INTERNATIONAL STANDARD

ISO 22125-1

First edition
2019-11

Water quality — Technetium-99 —

Part 1:
Test method using liquid scintillation counting

Qualité de l'eau — Technétium-99 —

Partie 1: Méthode d'essai par comptage des scintillations en milieu liquide

Reference number
ISO 22125-1:2019(E)

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Published in Switzerland

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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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of 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 www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

A list of all the parts in the ISO 22125 series can be found on the ISO website.

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

Radioactivity from several naturally-occurring and anthropogenic sources is present throughout the environment. Thus, water bodies (such as surface waters, ground waters, sea waters) 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, ^{210}Po and ^{210}Pb can be found in water for natural reasons (e.g. desorption from the soil and washoff by rain water) or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizers production and use).
- Human-made radionuclides such as transuranium elements (americium, plutonium, neptunium, curium), ^{3}H, ^{14}C, ^{90}Sr, and gamma emitting radionuclides can also be found in natural waters. Small quantities of these radionuclides are discharged from nuclear fuel cycle facilities into the environment as a result of authorized routine releases. Some of these radionuclides used for medical and industrial applications are also released into the environment after use. Anthropogenic radionuclides are also found in waters as a result of past fallout contaminations resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Radionuclide activity concentration in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear installation during planned, existing, and emergency exposure situations[1]. Drinking water may thus contain radionuclides at activity concentrations which could present a risk to human health.

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment[2] and water bodies. Drinking waters are monitored for their radioactivity content as recommended by the World Health Organization (WHO)[3] so that proper actions can be taken to ensure that there is no adverse health effect to the public. Following these international recommendations, national regulations usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for waterbodies and drinking waters for planned, existing, and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as specified by ISO/IEC Guide 98-3 and ISO 5667-20[4].

Depending on the exposure situation, there are different limits and guidance levels that would result in an action to reduce health risk. As an example, during planned or existing situation, the WHO guidelines for guidance level in drinking water is 100 Bq·l^{-1} for ^{99}Tc activity concentration.

NOTE 1 The guidance level is the activity concentration with an intake of 2 l/d of drinking water for one year that results in an effective dose of 0,1 mSv/a for members of the public. This is an effective dose that represents a very low level of risk and which is not expected to give rise to any detectable adverse health effects[3].

In the event of a nuclear emergency, the WHO Codex Guideline Levels[5] mentioned that the activity concentration on contaminated food might not be greater than 10 000 Bq·kg^{-1} for ^{99}Tc.

NOTE 2 The Codex guidelines levels (GLs) apply to radionuclides contained in foods destined for human consumption and traded internationally, which have been contaminated following a nuclear or radiological emergency. These GLs apply to food after reconstitution or as prepared for consumption, i.e. not to dried or concentrated foods, and are based on an intervention exemption level of 1 mSv in a year for members of the public (infant and adult)[5].

Thus, the test method can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the radionuclide activity concentrations test results can be verified to be below the guidance levels required by a national authority for either planned/existing situations or for an emergency situation[5][6][7].

Usually, the test methods can be adjusted to measure the activity concentration of the radionuclide(s) in either wastewaters before storage or in liquid effluents before being discharged to the environment.

The test results will enable the plant/installation operator to verify that, before their discharge, wastewaters/liquid effluent radioactive activity concentrations do not exceed authorized limits.

The test method(s) described in this document may be used during planned, existing and emergency exposure situations as well as for wastewaters and liquid effluents with specific modifications that can increase the overall uncertainty, detection limit, and threshold.

The test method(s) may be used for water samples after proper sampling, sample handling, and test sample preparation (see the relevant part of the ISO 5667 series).

This document has been developed to answer the need of test laboratories carrying out these measurements, that are sometimes required by national authorities, as they may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

This document is one of a set of International Standards on test methods dealing with the measurement of the activity concentration of radionuclides in water samples.

Water quality — Technetium-99 —

Part 1:
Test method using liquid scintillation counting

WARNING — Persons using this document should be familiar with normal laboratory practices. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

IMPORTANT — It is absolutely essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies a method for the measurement of ^{99}Tc in all types of waters by liquid scintillation counting (LSC).

The method is applicable to test samples of supply/drinking water, rainwater, surface and ground water, as well as cooling water, industrial water, domestic, and industrial wastewater after proper sampling and handling, and test sample preparation. A filtration of the test sample is necessary.

The detection limit depends on the sample volume and the instrument used. The method described in this document, using currently available LSC instruments, has a detection limit of approximately 5 Bq·kg^{-1} to 20 Bq·kg^{-1}, which is lower than the WHO criteria for safe consumption of drinking water (100 Bq l^{-1})[3]. These values can be achieved with a counting time of 30 min for a sample volume varying between 14 ml to 40 ml. The method presented in this document is not intended for the determination of ultra-trace amount of ^{99}Tc.

The activity concentration values in this document are expressed by sample mass unit instead of sample volume unit as it is usually the case in similar standards. The reason is that ^{99}Tc is measured in various matrix types such as fresh water or sea water, which have significant differences in density. The activity concentration values can be easily converted to sample volume unit by measuring the sample volume. However, it increases the uncertainty on the activity concentration result.

The method described in this document is applicable in the event of an emergency situation, but not if ^{99m}Tc is present at quantities that could cause interference and not if ^{99m}Tc is used as a recovery tracer.

The analysis of Tc adsorbed to suspended matter is not covered by this method.

It is the user's responsibility to ensure the validity of this test method for the water samples tested.

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/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 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste waters*

ISO 10703, *Water quality — Determination of the activity concentration of radionuclides — Method by high resolution gamma-ray spectrometry*

ISO 11929, *Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation — Fundamentals and application*

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

ISO 19361, *Measurement of radioactivity — Determination of beta emitters activities — Test method using liquid scintillation counting*

ISO 20042, *Measurement of radioactivity — Gamma emitting radionuclides — Generic test method using gamma spectrometry*

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

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 80000-10, ISO 11929, ISO/IEC Guide 98-3 and ISO/IEC Guide 99 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 http://www.electropedia.org/

3.2 Symbols

For the purposes of this document, the symbols and designations given in ISO 80000-10, ISO 11929, ISO/IEC Guide 98-3, ISO/IEC Guide 99 and the following apply.

Symbol	Term	Unit
c_A^*	decision threshold	$\mathrm{Bq \cdot kg^{-1}}$
$c_A^\#$	detection limit	$\mathrm{Bq \cdot kg^{-1}}$
$c_A^\triangleleft$, $c_A^\triangleright$	lower and upper limits of the confidence interval	$\mathrm{Bq \cdot kg^{-1}}$
$c_{A\rho}^\#$	detection limit in mass concentration	$\mathrm{g \cdot kg^{-1}}$
A	activity of the calibration source	Bq
A_T	tracer activity	Bq
A_Tm	tracer activity measured	Bq
c_A	activity concentration	$\mathrm{Bq \cdot kg^{-1}}$
c_m	mass concentration	$\mathrm{g \cdot kg^{-1}}$
$\mathrm{C_s}$	specific activity	$\mathrm{Bq \cdot g^{-1}}$

Symbol	Term	Unit
DPM	disintegrations per minute	
f_q	quench factor	
m	test sample mass	kg
m_1	sub sample mass of the eluate for Tc measurement by LSC	g
m_2	sub sample mass of the eluate for recovery measurement	g
m_e	eluate mass	g
m_T	tracer mass	g
m_{TB}	mass of tracer added to the reagent blank for the calculation of $\mathrm{r_b}$	g
m_{te}	empty container mass of the eluate	g
m_{tf}	full container mass of the eluate	g
m_{Tm}	tracer mass measured	g
m_{TS}	tracer solution mass	g
r_b	reagent blank count rate	counts·s^{-1}
R_c	chemical recovery	
r_g	sample count rate	counts·s^{-1}
$\mathrm{R_m}$	mass ratio	
r_s	calibration count rate	counts·s^{-1}
r_{sp}	spiked reagent blank count rate for $\mathrm{r_o}$ calculation	counts·s^{-1}
r_T	^{99}Tc count rate from the tracer	counts·s^{-1}
r_{us}	unspiked reagent blank count rate for $\mathrm{r_o}$ calculation	counts·s^{-1}
SQPE	spectral quench parameter of the external standard	
t_0	background counting time	s
TDCR	triple to double counts ratio	
t_g	sample counting time	s
t_s	calibration counting time	s
tSIE	transformed spectral index of the external standard	
$\tilde{u}(\tilde{C}_A)$	characteristic limits	Bq·kg^{-1}
U	expanded uncertainty, calculated by $U = ku(c_A)$ with $k = 1, 2 \ldots$,	Bq·kg^{-1}
$u(c_A)$	standard uncertainty associated with the measurement result	Bq·kg^{-1}
V	test sample volume	l
ε	detection efficiency	
ρ	sample density	kg·l^{-1}

4 Principle

Technetium is mainly an anthropogenic element, but trace amounts are found in uranium ores. It has no stable isotope. ^{99}Tc is a significant fission product of ^{235}U (approximatively 6 % yield[8]) with a maximum beta-energy of (294 ± 1) keV and a half-life of (2,1 ± 0,1) × 10^5 years[9].

To determine ^{99}Tc in water, a water sample is collected, filtered, acidified, and oxidized (see Clause 5). A tracer is added before the chemical separation to take into account the losses of recovery during the purification step. Enough tracer is added to obtain a good statistical precision and be easily distinguished from a blank sample. The tracers that can be used are stable Re, ^{95m}Tc and ^{99m}Tc. Stable Re is often used as a recovery tracer for Tc measurement due to its similar reactivity[8]. It has the advantages of being easily available and stable. Tc and Re do not behave similarly when heated in an acidic solution. Tc is more volatile[10][11]; thus Re cannot be used as a recovery tracer when the method includes a vaporization step.

- When Re is used as a chemical recovery tracer, a sub-sample (m_2) of known mass is taken before the LSC measurement for the recovery determination. It is recommended to complete the recovery determination before counting the sample.

Rhenium can be measured for example by:

- ICP-OES according to ISO 11885[12]
- AAS according to ISO 15586[13]
- UV-visible spectroscopy[14][15]
- When ^{99m}Tc or ^{95m}Tc is used as a chemical recovery tracer, the chemical recovery is determined by gamma spectrometry[8]. Enough activity of ^{99m}Tc or ^{95m}Tc is added to obtain 10 000 counts when counting the sample. The sample is directly placed in the gamma counter, without any sample pre-treatment. It is measured according to the instrument specifications and in accordance with ISO 10703 and ISO 20042.

^{95m}Tc or ^{99m}Tc should completely decay before measuring the sample by LSC. It can take several days for ^{99m}Tc and several months for ^{95m}Tc depending of the initial quantity added. The tracer ^{99m}Tc is usually preferred to ^{95m}Tc due to a faster decay and also because commercial ^{95m}Tc standard solutions may contain a significant amount of ^{99}Tc[8].

^{99}Tc is chemically purified from potential interferents, which consist of any isotope that can cause the liquid scintillator to emit light in the region of interest (ROI) of ^{99}Tc. Different methods for the purification of ^{99}Tc are presented in the Annexes A to C.

After removal of the potential interferents, the chemical recovery (R_c) is determined. The purified sample is mixed with the scintillation cocktail in a counting vial to obtain a homogenous medium. The vial is counted by LSC.

5 Sampling and storage

Sampling, handling, and storage of the water shall be done as specified in ISO 5667-1, ISO 5667-3 and ISO 5667-10 and guidance is given for the different types of water in References [16] to [23]. It is important that the laboratory receives a sample that is truly representative and has not been damaged or modified during transportation or storage.

The sample is filtered to remove suspended matter using a 0,45 µm filter. A smaller pore size filter can also be used, but the filtration might be more tedious and time consuming. Technetium (VII) is not strongly adsorbed to plastic or glass container, but it can be reduced by the organic matter in the sample to technetium oxide (TcO_2). After filtration, the sample is acidified with nitric acid (HNO_3) to 0,01 mol·l^{-1} HNO_3. Then, hydrogen peroxide (H_2O_2) is added to maintain Tc as TcO_4^- and reduce its adsorption to the container. An addition of H_2O_2 to bring the sample to a concentration of 0,02 mol l^{-1} is recommended for the sample.

6 Procedure

6.1 Sample preparation for measurement

Filter, acidify, and oxidize the samples and a blank sample prepared with ultrapure water as specified in Clause 5. A minimum of 1 blank sample is required for all the methods presented. However, the average of several blanks can be used. Also, measuring blank samples at regular interval enables to rapidly detect a background issue when measuring the samples (see quality assurance and quality control program in Clause 7). Add the tracer to the sample.

Purify the sample from potential interferents. Purification methods are described in the informative Annexes A to C. An equivalent method can be used but shall follow all the criteria stated in this document.

Determine the chemical recovery.

Measure the ^{99}Tc in the sample by LSC.

6.2 Sample measurement

Measure ^{99}Tc in the samples by LSC by following the instructions provided by the instrument manufacturer and the steps described in ISO 19361.

7 Quality assurance and quality control program

7.1 General

Quality control operations shall meet the requirements of ISO/IEC 17025. Measurement methods shall be performed by suitably skilled staff under a quality assurance program.

7.2 Variables that could influence the measurement

Special care shall be taken in order to limit as much as possible the influence of parameters that may bias the measurement and lead to a non-representative result. Failure to take sufficient precautions may require corrective factors to be applied to the measured result. The variables affecting each measurement method are discussed in ISO 13164-2[24] and ISO 13164-3[25].

Influencing variables can affect the following stages of the measurement process: sampling, transportation and storage, reagents, transfer, and the activity measurement.

The presence of luminescence prevents the proper measurement of the samples. To reduce the luminescence, the samples are left in the dark for a few hours before counting them. If a luminescence peak is observed, wait a few more hours until no luminescence is observed and re-count the samples.

7.3 Instrument verification

Major instrument parameters (efficiency, background) shall be periodically verified within a quality assurance program established by the laboratory and in accordance with the manufacturer's instructions.

7.4 Contamination

Verify for contamination of the reagents through the periodic performance of reagent blank analysis. Laboratory procedures shall ensure that laboratory and equipment contamination as well as sample cross contamination is avoided.

7.5 Interference control

It is the user's responsibility to ensure that all potential interferents have been removed. The removal of potential interferents is limited by the decontamination factor of the method and the instrumental capabilities.

7.6 Method verification

A periodic verification of the method accuracy should be performed. This may be accomplished by:

- participating in intercomparison exercises;

- analysing reference materials;
- analysing spiked samples.

The repeatability of the method should be verified (for example, by replicate measurements).

7.7 Demonstration of analyst capability

If an analyst has not performed this procedure before, a precision and bias test should be performed by running a duplicate measurement of a reference or spiked material. Acceptance limits should be defined by the laboratory.

A similar evaluation should be performed by the analysts who routinely apply this procedure, with a periodicity defined by the laboratory. Acceptance limits should be defined.

7.8 Sample measurement

Periodically, verify the measurement performances of the instruments using sources of constant activity, covering the energy range to be measured. The counting background of the system is measured for a period of at least equal to that of the counting time used for the test sample and standards. The count rate of the reagent blank is denoted r_b. The counting efficiency of ^{99}Tc is determined with a standard solution of ^{99}Tc of known activity and purity.

The samples collected after the purification and analysis by LSC should show a similar quenching index (such as tSIE, SQPE, TDCR, direct DPM) for a specific type of matrix as the chemical medium is very similar. However, a quench calibration curve can be constructed to cover the quenching index value range encountered. This curve is made by adding a known amount of ^{99}Tc and varying concentrations of a quenching agent to blank aliquots. A quench curve can be obtained by plotting detection efficiency against quenching index value.

8 Expression of results

8.1 Sample activity, recovery and uncertainties

In the particular case of the measurement by liquid scintillation, the uncertainties on the scintillation liquid volume or mass and the counting time can be neglected.

The sample activity concentration (c_A) of ^{99}Tc of the sample is calculated using Formula (1):

$$c_A = R_\mathrm{m} \cdot \left(r_\mathrm{g} - r_\mathrm{b}\right) / \left(m \cdot R_\mathrm{c} \cdot \varepsilon \cdot f_\mathrm{q}\right) = \left(r_\mathrm{g} - r_\mathrm{b}\right) \cdot w \qquad (1)$$

where

$$w = R_\mathrm{m} / \left(m \cdot R_\mathrm{c} \cdot \mu \cdot f_\mathrm{q}\right)$$

and

$$\varepsilon = \left(r_\mathrm{s} - r_\mathrm{b}\right) / A$$

If Re is used as a recovery tracer, r_b is equal to a method blank count rate. However, it is not the case when ^{95m}Tc or ^{99m}Tc is used as a recovery tracer, since these tracers might contain a significant amount of ^{99}Tc. To be able to calculate this contribution, 2 reagent blanks, with no tracer added, shall be prepared using the same method as for the samples. After separation, one of these method blanks is spiked with a known amount of the tracer (m_{TB}). The tracer is allowed to decay until it is undetectable. This can be done at the same time as the real samples to be more time efficient. The unspiked and spiked samples are then measured by LSC. The subtraction of the spiked (r_{sp}) and unspiked (r_{us}) count rate reagent blanks allows to determine the ^{99}Tc count rate (r_{T}) contribution from the tracer as in Formula (2):

$$r_{\mathrm{T}} = r_{\mathrm{sp}} - r_{\mathrm{us}} \tag{2}$$

The contribution of ^{99}Tc from the tracer (r_{T}) varies as a function of the sample recovery (R_{c}), but not the instrumental background. The reagent blank count rate (r_{b}) for each sample is determined using Formula (3):

$$r_{\mathrm{b}} = r_{\mathrm{us}} + \left(R_{\mathrm{c}} \cdot r_{\mathrm{T}} \cdot m_{\mathrm{T}} / m_{\mathrm{TB}}\right) \tag{3}$$

And the uncertainties on r_{b} is calculated using Formula (4):

$$u\left(r_{\mathrm{b}}\right) = \sqrt{\left(\mu\left(r_{\mathrm{us}}\right)\right)^2 + \left(\mu_{\mathrm{rel}}^2\left(R_{\mathrm{c}}\right) + \mu_{\mathrm{rel}}^2\left(r_{\mathrm{T}}\right) + \mu_{\mathrm{rel}}^2\left(m_{\mathrm{T}}\right) + \mu_{\mathrm{rel}}^2\left(m_{\mathrm{TB}}\right)\right)^2} \tag{4}$$

The eluate mass (m_e) is determined using Formula (5):

$$m_{\mathrm{e}} = m_{\mathrm{tf}} - m_{\mathrm{te}} \tag{5}$$

The sub-sample mass for LSC (m_1) measurement is determined using Formula (6):

$$m_1 = m_{\mathrm{e}} - m_2 \tag{6}$$

The mass ratio (R_m) is determined using Formula (7):

$$R_{\mathrm{m}} = m_{\mathrm{e}} / m_1 \tag{7}$$

The chemical recovery (R_c) is calculated using Formula (8):

$$R_{\mathrm{c}} = \left(m_{\mathrm{Tm}} / m_{\mathrm{T}}\right) \cdot \left(m_{\mathrm{e}} / m_2\right) \tag{8}$$

where

m_{Tm} is the tracer mass measured using one of the methods listed in Clause 4;

m_{T} is the tracer mass added to the sample;

m_2 is the sub sample mass.

If $^{99\mathrm{m}}$Tc or $^{95\mathrm{m}}$Tc are used as recovery tracers, the ratio m_e/m_2 = 1. The uncertainty on R_{c} (μR_c) is calculated using Formula (9):

$$\mu_{\mathrm{rel}}^2\left(R_{\mathrm{c}}\right) = \mu_{\mathrm{rel}}^2\left(m_{\mathrm{Tm}}\right) + \mu_{\mathrm{rel}}^2\left(m_{\mathrm{T}}\right) + \mu_{\mathrm{rel}}^2\left(m_{\mathrm{e}}\right) + \mu_{\mathrm{rel}}^2\left(m_2\right) \tag{9}$$

When $^{99\mathrm{m}}$Tc or $^{95\mathrm{m}}$Tc are used as recovery tracers, the amount of tracer added and measured is most likely expressed in activity rather than in mass. In that case, the ratio tracer mass measured on tracer mass added ($m_{\mathrm{Tm}}/m_{\mathrm{T}}$) can be equally replaced by the ratio tracer activity measured (A_{Tm}) on tracer activity added (A_T) as shown in Formula (10):

$$R_{\mathrm{c}} = (A_{\mathrm{Tm}}/A_{\mathrm{T}}) \cdot (m_{\mathrm{e}}/m_2) \tag{10}$$

And the uncertainty is calculated using Formula (11):

$$\mu_{\mathrm{rel}}^2(R_{\mathrm{c}}) = \mu_{\mathrm{rel}}^2(A_{\mathrm{Tm}}) + \mu_{\mathrm{rel}}^2(A_{\mathrm{T}}) + \mu_{\mathrm{rel}}^2(m_{\mathrm{e}}) + \mu_{\mathrm{rel}}^2(m_2) \tag{11}$$

When using $^{99\mathrm{m}}$Tc or $^{95\mathrm{m}}$Tc as a recovery tracer, it is important to remember to correct for the tracer radiological decay.

When $^{95\mathrm{m}}$Tc or $^{99\mathrm{m}}$Tc is used as a chemical recovery tracer, $m_{\mathrm{e}} = m_1$ and $m_2 = 0$, which implies that $R_m = 1$.

The uncertainty of the sample activity ($\mu[C_A]$) is calculated using Formula (12):

$$\mu[c_A] = \sqrt{w^2 \cdot \left(\mu^2(r_{\mathrm{g}}) + \mu^2(r_{\mathrm{b}})\right) + c_A{}^2 \cdot \mu_{\mathrm{rel}}^2(w)} = \sqrt{w^2 \cdot \left(r_{\mathrm{g}}/t_{\mathrm{g}} + r_{\mathrm{b}}/t_0\right) + c_A{}^2 \cdot \mu_{\mathrm{rel}}^2(w)} \tag{12}$$

where

$$\mu_{\mathrm{rel}}^2(w) = \mu_{\mathrm{rel}}^2(\varepsilon) + \mu_{\mathrm{rel}}^2(m) + \mu_{\mathrm{rel}}^2(f_{\mathrm{q}}) + \mu_{\mathrm{rel}}^2(R_{\mathrm{c}}) + \mu_{\mathrm{rel}}^2(R_{\mathrm{m}})$$

And the relative standard uncertainty of ε for each quenching value is calculated using Formula (13):

$$\mu_{\mathrm{rel}}^2(\varepsilon) = \mu_{\mathrm{rel}}^2(r_{\mathrm{s}} - r_{\mathrm{b}}) + \mu_{\mathrm{rel}}^2(A) = (r_{\mathrm{s}}/t_{\mathrm{s}} + r_{\mathrm{b}}/t_0)/(r_{\mathrm{s}} - r_{\mathrm{b}})^2 + \mu_{\mathrm{rel}}^2(A) \tag{13}$$

where $\mu_{\mathrm{rel}}{}^2(A)$ includes all the uncertainties related to the calibration source: that is in the standard solution and the preparation of the calibration source.

$\mu_{\mathrm{rel}}{}^2(f_{\mathrm{q}})$ depends on the mathematical model used to fit the quench curve.

If needed, the characteristic limits, $\tilde{u}(\tilde{c}_A)$, can be calculated using Formula (14) as explained in ISO 11929:

$$\tilde{u}[\tilde{c}_A] = \sqrt{w^2 \cdot \left(\left(\tilde{c}_A/(w + r_{\mathrm{b}})\right)/t_{\mathrm{g}} + r_{\mathrm{b}}/t_0\right) + \tilde{c}_A^2 \cdot \mu_{\mathrm{rel}}^2(w)} \tag{14}$$

Note that the results can be expressed in volume unit using the density of the water tested.

8.2 Decision threshold

The decision threshold, c_A^*, is obtained from Formula (15) for $\tilde{c}_A = 0$ (see ISO 11929). This yields:

$$c_A^* = k_{1-\alpha} \cdot \omega \cdot \sqrt{(r_{\mathrm{b}}/t_{\mathrm{g}}) + (r_{\mathrm{b}}/t_0)} \tag{15}$$

$\alpha = 0{,}05$ with $k_{1-\alpha} = 1{,}65$ are often chosen by default.

8.3 Detection limit

The detection limit $c_A^{\#}$ is calculated using Formula (16):

$$c_A^{\#} = c_A^{*} + k_{1-\beta} \cdot \tilde{\mu}\left(c_A^{\#}\right) = c_A^{*} + k_{1-\beta} \cdot \sqrt{w^2 \cdot \left(\left(\left(c_A^{\#}/w\right)+r_\mathrm{b}\right)/t_\mathrm{g}\right) + \left(r_\mathrm{b}/t_0\right) + c_A^{\#2} \cdot \mu_\mathrm{rel}^2(w)} \tag{16}$$

$\beta = 0{,}05$ with $k_{1-\beta} = 1{,}65$ are often chosen by default.

The detection limit can be calculated by solving the previous Formula for $c_A^{\#}$ or, more simply, by iteration with a starting approximation $c = 2 \cdot c_A^{*}$.

When taking $a = b$ then $k_{1-\alpha} = k_{1-\beta} = k$ and the solution of the detection limit is given by Formula (17):

$$c_A^{\#} = \left(2 \cdot c_A^{*} + \left(\left(w \cdot k^2\right)/t_\mathrm{g}\right)\right) / \left(1 - k^2 \cdot \mu_\mathrm{rel}^2(w)\right) \tag{17}$$

8.4 Confidence interval limits

The lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, confidence limits are calculated using Formulae (18) and (19) (see ISO 11929):

$$c_A^{\triangleleft} = c_A - k_\mathrm{p} \cdot \mu\left(c_A\right); p = \omega \cdot \left(1 - \gamma/2\right) \tag{18}$$

$$c_A^{\triangleright} = c_A + k_\mathrm{p} \cdot \mu\left(c_A\right); q = 1 - \omega \cdot \gamma/2 \tag{19}$$

where $\omega = \Phi(y/\mu(y))$,

where

Φ is the distribution function of the standardized normal distribution;

$1\text{-}\gamma/2$ is the probability for the confidence interval of the measure;

$\omega = 1$ may be set if $c_A \geq 4\,\mu(c_A)$.

In this case, see Formula (20):

$$c_A^{\triangleleft},\ c_A^{\triangleright} = c_A \pm k_{1-\gamma/2 \cdot \mu\left(c_A\right)} \tag{20}$$

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

8.5 Calculation using the activity per unit of volume

The activity concentration may be calculated by multiplying the activity per unit of mass by the density ρ in grams per litre, as shown in Formula (21):

$$c_A = \left(R_\mathrm{m} \cdot \rho \cdot \left(r_\mathrm{g} - r_\mathrm{b}\right)\right) / \left(m \cdot R_\mathrm{c} \cdot \varepsilon \cdot f_\mathrm{q}\right) = \left(r_\mathrm{g} - r_\mathrm{b}\right) \cdot w \tag{21}$$

where

$$w = (R_\mathrm{m} \cdot \rho) / (m \cdot R_\mathrm{c} \cdot \varepsilon \cdot f_\mathrm{q})$$

$$\mu_\mathrm{rel}^2(w) = \mu_\mathrm{rel}^2(\varepsilon) + \mu_\mathrm{rel}^2(m) + \mu_\mathrm{rel}^2(f_\mathrm{q}) + \mu_\mathrm{rel}^2(R_\mathrm{c}) + \mu_\mathrm{rel}^2(R_\mathrm{m}) + \mu_\mathrm{rel}^2(\rho) \tag{22}$$

The formulae for the uncertainty, the characteristics limits and the limits of the confidence interval are calculated using the same formula as defined with the mass.

8.6 Conversion of activity concentration to mass concentration

The results can be expressed in mass concentration by dividing the activity concentration by the specific activity of ^{99}Tc (C_s), which is 6,3 ± 0,2 × 10^8 Bq·g^{-1}.

The activity concentration (c_A) and detection limit ($c^\#_A$) can be converted to mass concentration (c_m) by dividing the values obtained with the specific activity of ^{99}Tc (C_s) as in Formulae (23) and (24).

$$c_\mathrm{m} = c_A / C_\mathrm{s} \tag{23}$$

$$c^\#_{A\rho} = c^\#_A / C_s \tag{24}$$

$$\mathrm{Cs} = 6{,}317 \pm 0{,}033 \times 10^8\ \mathrm{Bq \cdot g^{-1}}$$

The uncertainty of the mass concentration is calculated using Formula (25):

$$\mu[\rho] = \rho \sqrt{\mu_\mathrm{rel}^2(C_A) + \mu_\mathrm{rel}^2(C_s)} \tag{25}$$

There is no need to calculate the uncertainties on the $c^\#_A$ and $c^\#_{A\rho}$ because they are estimated values.

8.7 Conversion of mass concentration to volume unit

To express the concentration by sample mass to sample volume, the mass (m) and volume (V) of the sample shall be recorded when performing the measurement. The activity concentration by sample mass c_A(Bq·kg^{-1}) may be calculated by sample volume c_A(Bq·l^{-1}) using Formula (26):

$$c_{A\left(\mathrm{Bq \cdot l^{-1}}\right)} = c_{A\left(\mathrm{Bq \cdot kg^{-1}}\right)} \cdot m / V \tag{26}$$

And the uncertainty can be calculated using Formula (27):

$$\mu\left[c_{A\left(\mathrm{Bq \cdot l^{-1}}\right)}\right] = c_{A\left(\mathrm{Bq \cdot l^{-1}}\right)} \sqrt{\mu_\mathrm{rel}^2\left(c_{A\left(\mathrm{Bq \cdot kg^{-1}}\right)}\right) + \mu_\mathrm{rel}^2(m) + \mu_\mathrm{rel}^2(V)} \tag{27}$$

9 Test report

The test report shall conform to the requirements of ISO/IEC 17025 and shall contain at least the following information:

a) a reference to this document, i.e. ISO 22125-1:2019;

b) all information necessary for the complete identification of the samples;

c) units in which the results are expressed;

d) test result, $C_A \pm \mu(C_A)$ or $C_A \pm U$, with the associated k value.

Complementary information can be provided such as:

e) probabilities α, β and $(1-\gamma)$;

f) decision threshold and the detection limit;

g) depending on the customer request there are different ways to present the results:

  - when the activity concentration C_A is compared with the decision threshold [see ISO 11929 (all parts)], the result of the measurement should be expressed as $\leq C_A^*$ when the result is below or equal to the decision threshold;
  - when the activity concentration C_A is compared with the detection limit, the result of the measurement can be expressed as $\leq C_A^\#$ when the result is below or equal to the detection limit. If the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

h) mention of any relevant information likely to affect the results.

Annex A
(informative)

Method 1 — TEVA[1) resin

A.1 Principle

The sample is filtered, acidified, and oxidized as described in Clause 5. The tracer is added. ^{99}Tc is purified from potential interferents by passing the solution through a TEVA resin, which contains a quaternary amine that selectively extract Tc. Then ^{99}Tc is measured by LSC.

^{95m}Tc or ^{99m}Tc can be used as a recovery tracer for this method. An approximate detection limit of 5 Bq·kg^{-1} is usually obtained using this method.

A.2 Reagents and apparatus

A.2.1 Reagents

Use only reagents of recognized analytical grade.

A.2.1.1 Nitric acid solution, $c(HNO_3) = 0{,}01$ mol·l^{-1}.

A.2.1.2 Nitric acid solution, $c(HNO_3) = 0{,}1$ mol·l^{-1}.

A.2.1.3 Nitric acid solution, $c(HNO_3) = 12$ mol·l^{-1}.

A.2.1.4 Nitric acid + hydrofluoric acid solution, $c(HNO_3) = 0{,}02$ mol·l^{-1} + c(HF) = 0,5 mol·l^{-1}.

A.2.1.5 ^{95m}Tc or ^{99m}Tc standard solution.

A.2.1.6 Chromatographic extraction resin TEVA.

A.2.1.7 Laboratory water, distilled or deionized, complying with ISO 3696 grade 3.

A.2.1.8 ^{99}Tc standard solution.

A.2.1.9 Liquid scintillation cocktail, chosen accordingly to the characteristics of the sample to be analysed and the properties of the detection equipment. The characteristics of the scintillation cocktail shall allow the mixture to be homogeneous and stable.

A.2.2 Apparatus

Usual laboratory equipment including the following:

A.2.2.1 Vacuum filtration system.

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1) TEVA resin is the trademark of a product supplied by Eichrom Technologies and TrisKem international. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

A.2.2.2 Filters, of pore size 0,45 µm.

A.2.2.3 Multi-holes vacuum box, e.g. 12 positions.

A.2.2.4 Analytical balance, accuracy 0,1 mg.

A.2.2.5 Disposable polypropylene centrifuge container, minimum volume of 50 ml.

A.2.2.6 Pipettes.

A.2.2.7 Hot plate.

A.2.2.8 Liquid scintillator counter.

A.3 Procedure

A.3.1 Sample preparation

Weigh approximately 40 ml of the filtered sample (*m*) in a 50 ml disposable plastic centrifuge container. Record the sample volume (*V*) if it is desired to express the final concentration in volume unit.

Add the tracer to the sample and record the mass of solution added (m_{TS}). Add enough ^{95m}Tc or ^{99m}Tc tracer to give 10 000 counts by gamma spectrometry when counting the sample.

A.3.2 Sample purification by extraction chromatography

Place a 2 ml TEVA resin on top of a multi-holes vacuum box using the appropriate connectors and reservoirs to pass the reagents through the resin.

Precondition the extraction resin with 5 ml of the HNO_3 solution of $c(HNO_3) = 0{,}1\ mol{\cdot}l^{-1}$.

Pass the sample through the resin at a flow rate of 1 ml·min^{-1} to 2 ml·min^{-1}.

Rinse the resin twice with 25 ml (total 50 ml) of the HNO_3 solution of $c(HNO_3) = 0{,}01\ mol{\cdot}l^{-1}$.

If ^{234}Th is present, rinse the resin another time with 25 ml of the solution of HNO_3 + HF of $c(HNO_3) = 0{,}02\ mol{\cdot}l^{-1} + c(HF) = 0{,}5\ mol{\cdot}l^{-1}$.

If a high amount of Ru and/or Mo is present, rinse the resin another time twice with 20 ml (total 40 ml) of the HNO_3 solution of $c(HNO_3) = 2\ mol{\cdot}l^{-1}$.

Elute Tc from the resin into a glass beaker using 25 ml HNO_3 solution of $c(HNO_3) = 12\ mol{\cdot}l^{-1}$.

A.3.3 Sample preparation for LSC measurement

Vaporize the sample solution on a hot plate until 0,5 ml is left. It is suggested not to heat at a temperature above 80 °C to minimize the chemical recovery losses.

Transfer the 0,5 ml sample to a LSC vial. Rinse the container with up to 4,5 ml of water and transfer this rinse solution to the LSC vial and adjust to 5 ml if needed.

A.3.4 Measurement

Measure the tracer in the samples by gamma spectrometry and calculate the chemical recovery (R_c).

Let ^{95m}Tc or ^{99m}Tc decay completely.

Add 15 ml of LSC cocktail in a 20 ml liquid scintillation vial and mix the sample.

Let the sample stand in the instrument rack to reduce the luminescence by dark adaptation.

Measure ^{99}Tc in the samples by LSC.

Annex B
(informative)

Method 2 — TRU[2] resin

B.1 Principle

The sample is filtered, acidified, and oxidized as described in Clause 5. The tracer is added. ^{99}Tc is purified from potential interferents by proceeding to a calcium phosphate co-precipitation followed by a solid phase extraction using an extraction chromatography resin (TRU resin) containing tributyl phosphate (TBP). Then ^{99}Tc is measured by LSC.

Re, ^{95m}Tc and ^{99m}Tc can be used as a recovery tracer for this method.

An approximate detection limit of 5 Bq·kg^{-1} is usually obtained using this method.

B.2 Reagents and apparatus

B.2.1 Reagents

Use only reagents of recognized analytical grade.

B.2.1.1 Phosphoric acid solution, $c(H_3PO_4) = 14{,}8$ mol·l^{-1}.

B.2.1.2 Sulfuric acid solution, $c(H_2SO_4) = 18$ mol·l^{-1}.

B.2.1.3 Sulfuric acid solution, $c(H_2SO_4) = 2$ mol·l^{-1}.

B.2.1.4 Calcium chloride solution, $c(CaCl_2) = 1$ mol·l^{-1}.

B.2.1.5 Ammonium hydroxide solution, $c(NH_4OH) = 14{,}5$ mol·l^{-1}.

B.2.1.6 Hydrogen peroxide solution, $c(H_2O_2) = 8{,}82$ mol·l^{-1}.

B.2.1.7 Re standard solution, $c(NH_4ReO_4) = 8{,}06 \times 10^{-6}$ mol·l^{-1} or ^{95m}Tc or ^{99m}Tc standard solution.

B.2.1.8 Chromatographic extraction resin TRU.

B.2.1.9 Laboratory water, distilled or deionised, complying with ISO 3696 grade 3.

B.2.1.10 ^{99}Tc standard solution.

B.2.1.11 Liquid scintillation cocktail, chosen accordingly to the characteristics of the sample to be analysed and the properties of the detection equipment. The characteristics of the scintillation cocktail shall allow the mixture to be homogeneous and stable.

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[2] TRU resin is the trademark of a product supplied by Eichrom Technologies and TrisKem international. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

B.2.2 Apparatus

Usual laboratory equipment including the following:

B.2.2.1 Vacuum filtration system.

B.2.2.2 Filters, of pore size 0,45 µm.

B.2.2.3 Centrifuge.

B.2.2.4 Multi-holes vacuum box, e.g. 12 positions.

B.2.2.5 Analytical balance, accuracy 0,1 mg.

B.2.2.6 Disposable polypropylene centrifuge containers, minimum volume of 50 ml.

B.2.2.7 Pipettes.

B.2.2.8 Hot plate.

B.2.2.9 Liquid scintillation counter.

B.3 Procedure

B.3.1 Sample preparation

Weigh approximately 40 ml of the filtered sample (m) in a 50 ml disposable plastic centrifuge container. Record the sample volume (V) if it is desired to express the final concentration in volume unit.

Add the tracer to the sample and record the mass of solution (m_{TS}). If Re is used, add 8,06 × 10^{-10} mol of Re tracer (m_T) (0,1 ml of Re standard solution, $c(NH_4ReO_4) = 8{,}06 \times 10^{-6}$ mol·l^{-1}). If ^{95m}Tc or ^{99m}Tc is used, add enough ^{95m}Tc or ^{99m}Tc tracer to give 10 000 counts by gamma spectrometry when counting the sample.

Add 5 × 10^{-4} mol of Ca^{2+} (0,5 ml of calcium chloride solution, $c(CaCl_2) = 1$ mol·l^{-1}) (except for sea water, since the amount of calcium is already sufficient), 2,96 × 10^{-3} mol of H_3PO_4 (0,2 ml of H_3PO_4 solution, $c(H_3PO_4) = 14{,}8$ mol·l^{-1}), and 8,82 × 10^{-4} mol of H_2O_2 (0,1 ml of H_2O_2 solution, $c(H_2O_2) = 8{,}82$ mol·l^{-1}). Mix the sample to homogenize and wait 5 min.

B.3.2 Calcium phosphate precipitation

Add 1,45 × 10^{-2} mol of NH_4OH (1 ml of 14,5 mol·l^{-1} NH_4OH solution, $c(NH_4OH) = 14{,}5$ mol·l^{-1}) and mix the sample. Wait 5 min for the precipitate to be formed.

Centrifuge the sample.

Transfer the supernatant in a disposable 50 ml plastic container and add 7,92 × 10^{-2} mol of H_2SO_4 (4,4 ml of H_2SO_4 solution, $c(H_2SO_4) = 18$ mol·l^{-1}) to the supernatant. Mix the sample and wait 30 min to let the sample cool to room temperature.

CAUTION — The dissolution of H_2SO_4 in water is highly exothermic, which could make the plastic softer. It is important to be careful when closing the container cap.