml of bubbler sample solution are taken for the measurement as test samples. The water volume of bubblers is completed at 0,160 l before starting a new tritium transfer cycle.



Key

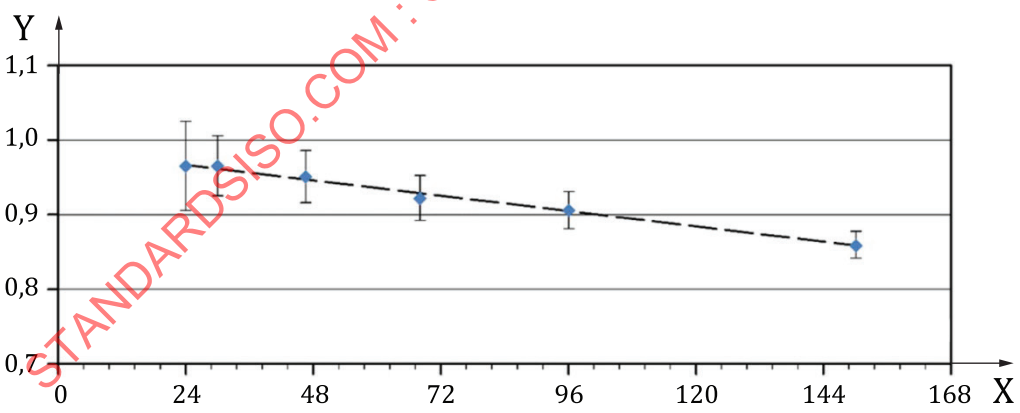
X sampled air volume in m^3

Y transfer rate in %

NOTE Initial water volume 0,160 l, air flow rate 30 $l \cdot h^{-1}$, ambient temperature (19,8 ± 0,7) °C and absolute air humidity (8,9 ± 1,0) $g \cdot m^{-3}$ at standard conditions.

Figure B.1 — Tritium activity transfer rate from bubbler B1 to bubbler B2 as a function of sampled air in controlled conditions

Figure B.2 shows an example of variation of first bubbler sample trapping efficiency as a function of the sampling period. The extrapolation of the curve in Figure B.2 for a shorter sampling duration has not been demonstrated in this example. For a sampling duration less than 24 h, it is recommended to determine the trapping efficiency of the first bubbler experimentally. By default, the following values of trapping efficiency of bubbler sample B1 can be used: $\varepsilon_{B1} = 0,9820$ and $u_{rel}(\varepsilon_{B1}) = 0,0035$ (k=1) (see Reference [11]).



Key

X sampling duration in h

Y trapping efficiency ε_{B1}

NOTE Initial water volume 0,160 l, air flow rate 30 $l \cdot h^{-1}$, ambient temperature (20,1 ± 0,8) °C and absolute air humidity (9,0 ± 1,1) $g \cdot m^{-3}$ at standard conditions.

Figure B.2 — Trapping efficiency of bubbler samples as a function of sampling duration in controlled conditions

Annex C
(informative)

Preserving of tritiated water solutions

C.1 Tritiated trapping solutions tests

The tests were conducted with the aim to quantify the integrity of the tritiated water samples, in terms of activity, when bubbler samples are stored in a ventilated room at ambient laboratory conditions over a period of 35 days.

To carry out this study, the four bubbler samples, closed by the original PVC cap, were brought back to the storage room after the weekly routine sampling. Then, bubbler samples are stored in the ventilated cupboard of an air-conditioned room at 19 °C. Water samples were stored in their original bubbler samples at ambient temperature and brightness room. During the storage period test samples were taken at regular intervals and analysed for tritium. The beta measurements of tritium activity concentration with relative uncertainty of 5 % have been carried out according to ISO 9698.

Analysis results showed that there was no significant evolution of tritium activity from bubbler samples B1 and B3 (HTO and no-HTO, respectively), over a period of 35 days of storage. Under these conditions, cold storage of bubbler samples is not necessary.

C.2 Tritiated water solution tests

Other multiparametric studies of tritiated water conservation stability in Abatilles water (water with a low level of tritium activity concentration) were carried out to assess the impact of preserving conditions on tritiated water samples. Water samples from Abatilles spiked with HTO have been stored in bottles of different materials (glass, high-density polyethylene, Teflon™ and polycarbonate) and stored under different conditions:

— in the dark at the refrigerator temperature of (3 ± 2) °C and

— on a work surface in the atmosphere of the test laboratory at the ambient temperature of (25 ± 5) °C and exposed to day-night cycles.

The tritiated water and blank samples (untritiated control sample) were hermetically sealed with original caps and kept for 60 days. The untritiated control samples were used to verify the absence of contamination by the storage site atmosphere and between samples, including possible diffusion and migration phenomena.

Tests samples and measurements were carried out at t_0, t_0 + 3 days, t_0 + 14 days, t_0 + 31 days and t_0 + 60 days. Over two months of preserving, no significant trends of tritium activity concentration variation were observed (relative deviation less than 4 % and standard deviation less than 0,2 (unit) compared with t_0 results). These results show that water samples with low level tritium activity concentration or tritiated can be maintained under laboratory ambient conditions before measurement.

C.3 Conclusion

These tests show that tritiated water solutions may be stored at room temperature, less than 30 °C, until 60 days.

Annex D
(informative)

Example of sampling and calculations forms

D.1 Sampling forms

Sampling system reference

Internal number of the laboratory sampling system	

Air sampling location

Name or number of monitored site	
State and town or village	
Name of sampling location	

Geographic coordinates of air sampling location

Latitude	
Longitude	

Trapping water solution

Nature of sampling solution	*example: low-level tritium ground water*

Note This solution shall be exactly the same that measurement solution

Parameters values at the beginning of sampling

Date of sampling start	**a**	**a**	**a**	**a**	**m**	**m**	**d**	**d**	**h**	**h**	**m**	**m**
Date and time												

Sampling system parameters	Unit	Expected value	Recorded value
Air flow rate	$l \cdot h^{-1}$		
Furnace temperature*	°C		
Cooling system temperature (°C)	°C		
Cooling system operational ?	Yes ☐	No ☐	
Bubbles present into each bubbler ?	Yes ☐	No ☐	
Nature of catalyst for catalytic oxidizing	information		

[a] *If no-HTO is required*

At the beginning of sampling air, *note volumes of bubbler samples in the corresponding table*

Parameters values at the end of sampling

Date of sampling start	**a**	**a**	**a**	**a**	**m**	**m**	**d**	**d**	**h**	**h**	**m**	**m**
Date and time												

Sampling system parameters	Unit	Recorded value
Air flow rate reading	$l \cdot h^{-1}$	
Air volume sampled (pumped)	l	
Furnace temperature reading	°C	
Cooling system temperature (°C)	°C	
Cooling system operational ?	Yes ☐	No ☐
Are bubbles present into each bubbler ?	Yes ☐	No ☐
	If no, number(s) of bubbler sample:	

Recorded values of bubbler samples	V_{Bref}	V_{Bend}	Unit	Sample number
B1 (HTO only)			l or kg	
B2 (HTO only)			l or kg	
B3 (no-HTO and/or residual HTO)[a]			l or kg	
B4 (no-HTO and/or residual HTO)[a]			l or kg	

[a] If no-HTO species are required.

NOTE V_{Bref} and V_{Bend} respectively amount of trapping water at the beginning and at the end of air sampling

Observations [see Clause 9 j)]:

Responsible for sampling identification *(contact details)*: Name, Department, phone number, e-mail…

Signature:

D.2 Calculation forms

Sampling system used parameters	Value
Uncertainty of sampling system flow rate (k = 1), in $l \cdot h^{-1}$	
Total air volume sampled, in m^3	
Relative uncertainty of total air volume sampled (k = 1)	
Trapping efficiency of bubbler samples B1	
Trapping efficiency of bubbler samples B3	
Relative uncertainty of trapping efficiency of bubbler samples B1 (k = 1)	
Relative uncertainty of trapping efficiency of bubbler samples B3 (k = 1)	
Catalytic oxidizing efficiency	
Uncertainty of catalytic oxidizing efficiency (k = 1)	
Relative uncertainty of volume or mass bubbling solutions at the end of sampling duration (k = 1)	