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Water quality — Nickel-59 and nickel-63 —

Part 1:
Test method using liquid scintillation counting

Qualité de l'eau — Nickel 59 et Nickel 63 —

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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 23655 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 (e.g. 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 can thus contain radionuclides at activity concentrations which can 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 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[4] and ISO 5667-20[5].

Depending on the exposure situation, there are different limits and guideline levels (GLs) that would result in an action to reduce health risk. As an example, during a planned or existing situation, the WHO GL for drinking water is 1 000 Bq·l^{-1} for Ni activity concentration.

NOTE 1   The GL is the activity concentration with an intake of 2 l·d^{-1} of drinking water for one year that results in an effective dose of 0,1 mSv·a^{-1} 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 GLs[6] mentioned that the activity concentration might not be greater than 10 000 Bq·l^{-1} for Ni.

NOTE 2   The Codex 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)[6].

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[7],[8].

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

This document has been developed to support the need of test laboratories carrying out these measurements, that are sometimes required by national authorities, as they can need 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 — Nickel-59 and nickel-63 —

Part 1:
Test method using liquid scintillation counting

WARNING — Persons using this document should be familiar with normal laboratory practice. 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.

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

1 Scope

This document specifies the determination of nickel-59 and nickel-63 (^{59}Ni and ^{63}Ni) activity concentration in samples of all types of water using liquid scintillation counting (LSC). Using currently available liquid scintillation counters, this test method can measure ^{59}Ni activity concentrations of 50 mBq·l^{-1} and ^{63}Ni activity concentrations of 20 mBq·l^{-1} with a counting time of 200 min and a sample volume of 1,5 l.

NOTE   These performance indicators are wholly dependent on the measurement regimes in individual laboratories; in particular, the detection limits for ^{59}Ni are entirely dependent on the levels of ^{63}Ni that can be present.

The range of application depends on the amount of dissolved material in the water and on the performance characteristics of the measurement equipment (background count rate and detection efficiency).

It is the laboratory's responsibility to ensure the suitability 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 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/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 and definitions

For the purposes of this document, the terms and definitions given in ISO 80000-10 apply.

ISO and IEC maintain terminology 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/

4 General symbols and nickel-59 and nickel-63 specific symbols

Table 1 provides the general symbols used in this document and Table 2 provides the ^{59}Ni and ^{63}Ni specific symbols used in this document.

Table 1 — General symbols and units

Symbol	Description	Unit
c_A	Activity concentration of the measurand	$Bq \cdot l^{-1}$
c_A^*	Decision threshold, expressed as an activity concentration	$Bq \cdot l^{-1}$
$c_A^\#$	Detection limit, expressed as an activity concentration	$Bq \cdot l^{-1}$
$c_A^\triangleleft$	Lower limit of the probabilistically symmetric coverage interval	$Bq \cdot l^{-1}$
$c_A^\triangleright$	Upper limit of the probabilistically symmetric coverage interval	$Bq \cdot l^{-1}$
$c_A^<$	Lower limit of the shortest coverage interval	$Bq \cdot l^{-1}$
$c_A^>$	Upper limit of the shortest coverage interval	$Bq \cdot l^{-1}$
E	Beta particle energy	keV
$f(Q_p)$	Empirical function linking a quench parameter, Q_p, to a detection efficiency, ε	—
$k_{1-\alpha}$	Quantiles of the standardised normal distribution for the probabilities $1-\alpha$	—
$k_{1-\beta}$	Quantiles of the standardised normal distribution for the probabilities $1-\beta$	—
$r_{g,A}$	Count rate of sample for energy region (2–20) keV	s^{-1}
$r_{g,B}$	Count rate of sample for energy region (20–100) keV	s^{-1}
$r_{b,A}$	Count rate of reagent blank for energy region (2–20) keV	s^{-1}
$r_{b,B}$	Count rate of reagent blank for energy region (20–100) keV	s^{-1}
$r_{0,A}$	Detector background for energy region (2–20) keV	s^{-1}
$r_{0,B}$	Detector background for energy region (20–100) keV	s^{-1}
$r_{net,A}$	Net count rate for energy region (2–20) keV	s^{-1}
$r_{net,B}$	Net count rate for energy region (20–100) keV	s^{-1}
R_{Ni}	Nickel recovery	—
S_E	Energy distribution for beta particles emitted by a particular radionuclide	—
t_s	Standard count time	s
t_g	Sample count time	s
t_b	Blank count time	s
t_0	Background count time	s
Q_p	Liquid scintillation quench parameter	—
$u_{R_{Ni}}$	nickel recovery uncertainty	—
u_x	Uncertainty of the parameter "x"	unit of x
u_y	Standard uncertainty of the estimate of the measurand	$Bq \cdot l^{-1}$
v_m	Liquid scintillation counting free parameter	—
V_g	Sample volume	l

Table 1 *(continued)*

Symbol	Description	Unit
x	Generic input quantity	—
y	Estimate of the measurand, primary measurement result of the measurand	$Bq \cdot l^{-1}$
α	Probability of reporting a false-positive result	—
β	Probability of reporting a false-negative result	—
ε	General term for detection efficiency	$s^{-1} \cdot Bq^{-1}$
γ	Proportion of data outside the coverage interval of the measurand	—
Φ	Distribution function of the standardised normal distribution	—
ω	Distribution function of y, where the standard measurement uncertainty is $u(y)$	—

Table 2 — Symbols and units specific to ^{59}Ni and ^{63}Ni analysis

Symbol	Description	Unit
A_{59Ni}	Activity concentration of the ^{59}Ni calibration standard solution	$Bq \cdot g^{-1}$
A_{63Ni}	Activity concentration of the ^{63}Ni calibration standard solution	$Bq \cdot g^{-1}$
$c_{A,59Ni}$	Activity concentration of ^{59}Ni in sample	$Bq \cdot l^{-1}$
$\tilde{c}_{A,59Ni}$	True value of the activity concentration of ^{59}Ni in sample	—
$c_{A,63Ni}$	Activity concentration of ^{63}Ni in sample	$Bq \cdot l^{-1}$
$C_{c,Ni}$	Mass concentration of stable nickel carrier	$g \cdot g^{-1}$
$C_{g,Ni}$	Mass concentration of stable nickel of sample	$g \cdot g^{-1}$
$C_{y,Ni}$	Mass concentration of stable nickel in the yield solution	$g \cdot g^{-1}$
D_{63Ni}	Decay of ^{63}Ni between sampling and measurement; $D_{63Ni} = e^{\left(\frac{\ln 0,5 \cdot t_d}{T_{63Ni}} \right)}$	—
$m_{c,Ni}$	Mass of stable nickel carrier	g
$m_{Ni,1}$	Mass of solution recovered for source preparation	g
$m_{Ni,2}$	Mass of solution used to determine stable nickel content in source solution	g
$m_{Ni,3}$	Mass of diluted solution for stable nickel content determination	g
$m_{Ni,4}$	Mass of solution counted	g
$m_{s,59Ni}$	Mass of ^{59}Ni calibration standard solution used	g
$m_{s,63Ni}$	Mass of ^{63}Ni calibration standard solution used	g
R_{Ni}	Recovery of nickel	—
$r_{s,59Ni,A}$	Gross count rate of the ^{59}Ni source in region A	s^{-1}
$r_{s,63Ni,A}$	Gross count rate of the ^{63}Ni source in region A	s^{-1}
$r_{s,63Ni,B}$	Gross count rate of the ^{63}Ni source in region B	s^{-1}
t_d	Time elapsed between sampling and measurement	s
t_{Ni}	Count time of source	s
T_{63Ni}	Radioactive half-life of ^{63}Ni	s
$\tilde{u}_{\tilde{c}A,59Ni}$	Combined standard uncertainty of $\tilde{c}_{A,59Ni}$	—
w_{59Ni}	Multiplier linking net count rate of ^{59}Ni to the measured activity concentration of ^{59}Ni, where: $w_{59Ni} = \dfrac{m_{Ni,1}}{\varepsilon_{59Ni,A} \cdot R_{Ni} \cdot m_{Ni,4} \cdot V_g}$	$Bq \cdot l^{-1} \cdot s$

Table 2 *(continued)*

Symbol	Description	Unit
$w_{63\text{Ni}}$	Multiplier linking net count rate of ^{63}Ni to the measured activity concentration of ^{63}Ni, where: $w_{63\text{Ni}} = \dfrac{m_{\text{Ni},1}}{\varepsilon_{63\text{Ni},A} \cdot R_{\text{Ni}} \cdot m_{\text{Ni},4} \cdot V_{g}}$	Bq·l^{-1}·s
$\varepsilon_{59\text{Ni},A}$	Detection efficiency of ^{59}Ni in region A	s^{-1}·Bq^{-1}
$\varepsilon_{63\text{Ni},A}$	Detection efficiency of ^{63}Ni in region A	s^{-1}·Bq^{-1}
$\varepsilon_{63\text{Ni},B}$	Detection efficiency of ^{63}Ni in region B	s^{-1}·Bq^{-1}
χ	Ratio between the detection efficiency of ^{63}Ni in channel A and the detection efficiency if ^{63}Ni in channel B	
$T(\chi)$	Uncertainty term in channel A, arising from counts in channel B arising from ^{63}Ni	s^{-2}

5 Principle

Nickel-59 is an anthropogenic radionuclide with a half-life of 76 000 years[9] that decays to ^{59}Co by electron capture, with the associated emission of cobalt K- and L- X-rays, with energies of 6,9 keV and 7,7 keV. ^{59}Ni is generated by neutron capture of the stable isotope ^{58}Ni.

Nickel-63 is an anthropogenic radionuclide with a half-life of 98,7 years[10] that decays to ^{63}Cu by beta particle emission with a maximum beta energy of 67,0 keV. ^{63}Ni is generated by neutron capture of the stable isotope ^{62}Ni.

Freshly irradiated natural nickel can have an ^{59}Ni/^{63}Ni activity ratio of 0,009 and this increases to 0,01 after 20 years, to 0,012 after 50 years and to 0,018 after 100 years, although these values are very dependent on the irradiation history and any subsequent processing of the material being measured.

Both ^{59}Ni and ^{63}Ni are separated from an aliquot of the sample matrix by precipitation, extraction chromatography or ion exchange chromatography and their activities are measured simultaneously by liquid scintillation counting against suitable calibration standards of ^{59}Ni and ^{63}Ni.

For samples with high activity concentration, dilution of the sample is required to avoid resin and detector saturation during the separation and counting steps, respectively.

Suspended material is removed prior to analysis by filtration using 0,45 µm filters. The analysis of the insoluble fraction requires a mineralization step that is not covered by this document.

NOTE   General guidance on sample pre-treatment is given in ISO 18589-2[11].

It is necessary to know the concentration of stable nickel in the sample in order to determine the mass of the iron and nickel carriers to add and to calculate the chemical yield for the separation of ^{59}Ni and ^{63}Ni.

When suspended matters are significant, a filtration step is required and ^{59}Ni and ^{63}Ni activities can also be determined in the filter deposit.

6 Reagents

All reagents shall be of recognized analytical grade and shall not contain any detectable alpha and beta activity, except for radioactive standard solutions.

6.1 Standard solutions

6.1.1 Nickel-59 and ^{63}Ni standards

Nickel-59 and ^{63}Ni standards should be traceable to national or international measurement standards, and can be obtained from a number of commercial suppliers and national metrology institutes.

6.1.2 Stable nickel standards

Stable nickel standards can be obtained from a number of commercial suppliers at a range of concentrations.

6.2 Chemical quenching agent

A suitable chemical should be used, such as nitromethane, CH_3NO_2.

6.3 Colour quenching agent

A suitable chemical should be used, such as tartrazine, $C_{16}H_9N_4Na_3O_9S_2$.

6.4 Holdback carrier

Prepare a mixed solution of antimony, caesium, calcium, cerium, chromium, cobalt, iron, manganese, ruthenium, silver, strontium and zinc, containing approximately 10 mg g^{-1} of each element. It is not necessary to calibrate this solution.

6.5 Water

Water complying with grade 3 of ISO 3696.

6.6 Specific reagents for chemical separation

6.6.1 Ammonium citrate solution, $c_{C6H14N2O7}$ = 1 mol·l^{-1}

Dissolve 22,62 g of ammonium citrate ($C_6H_{14}N_2O_7$) in 80 ml of water and dilute to 100 ml with water (6.5).

6.6.2 Ammonium citrate solution, $c_{C6H14N2O7}$ = 0,2 mol·l^{-1}

Dissolve 4,52 g of ammonium citrate ($C_6H_{14}N_2O_7$) in 80 ml of water and dilute to 100 ml with water (6.5).

6.6.3 Ammonium hydroxide solution, c_{NH4OH} = 6 mol·l^{-1}

Dilute 500 ml of concentrated ammonia (NH_4OH) solution to 1 l with water (6.5).

6.6.4 Dimethylglyoxime solution, 1 %, $c_{C4H8N2O2}$ = 0,086 mol·l^{-1}

Dissolve 1 g dimethylglyoxime ($C_4H_8N_2O_2$) in 100 ml ethanol.

6.6.5 Hydrochloric acid solution, c_{HCl} = 6 mol·l^{-1}

Dilute 500 ml of concentrated hydrochloric acid (HCl) to 1 l with water (6.5).

6.6.6 Hydrochloric acid solution, c_{HCl} = 1 mol·l^{-1}

Dilute 83 ml of concentrated hydrochloric acid (HCl) to 1 l with water (6.5).

6.6.7   Iron chloride solution, $c(FeCl_3)$ = 0,02 mol·l^{-1}

Dissolve 0,54 g of iron(III)chloride hexahydrate in 100 ml of hydrochloric acid (6.6.6).

6.6.8   Nitric acid solution, c_{HNO3} = 16 mol·l^{-1}

Use commercially available concentrated nitric acid (HNO$_3$).

6.6.9   Nitric acid solution, c_{HNO3} = 7,2 mol·l^{-1}

Dilute 450 ml of concentrated nitric acid (HNO$_3$) (6.6.8) to 1 l with water (6.5).

6.6.10   Nitric acid solution, c_{HNO3} = 3 mol·l^{-1}

Dilute 190 ml of concentrated nitric acid (HNO$_3$) to 1 l with water (6.5).

6.6.11   Sodium hydroxide solution, c_{NaOH} = 4 mol·l^{-1}

Dissolve 160 g of sodium hydroxide (NaOH) in water (6.5) and dilute the solution to 1 l.

WARNING — Eye protection should be worn.

6.6.12   Stable nickel carrier solution

Procure a calibrated solution of (10 ± 1) g·l^{-1} from a suitable supplier. Alternatively, prepare and calibrate a tracer solution in-house from, for example, Ni(NO$_3$)$_2$·6H$_2$O.

7   Equipment

7.1   Laboratory equipment for direct evaporation

Usual laboratory apparatus to store and prepare the sample as specified in ISO 5667-3.

A hot plate, an automatic evaporator or any other appropriate apparatus.

7.2   Liquid scintillation vials

The vials shall be either in plastic or glass.

7.3   Measurement equipment: Liquid scintillation counter

Both ^{59}Ni and ^{63}Ni can be counted with a commercial liquid scintillation counter. These can include:

—   "conventional" twin photomultiplier tube systems where either standard quench curves or CIEMAT-NIST efficiency tracing routines (CIEMAT/NIST measurements require additional software for data analysis) can be used to determine detection efficiency;

—   triple-to-double coincidence ratio systems (TDCR measurements require additional software for data analysis).

General guidance on liquid scintillation counting is given in ISO 19361[22].

8   Sampling

Sampling, handling and storage of the water samples shall be done as specified in ISO 5667-1 and ISO 5667-3.

The water sample should be acidified with concentrated nitric acid but hydrochloric acid shall be avoided.

9 Liquid scintillation set up and calibration

9.1 Window setting

Both ^{59}Ni and ^{63}Ni measurements require measurements of low energy photon emitters (^{59}Ni) and low energy beta emitters (^{63}Ni) and so two measurement regions need to be set.

This can be carried out using ^{59}Ni and ^{63}Ni sources, neither of which need to be calibrated. However, if ^{59}Ni is not being reported, tritium can be used as a satisfactory substitute.

Table 3 — Counting conditions

Region	Energy range	Comments
A	2 keV to 20 keV	This region captures most of the ^{59}Ni data, with electronic noise being largely excluded by setting the lower energy limit to 2 keV.
B	20 keV to 100 keV	This region captures most of the ^{63}Ni data.

9.2 Background

Measure the background activity using an identical clean liquid scintillation vial containing iron or nickel carrier as appropriate. Repeated counts confirm the stability of the background level.

For method blanks, measure the blank activity using clean water and reagents under conditions representative of the measurement method. Repeated counts confirm the stability of the blank level.

9.3 Calibration

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, $r_{b,A}$ for the low energy region (^{59}Ni) and $r_{b,B}$ for the high energy region (^{63}Ni) which can be replaced by the appropriate background count rate value, $r_{0,A}$ and $r_{0,B}$ if these values are equivalent.

The detection efficiency of ^{59}Ni is determined in region A, $\varepsilon_{59\text{Ni,A}}$ with a standard ^{59}Ni solution of known activity and purity; the detection efficiency in region B is zero for ^{59}Ni. The detection efficiency is determined by dividing the net count rate in region A by the activity of the source $A_{59\text{Ni}}$:

$$\varepsilon_{59\text{Ni,A}} = \frac{\left[r_{s,59\text{Ni,A}} - r_{0,A} \right]}{A_{59\text{Ni}} \cdot m_{s,59\text{Ni}}} \tag{1}$$

The detection efficiency of ^{63}Ni is determined in region A, $\varepsilon_{63\text{Ni,A}}$, with a standard ^{63}Ni solution of known activity and purity. The detection efficiency is determined by dividing the net count rate in region A by the activity of the source, $A_{63\text{Ni}}$, as given in Formula (2):

$$\varepsilon_{63\text{Ni,A}} = \frac{\left[r_{s,63\text{Ni,A}} - r_{0,A} \right]}{A_{63\text{Ni}} \cdot m_{s,63\text{Ni}}} \tag{2}$$

The detection efficiency of ^{63}Ni is determined in region B, $\varepsilon_{63\text{Ni,B}}$, with a standard ^{63}Ni solution of known activity and purity. The detection efficiency is determined by dividing the net count rate in region B by the activity of the source, $A_{63\text{Ni}}$:

$$\varepsilon_{63\text{Ni,B}} = \frac{\left[r_{s,63\text{Ni,B}} - r_{0,\text{B}} \right]}{A_{63\text{Ni}} . m_{s,63\text{Ni}}} \tag{3}$$

In each case, a chemical quench correction curve shall be prepared by adding a suitable chemical quenching agent (e.g. nitromethane) to a series of sources of known activity. Also, a colour quench correction curve shall also be prepared by adding a suitable chemical quenching agent (e.g. tartrazine) to a series of sources of known activity. Each efficiency calibration source should be consistent with respect to:

— approximate activity;

— carrier mass;

— solution volume;

— scintillation fluid volume.

The shape of the quench correction curve cannot be predicted, but takes the general form given in Formula (4):

$$\varepsilon = f\left(Q_p\right) \tag{4}$$

Efficiency tracing routines should be used, if appropriate[12]. Efficiency tracing is a relative or tracing activity measurement method suitable for activity determination of pure beta, beta-gamma, pure EC and EC-gamma decaying radionuclide using a commercial liquid scintillation counter.

NOTE 1   Standard addition techniques can also be used but are outside the scope of this document.

The efficiency tracing requires one to know the experimental detection efficiency of one tracer radionuclide (tritium is usually employed for beta emitters) for different degrees of chemical quench and to compute the detection efficiency at the photocathode output for different values of the free parameter, ν_m, associated with the efficiency model in Formula (5):

$$\varepsilon = \int_0^E S(E).\left(1 - e^{-\nu_\text{m}}\right) d(E) \tag{5}$$

NOTE 2   The derivation of the free parameter, ν_m, is outside the scope of this document. See Reference [14], for an example.

To obtain a universal curve, which allows one to determine the detection efficiency for any radionuclide, a model for the detection efficiency as a function of the free parameter shall be developed for each radionuclide.

Acceptance limits for efficiency should be defined. It is advisable to check the method linearity. The efficiency should be assessed using calibration samples whose activities should cover the whole working range.

Efficiencies should be verified with a periodicity established by the laboratory and whenever changes in materials (e.g. scintillation cocktail) or when maintenance operations are performed on the scintillation counter.

A verification or a recalibration is necessary when requisites of instrument quality control are not met.

10 Procedure

10.1 Preliminary

10.1.1 Stable nickel content

Measure the nickel $(C_{g,Ni})$ concentrations in the sample according to various protocols already described in other International Standards. These protocols include the following:

— ICP-OES according to ISO 11885[18];

— ICP-MS according to ISO 17294-2[20];

— AAS according to ISO 15586[21].

10.1.2 Iron and nickel separation

Take a suitable aliquot of sample (V_g) and add a known mass of calibrated nickel $(C_{g,Ni}$ and $m_{c,Ni})$ carrier (6.6.12). Uncalibrated holdback carriers of antimony, caesium, calcium, cerium, chromium, cobalt, iron, manganese, ruthenium, silver, strontium and zinc can be added, depending on sample composition.

Add the sodium hydroxide solution (6.6.11) to the sample, until the pH of the solution is greater than 10. Warm the solution to coagulate the precipitate.

NOTE 1   Any iron hydroxide [Fe(OH)$_3$] precipitate is visible as a brown precipitate.

Centrifuge the solution at a suitable rate to effectively separate the supernate and precipitate, and reject the supernate. Wash the precipitate with water and recentrifuge; repeat the wash cycle twice.

It is advisable to wash any residual NaOH solution from the precipitate in order to reduce the volume of acid necessary for redissolution.

Re-dissolve the solid in nitric acid (6.6.9), warming it, if necessary. The temperature should not exceed 80 °C. Adjust the acid concentration to between 7 mol l^{-1} to 8 mol l^{-1} with respect to nitric acid in order to maximize the uptake of uranium and thorium.

Pass the solution through a suitable anion exchange resin (AG1-X8) or extraction chromatography resin (TEVA, UTEVA) to remove any actinide elements; at least 2 g of resin should be used. Wash the column with 3 bed volumes of nitric acid (6.6.9).

NOTE 2   This step removes any uranium and thorium from the sample.

Precipitate iron by adding ammonium hydroxide solution (6.6.3) to the solution, until the solution pH > 10, then warm to coagulate the precipitate; the temperature should not exceed 80 °C.

Centrifuge the solution at 2 000 min^{-1}, retain the supernate for ^{63}Ni analysis.

Purify the nickel fraction according to steps A.1.1 to A.1.8 or A.2.1 to A.2.8 as appropriate.

10.2 Liquid scintillation source preparation

Take the solution from step A.1.8 or A.2.8 as appropriate.

Record the solution mass, $m_{Ni,1}$.

Remove (0,5 ± 0,1) g of the solution, $m_{Ni,2}$ and dilute to (50 ± 0,5) g with nitric acid (6.6.10), recording the mass, $m_{Ni,3}$ of this 'Nickel yield solution'.

Weigh $(2,5 \pm 0,2)$ g of the solution into a clean plastic or glass scintillation vial, $m_{\mathrm{Ni},4}$. Add an appropriate scintillation cocktail and count, using the regions set in Clause 9.

A colour quench correction is needed due to the colour of $\mathrm{Ni^{2+}}$.

11 Quality control

Periodically check the measurement performances of the instruments using sources of constant activity, covering the energy range to be measured. This can usually be done with the background, ^{3}H and ^{14}C sealed check sources supplied with the counter. The results of such checks should be plotted on a Shewhart control chart and analysed using ISO 7870-2[17].

12 Expression of results

12.1 Nickel-59 measurements

12.1.1 Nickel recovery

Using the "nickel yield solution" (see 10.2), measure the nickel concentration in the solution used to prepare the counting sources, as in 10.1.1 $C_{\mathrm{y,Ni}}$.

The concentration of stable nickel in the counting solution is as given in Formula (6):

$$\frac{C_{\mathrm{y,Ni}} . m_{\mathrm{Ni},3}}{m_{\mathrm{Ni},2}} \tag{6}$$

Thus, the total amount of nickel recovered is as given in Formula (7):

$$\frac{C_{\mathrm{y,Ni}} . m_{\mathrm{Ni},3}}{m_{\mathrm{Ni},2}} . m_{\mathrm{Ni},1} \tag{7}$$

The total amount of nickel in the sample is as given in Formula (8):

$$C_{\mathrm{g,Ni}} . V_{\mathrm{g}} + C_{\mathrm{c,Ni}} . m_{\mathrm{c,Ni}} \tag{8}$$

Thus, the recovery of nickel, R_{Ni}, is as given in Formula (9):

$$R_{\mathrm{Ni}} = \frac{\left[\frac{C_{\mathrm{y,Ni}} . m_{\mathrm{Ni},3}}{m_{\mathrm{Ni},2}} . m_{\mathrm{Ni},1} \right]}{\left[C_{\mathrm{g,Ni}} . V_{\mathrm{g}} + C_{\mathrm{c,Ni}} . m_{\mathrm{c,Ni}} \right]} \tag{9}$$

12.1.2 Activity calculation

The net count rate of ^{59}Ni in region A is as given in Formula (10):

$$r_{\mathrm{net,A}} = r_{\mathrm{g,A}} - r_{0,A} - \chi . r_{\mathrm{net,B}} \quad \text{with} \quad \chi = \frac{\varepsilon_{63\mathrm{Ni,A}}}{\varepsilon_{63\mathrm{Ni,B}}} = \frac{r_{\mathrm{s,63Ni,A}} - r_{0,A}}{r_{\mathrm{s,63Ni,B}} - r_{0,B}} \tag{10}$$

The activity is calculated with Formula (11) and Formula (12):

$$c_{A,59\mathrm{Ni}} = \frac{r_{\mathrm{net,A}} . m_{\mathrm{Ni},1}}{\varepsilon_{59\mathrm{Ni,A}} . R_{\mathrm{Ni}} . m_{\mathrm{Ni},4} . V_{\mathrm{g}}} = r_{\mathrm{net,A}} . W_{59\mathrm{Ni}} \tag{11}$$

where $w_{59\text{Ni}} = \dfrac{m_{\text{Ni},1}}{\varepsilon_{59\text{Ni,A}} . R_{\text{Ni}} . m_{\text{Ni},4} . V_{\text{g}}}$ (12)

12.2 Nickel-63 measurements

The net count rate of ^{63}Ni in region B is as given in Formula (13):

$$r_{\text{net,B}} = r_{\text{g,B}} - r_{0,\text{B}}$$ (13)

The activity of ^{63}Ni can be calculated as:

$$c_{A,63\text{Ni}} = \frac{r_{\text{net,B}} . m_{\text{Ni},1}}{\varepsilon_{63\text{Ni,B}} . R_{\text{Ni}} . m_{\text{Ni},4} . D_{63\text{Ni}} . V_{\text{g}}} = r_{\text{net,B}} . W_{63\text{Ni}}$$ (14)

where $w_{63\text{Ni}} = \dfrac{m_{\text{Ni},1}}{\varepsilon_{63\text{Ni,A}} \cdot R_{\text{Ni}} \cdot m_{\text{Ni},4} \cdot D_{63\text{Ni}} \cdot V_{\text{g}}}$ (15)

12.3 Uncertainties and characteristic limits

12.3.1 Nickel recovery

The calculation of nickel recovery uncertainty $u_{R_{\text{Ni}}}$ from Formula (9) is given by Formula (16):

$$u_{R_{\text{Ni}}} = R_{\text{Ni}} \cdot \sqrt{\left(\frac{u_{C_{\text{y,Ni}}}}{C_{\text{y,Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{m_{\text{Ni},2}}}{m_{\text{Ni},2}}\right)^2 + \left(\frac{u_{m_{\text{Ni},3}}}{m_{\text{Ni},3}}\right)^2 + \frac{\left[\left(\frac{u_{C_{\text{g,Ni}}}}{C_{\text{g,Ni}}}\right)^2 + \left(\frac{u_{V_{\text{g}}}}{V_{\text{g}}}\right)^2\right] . \left[C_{\text{g,Ni}} . V_{\text{g}}\right]^2 + \left[\left(\frac{u_{c_{\text{,Ni}}}}{c_{\text{,Ni}}}\right)^2 + \left(\frac{u_{m_{\text{c,Ni}}}}{m_{\text{c,Ni}}}\right)^2\right] . \left[C_{\text{,Ni}} . m_{\text{c,Ni}}\right]^2}{\left[C_{\text{g,Ni}} . V_{\text{g}} + C_{\text{,Ni}} . m_{\text{c,Ni}}\right]^2}}$$

(16)

12.3.2 Nickel-59 measurements

12.3.2.1 Nickel-59 detection efficiency

The calculation of ^{59}Ni detection efficiency uncertainty $u_{\varepsilon_{59\text{Ni,A}}}$ from Formula (1) is given by the Formula (17):

$$u_{\varepsilon_{59\text{Ni,A}}} = \varepsilon_{59\text{Ni,A}} \cdot \sqrt{\frac{\left(\frac{r_{\text{s,59Ni,A}}}{t_{\text{s}}} + \frac{r_{0,\text{A}}}{t_0}\right)}{\left(r_{\text{s,59Ni,A}} - r_{0,\text{A}}\right)^2} + \left(\frac{u_{A_{59\text{Ni}}}}{A_{59\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{s,59Ni}}}}{m_{\text{s,59Ni}}}\right)^2}$$ (17)

12.3.2.2 Nickel-59 activity

The calculation of the activity concentration uncertainty $u_{c_{A,59\text{Ni}}}$ from Formula (11) is given by Formula (18):

$$u_{c_{A,59\text{Ni}}} = \sqrt{w_{59\text{Ni}}^2 \cdot \left(u_{r_{\text{g},A}}^2 + u_{r_{0,A}}^2 + T(\chi)\right) + c_{A,59\text{Ni}}^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{59\text{Ni},A}}}{\varepsilon_{59\text{Ni},A}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_{\text{g}}}}{V_{\text{g}}}\right)^2\right]} \tag{18}$$

that can be developed as given in Formula (19), Formula (20) and Formula (21):

$$u_{c_{A,59\text{Ni}}} = \sqrt{w_{59\text{Ni}}^2 \cdot \left(\frac{r_{\text{g},A}}{t_{\text{g}}} + \frac{r_{0,A}}{t_0} + T(\chi)\right) + c_{A,59\text{Ni}}^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{59\text{Ni},A}}}{\varepsilon_{59\text{Ni},A}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_{\text{g}}}}{V_{\text{g}}}\right)^2\right]} \tag{19}$$

where

$$T(\chi) = \left(r_{\text{g},B} - r_{0,B}\right)^2 \cdot u^2(\chi) + \chi^2 \cdot \left(\frac{r_{\text{g},B}}{t_{\text{g}}} + \frac{r_{0,B}}{t_0}\right) \tag{20}$$

and

$$u(\chi) = \sqrt{\frac{\dfrac{r_{\text{s},63\text{Ni},A}}{t_{\text{s}}} + \dfrac{r_{0,A}}{t_0}}{\left(r_{\text{s},63\text{Ni},A} - r_{0,A}\right)^2} + \frac{\dfrac{r_{\text{s},63\text{Ni},B}}{t_{\text{s}}} + \dfrac{r_{0,B}}{t_0}}{\left(r_{\text{s},63\text{Ni},B} - r_{0,B}\right)^2}} \tag{21}$$

For the calculation of the characteristic limits (see ISO 11929-1[19]), $\tilde{u}_{\tilde{c}A,59\text{Ni}}$ is needed, i.e. the combined standard uncertainty of $c_{A,59\text{Ni}}$ as a function of its true value.

For a true value of $\tilde{c}_{A,59\text{Ni}}$, it is expected $r_{\text{g},A}/t_{\text{g}} = \left(\tilde{c}_{A(\text{Ni}-59)}/w_{(\text{Ni}-59)} + \chi\left(r_{g,B} - r_{0,B}\right) + r_{0,A}\right)/t_g$, for the following to be obtained:

$$\tilde{u}_{\tilde{c}_{A,59\text{Ni}}} = \sqrt{w_{59\text{Ni}}^2 \cdot \left[\frac{\dfrac{\tilde{c}_{A,59\text{Ni}}}{w_{59\text{Ni}}} + \chi\left(r_{\text{g},B} - r_{0,B}\right) + r_{0,A}}{t_{\text{g}}} + \frac{r_{0,A}}{t_0} + T(\chi)\right] + \tilde{c}_{A,59\text{Ni}}^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{59\text{Ni},A}}}{\varepsilon_{59\text{Ni},A}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_{\text{g}}}}{V_{\text{g}}}\right)^2\right]} \tag{22}$$

12.3.2.3 Nickel-59 decision threshold and detection limit

The decision threshold, $c_{A,59\text{Ni}}^*$, is obtained from Formula (22) for $\tilde{c}_{A,59\text{Ni}} = 0$ according to ISO 11929-1[19] as given in Formula (23):

$$c_{A,59\text{Ni}}^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w_{59\text{Ni}} \cdot \sqrt{\frac{\chi\left(r_{\text{g},B} - r_{0,B}\right) + r_{0,A}}{t_{\text{g}}} + \frac{r_{0,A}}{t_0} + T(\chi)} \tag{23}$$

where $\alpha = 0{,}05$, and then, $k_{1-\alpha} = 1{,}65$ is often chosen by default.

The detection limit, $c_A^{\#}$, is calculated using the implicit Formula (22) according to ISO 11929-1[19] and ISO 11929-3[19] as given in Formula (24):

$$c_{A,59\text{Ni}}^{\#} = c_{A,59\text{Ni}}^{*} + k_{1-\beta} \cdot \tilde{u}_{c_{A,59\text{Ni}}^{\#}} \tag{24}$$

$$c_{A,59\text{Ni}}^{\#} = c_{A,59\text{Ni}}^{*} + k_{1-\beta} \cdot \sqrt{w_{59\text{Ni}}^2 \cdot \left[\frac{\frac{c_{A,59\text{Ni}}^{\#}}{w_{59\text{Ni}}} + \chi\left(r_{g,B} - r_{0,B}\right) + r_{0,A}}{t_g} + \frac{r_{0,A}}{t_0} + T(\chi) \right] + c_{A,59\text{Ni}}^{\#2} \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}} \right)^2 + \left(\frac{u_{\varepsilon_{59\text{Ni,A}}}}{\varepsilon_{59\text{Ni,A}}} \right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}} \right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}} \right)^2 + \left(\frac{u_{V_g}}{V_g} \right)^2 \right]}$$

(25)

where $\beta = 0{,}05$ and then, $k_{1-\beta} = 1{,}65$ is often chosen by default.

The detection limit can be calculated by solving Formula (25) for $c_{A,59\text{Ni}}^{\#}$ or, more simply, by iteration with a starting approximation $c_{A,59\text{Ni}}^{\#} = 2 \cdot c_{A,59\text{Ni}}^{*}$

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Formula (25) is given by Formula (26):

$$c_{A,59\text{Ni}}^{\#} = \frac{2 \cdot c_{A,59\text{Ni}}^{*} + \frac{\left(k^2 \cdot w_{59\text{Ni}}\right)}{t_g}}{1 - k^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}} \right)^2 + \left(\frac{u_{\varepsilon_{59\text{Ni,A}}}}{\varepsilon_{59\text{Ni,A}}} \right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}} \right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}} \right)^2 + \left(\frac{u_{V_g}}{V_g} \right)^2 \right]} \tag{26}$$

12.3.3 Nickel-63 measurements

12.3.3.1 General

The recovery of nickel is given in 12.3.1.

12.3.3.2 Nickel-63 detection efficiency

The calculation of ^{63}Ni detection efficiency uncertainty $u_{\varepsilon_{63\text{Ni,A}}}$ from Formula (3) is given by the Formula (27):

$$u_{\varepsilon_{63\text{Ni,B}}} = \varepsilon_{63\text{Ni,B}} \cdot \sqrt{\frac{\left[\frac{r_{s,63\text{Ni,B}}}{t_s} + \frac{r_{0,B}}{t_0} \right]}{\left[r_{s,63\text{Ni,B}} - r_{0,B} \right]^2} + \left(\frac{u_{A_{63\text{Ni}}}}{A_{63\text{Ni}}} \right)^2 + \left(\frac{u_{m_{s,63\text{Ni}}}}{m_{s,63\text{Ni}}} \right)^2} \tag{27}$$

12.3.3.3 Nickel-63 activity

The calculation of the activity concentration uncertainty $u_{c_{A,63\text{Ni}}}$ from Formula (14) and Formula (15) is given by the Formula (28):

$$u_{c_{A,63\text{Ni}}} = \sqrt{w_{63\text{Ni}}^2 \cdot \left(u^2\left(r_{g,B}\right) + u^2\left(r_{0,B}\right) \right) + c_{A,63\text{Ni}}^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{63\text{Ni},B}}}{\varepsilon_{63\text{Ni},B}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_g}}{V_g}\right)^2 \right]}$$

(28)

that can be developed as given in Formula (29):

$$u_{c_{A,63\text{Ni}}} = \sqrt{w_{63\text{Ni}}^2 \cdot \left(\frac{r_{g,B}}{t_g} + \frac{r_{0,B}}{t_0} \right) + c_{A,63\text{Ni}}^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{63\text{Ni},A}}}{\varepsilon_{63\text{Ni},A}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_g}}{V_g}\right)^2 \right]}$$

(29)

For the calculation of the characteristic limits (see ISO 11929-1[19]), $\tilde{u}_{\tilde{c}_{A,63\text{Ni}}}$ is needed, i.e. the combined standard uncertainty of $c_{A,63\text{Ni}}$ as a function of its true value. For a true value of $\tilde{c}_{A,63\text{Ni}}$ it is expected

that $\dfrac{r_{g,B}}{t_g} = \dfrac{\left(\dfrac{\tilde{c}_{A,63\text{Ni}}}{w_{63\text{Ni}}} + r_{0,B} \right)}{t_g}$, the following is obtained:

$$\tilde{u}_{\tilde{c}_{A,63\text{Ni}}} = \sqrt{w_{63\text{Ni}}^2 \cdot \left[\frac{\frac{\tilde{c}_{A,63\text{Ni}}}{w_{63\text{Ni}}} + r_{0,B}}{t_g} + \frac{r_{0,B}}{t_0} \right] + \tilde{c}_{A,63\text{Ni}}^2 \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{63\text{Ni},A}}}{\varepsilon_{63\text{Ni},A}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_g}}{V_g}\right)^2 \right]}$$

(30)

12.3.3.4 Nickel-63 decision threshold and detection limit

The decision threshold, $c_{A,63\text{Ni}}^*$, is obtained from Formula (30) for $\tilde{c}_{A,63\text{Ni}} = 0$ according to ISO 11929-1[19] as given in Formula (31) and Formula (32):

$$c_{A,63\text{Ni}}^* = k_{1-\alpha} \cdot \tilde{u}(0) = k_{1-\alpha} \cdot w_{63\text{Ni}} \sqrt{\cdot \left(\frac{r_{0,B}}{t_g} + \frac{r_{0,B}}{t_0} \right)}$$

(31)

where $\alpha = 0,05$ and then, $k_{1-\alpha} = 1,65$ is often chosen by default.

The detection limit, $c_{A,63\text{Ni}}^\#$ is calculated using the implicit Formula (30) according to ISO 11929-1[19]:

$$c_{A,63\text{Ni}}^\# = c_{A,63\text{Ni}}^* + k_{1-\beta} \cdot \tilde{u}_{c_{A,63\text{Ni}}^\#}$$

(32)

$$c_{A,63\text{Ni}}^\# = c_{A,63\text{Ni}}^* + k_{1-\beta} \cdot \sqrt{w_{63\text{Ni}}^2 \cdot \left(\frac{\frac{c_{A,63\text{Ni}}^\#}{w_{63\text{Ni}}} + r_{0,A}}{t_g} + \frac{r_{0,A}}{t_0} \right) + c_{A,63\text{Ni}}^{\#2} \cdot \left[\left(\frac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\frac{u_{\varepsilon_{63\text{Ni},B}}}{\varepsilon_{63\text{Ni},B}}\right)^2 + \left(\frac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\frac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\frac{u_{V_g}}{V_g}\right)^2 \right]}$$

(33)

where $\beta = 0,05$ and then, $k_{1-\beta} = 1,65$ is often chosen by default.

The detection limit can be calculated by solving Formula (33) for $c_{A,63\text{Ni}}^{\#}$ or, more simply, by iteration with a starting approximation $c_{A,63\text{Ni}}^{\#} = 2 \cdot c_{A,63\text{Ni}}^{*}$

When taking $k_{1-\alpha} = k_{1-\beta} = k$, the solution of Formula (33) is given by Formula (34):

$$c_{A,63\text{Ni}}^{\#} = \frac{2 \cdot c_{A,63\text{Ni}}^{*} + \dfrac{\left(k^2 \cdot w_{63\text{Ni}}\right)}{t_\text{g}}}{1 - k^2 \cdot \left[\left(\dfrac{u_{m_{\text{Ni},1}}}{m_{\text{Ni},1}}\right)^2 + \left(\dfrac{u_{\varepsilon_{63\text{Ni,A}}}}{\varepsilon_{63\text{Ni,A}}}\right)^2 + \left(\dfrac{u_{R_{\text{Ni}}}}{R_{\text{Ni}}}\right)^2 + \left(\dfrac{u_{m_{\text{Ni},4}}}{m_{\text{Ni},4}}\right)^2 + \left(\dfrac{u_{V_\text{g}}}{V_\text{g}}\right)^2\right]} \tag{34}$$

12.4 Limits of the coverage interval

12.4.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^{\triangleleft}$ and upper, $c_A^{\triangleright}$ coverage limits are calculated using Formula (35) and Formula (36) according to ISO 11929 series[19]:

$$c_A^{\triangleleft} = c_A - k_p \cdot u_{cA}; \ p = \omega \cdot \left(1 - \frac{\gamma}{2}\right) \tag{35}$$

$$c_A^{\triangleright} = c_A + k_q \cdot u_{cA}; \ q = 1 - \left(\frac{\omega \cdot \gamma}{2}\right) \tag{36}$$

where

- ω equals $\Phi\left[\frac{y}{u_y}\right]$, Φ and is the distribution function of the standardized normal distribution; $\omega = 1$ can be set if $c_A > 4 \cdot u_{cA}$;

- γ is the proportion of data outside the coverage interval of the measurand.

In this case:

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\frac{\gamma}{2}} \cdot u_{cA} \tag{37}$$

Often, a probability of 0,05 is chosen. In this case, $\gamma = 0,05$ and then, $k_{1-\frac{\gamma}{2}} = 1,96$ is often chosen by default.

12.4.2 Shortest coverage interval

As described in detail in ISO 11929 series[19], the lower limit of the shortest coverage interval, $c_A^<$, and the upper limit of the shortest coverage interval, $c_A^>$, are calculated from a primary measurement result, c_A, of the measurand and the standard uncertainty, u_{cA}, associated with c_A, either Formula (38):

$$c_A^<, c_A^> = c_A \pm k_p \cdot u_{cA}; \quad p = \frac{[1 + \omega \cdot (1 - \gamma)]}{2} \tag{38}$$

or if $c_A^< < 0$ were the result, by as given in Formula (39):

$$c_A^< < 0; \quad c_A^> = c_A + k_q \cdot u_{cA}; \quad q = 1 - \omega \cdot \gamma \tag{39}$$

where $\omega = \Phi\left[\dfrac{y}{u_y}\right]$ and Φ is the distribution function of the standardized normal distribution.

When these relations apply, the approximation of Formula (37) is valid.

13 Test report

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

a)   reference to this document (ISO 23655-1:2022);

b)   identification of the sample;

c)   units in which the results are expressed;

d)   the test result;

  1)   when the activity concentration, c_A is compared with the decision threshold (see ISO 11929 series[19]);

  —   if the result is less than the decision threshold, the result of the measurement is expressed as $\leq c_A^*$

  —   if the result is greater than the decision threshold, the result of the measurement is expressed as $c_A \pm u(c_A)$ or $c_A \pm U(c_A)$ with the associated k value,

  2)   when the activity concentration, c_a is compared with the detection limit

  —   if the result is less than the detection limit, the result of the measurement is expressed as $\leq c_A^\#$, or

  —   if the result is greater than the detection limit, the result of the measurement is expressed as a $c_A \pm u(c_A)$ or $c_A \pm U(c_A)$ with the associated k value.

e)   the method used (if the standard includes several);

f)   any deviations from the procedure;

g)   any unusual features observed;

h)   the date of the test.