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Water quality — Nickel-59 and nickel-63 —

Part 2:
Test method using ICP-MS

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

Partie 2: Méthode d'essai par ICP-MS

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Contents

Page

Foreword .... **iv**
Introduction .... **v**
1 Scope **1**
2 Normative references **1**
3 Terms, definitions and symbols **2**
  3.1 Terms and definitions 2
  3.2 Symbols 2
4 Principle **4**
5 Reagents **4**
  5.1 Standard solutions 4
    5.1.1 Nickel-59 and ^{63}Ni standards 4
    5.1.2 Stable nickel standards 5
  5.2 Holdback carrier 5
  5.3 Water 5
  5.4 Specific reagents for chemical separation 5
6 Equipment **6**
  6.1 Laboratory equipment for direct evaporation 6
  6.2 Mass spectrometry vials 6
  6.3 Measurement equipment: Inductively coupled plasma mass spectrometry 6
7 Sampling **6**
8 ICP-MS setup and calibration **6**
  8.1 Background 6
  8.2 Calibration 7
  8.3 Mass bias 7
  8.4 Background signal 7
9 Procedure **8**
  9.1 Preliminary 8
    9.1.1 Stable element interferences content[12] 8
    9.1.2 Iron and nickel separation 8
  9.2 Nickel measurement solution preparation 8
10 Quality control **9**
11 Expression of results **9**
  11.1 Nickel recovery 9
  11.2 Nickel-59 activity calculation 10
  11.3 Nickel-63 activity calculation 10
  11.4 Uncertainties and characteristic limits[14] 10
    11.4.1 Nickel-59 measurements 10
    11.4.2 Nickel-63 measurements 11
12 Test report **11**
Annex A (normative) **Isolation and purification of nickel** **13**
Bibliography **15**

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 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 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 wash off 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 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 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].

NOTE 1 The guideline level (GL) is the activity concentration with an intake of 2 $\mathrm{l{\cdot}d^{-1}}$ of drinking water for one year that results in an effective dose of 0,1 $\mathrm{mSv{\cdot}a^{-1}}$ 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].

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[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 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 the 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 be required 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 2:
Test method using ICP-MS

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 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 the determination of nickel-59 and nickel-63 (^{59}Ni and ^{63}Ni) activity concentration in samples of all types of water using inductively coupled plasma mass spectrometry (ICP-MS).

Using currently available ICP-MS, this test method can measure ^{59}Ni activity concentrations of 300 mBq·l^{-1} and ^{63}Ni activity concentrations of 200 Bq·l^{-1}. These values can be achieved with a sample volume of 1,0 l. Higher activity concentrations can be measured by either diluting the sample or using smaller sample aliquots or both.

NOTE These performance indicators are wholly dependent on the measurement regimes in individual laboratories; in particular, the detection limit is influenced by amount of stable nickel 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 counting 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 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 15586, *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace*

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

ISO 17294-2, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of selected elements including uranium isotopes*

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 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/

3.2 Symbols

The symbols used in this document are explained in Table 1.

Table 1 — Symbols and units

Symbol	Description	Unit
b_{59}	Mass bias for ^{59}Ni (relative to ^{58}Ni)	—
b_{63}	Mass bias for ^{63}Ni (relative to ^{63}Ni)	—
c	Concentration	mol·l^{-1}
$C_{A,59\text{Ni}}$	^{59}Ni activity concentration	Bq·l^{-1}
$C_{A,63\text{Ni}}$	^{63}Ni activity concentration	Bq·l^{-1}
$C_{\text{S},59\text{Ni}}$	^{59}Ni calibration standard solution activity concentration	Bq·g^{-1}
$C_{\text{S},63\text{Ni}}$	^{63}Ni calibration standard solution activity concentration	Bq·g^{-1}
$C_{\text{c,Ni}}$	Mass concentration of stable nickel carrier	g·g^{-1}
$C_{\text{m,Ni}}$	Mass concentration of stable nickel in the measurement solution	g·g^{-1}
$C_{\text{y,Ni}}$	Mass concentration of stable nickel in the yield solution	g·g^{-1}
$C_{\text{g,Ni}}$	Mass concentration of natural nickel in the sample	g·g^{-1}
$\varepsilon_{59\text{Ni}}$	Response of the ICP-MS to ^{59}Ni at $\frac{m}{z}=59$	s^{-1}·g^{-1}
$\varepsilon_{63\text{Ni}}$	Response of the ICP-MS to ^{63}Ni at $\frac{m}{z}=63$	s^{-1}·g^{-1}
I_{58}	Isotopic abundance of ^{58}Ni: 0,680 77 (natural isotopic abundance is assumed)	—
k	Associated coverage factor	—
L_A	Avogadro constant: 6,022 140 76 × 10^{23} atoms per mole (defined as an exact quantity, with zero uncertainty)	mol^{-1}
L_D	Detection limit	—
L_Q	Limit of quantification	—
m	Mass of an ion	—
$m_{\text{a},59\text{Ni}}$	Atomic mass of ^{59}Ni 58,934 346 7	g·mol^{-1}
$m_{\text{a},63\text{Ni}}$	Atomic mass of ^{63}Ni 62,929 669 4	g·mol^{-1}
$m_{\text{c,Ni}}$	Mass of stable nickel carrier used	g

Table 1 *(continued)*

Symbol	Description	Unit
$m_{s,59Ni}$	Mass of ^{59}Ni calibration standard solution used	g
$m_{s,63Ni}$	Mass of ^{63}Ni calibration standard solution used	g
$m_{Ni,1}$	Mass of measurement solution	g
$m_{Ni,2}$	Mass of measurement solution used for nickel yield measurement	g
$m_{Ni,3}$	Mass of nickel yield solution	g
$m_{r,Ni}$	Mass of nickel recovered	g
$m_{t,Ni}$	Total amount of nickel recovered	g
$p_{b,58}$	Blank signal at $\frac{m}{z}=58$	s^{-1}
$p_{b,59}$	Blank signal at $\frac{m}{z}=59$	s^{-1}
$p_{b,63}$	Blank signal at $\frac{m}{z}=63$	s^{-1}
$r_{s,58Ni}$	Gross count rate of the stable nickel solution $\frac{m}{z}=58$	s^{-1}
$r_{s,59Ni}$	Gross count rate of the ^{59}Ni source at $\frac{m}{z}=59$	s^{-1}
$r_{s,63Ni}$	Gross count rate of the ^{63}Ni source at $\frac{m}{z}=63$	s^{-1}
r_{59}	Gross count rate of measurement solution at $\frac{m}{z}=59$	s^{-1}
r_{63}	Gross count rate of measurement solution at $\frac{m}{z}=63$	s^{-1}
$r_{net,59}$	Net count rate of measurement solution at $\frac{m}{z}=59$	s^{-1}
$r_{net,63}$	Net count rate of measurement solution at $\frac{m}{z}=63$	s^{-1}
$r_{net,0,59}$	Net count rate of a blank sample solution at $\frac{m}{z}=59$	s^{-1}
$r_{net,0,63}$	Net count rate of a blank sample solution at $\frac{m}{z}=63$	s^{-1}
R_{Ni}	Recovery of nickel	—
$s_{r0,59}$	Standard deviation of the measurement of a blank $\frac{m}{z}=59$	s^{-1}
$s_{r0,63}$	Standard deviation of the measurement of a blank $\frac{m}{z}=63$	s^{-1}
$s_{r0,59,10}$	Standard deviation of the measurement of 10 test portions of a blank sample at $\frac{m}{z}=59$	s^{-1}
$s_{r0,63,10}$	Standard deviation of the measurement of 10 test portions of a blank sample at $\frac{m}{z}=63$	s^{-1}
$T_{59,Ni}$	Radioactive half-life of ^{59}Ni	s
$T_{63,Ni}$	Radioactive half-life of ^{63}Ni	s
u	Unexpanded uncertainty	—

Table 1 *(continued)*

Symbol	Description	Unit
U	Expanded uncertainty	—
u_{rel}	Relative uncertainty NOTE $u_{\text{rel}}(x) = u(x)/x$.	—
V_g	Sample volume	l
$w_{\text{net},59}$	Net response of an ICP-MS system to a given mass concentration of ^{59}Ni	s^{-1}
$w_{\text{net},63}$	Net response of an ICP-MS system to a given mass concentration of ^{63}Ni	s^{-1}
w_{59}	Overall response of an ICP-MS system to a given mass concentration of ^{59}Ni	s^{-1}
z	Electric charge of an ion	—

4 Principle

Nickel-59 is an anthropogenic radionuclide 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 and a half-life of (76 000 ± 5 000) years[8]. Nickel-59 is generated by neutron capture of ^{58}Ni.

Nickel-63 is an anthropogenic radionuclide that decays to ^{63}Cu by beta particle emission with a maximum beta energy of 67,0 keV and a half-life of (98,7 ± 2,4) years[9]. Nickel-63 is generated by neutron capture of ^{62}Ni.

Freshly irradiated natural nickel can have an ^{59}Ni/^{63}Ni mass ratio of approximately 6,9 and this increases to approximately 7,7 after 20 years, to approximately 9,2 after 50 years and to approximately 14 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 concentrations are measured separately by ICP-MS against suitable calibration standards of ^{59}Ni and ^{63}Ni[10].

For samples with high activity concentration, dilution of the sample is required to avoid resin and mass spectrometer 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 A suitable mineralization step is specified in ISO 18589-2[11].

It is necessary to know the concentration of the 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.

5 Reagents

All reagents shall be of recognized analytical grade.

5.1 Standard solutions

5.1.1 Nickel-59 and ^{63}Ni standards

These should be traceable to national or international measurement standards and can be obtained from a number of commercial suppliers and national measurement institutes.

5.1.2 Stable nickel standards

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

5.2 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.

5.3 Water

Water complying with grade 3 of ISO 3696.

5.4 Specific reagents for chemical separation

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

Dissolve 22,62 g of ammonium citrate in 80 ml of water and dilute to 100 ml with water (5.3).

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

Dissolve 4,52 g of ammonium citrate in 80 ml of water and dilute to 100 ml with water (5.3).

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

Dilute 500 ml of concentrated ammonia solution to 1 l with water (5.3).

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

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

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

Dilute 500 ml of concentrated hydrochloric acid to 1 l with water (5.3).

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

Dilute 83 ml of concentrated hydrochloric acid to 1 l with water (5.3).

5.4.7 Iron chloride solution, c_{FeCl3} = 0,02 mol·l^{-1}

Dissolve 0,54 g of iron(III)chloride hexahydrate in 100 ml 0,01 mol·l^{-1} hydrochloric acid (5.4.6).

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

Use a concentrated nitric acid solution.

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

Dilute 450 ml of concentrated nitric acid to 1 l with water (5.3).

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

Dilute 125 ml of concentrated nitric acid to 1 l with water (5.3).

5.4.11 Sodium hydroxide solution, $c_{\mathrm{NaOH}} = 4\ \mathrm{mol{\cdot}l^{-1}}$

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

WARNING — Eye protection should be worn.

5.4.12 Stable nickel carrier solution

Procure a calibrated solution of (10 ± 1) $\mathrm{g{\cdot}l^{-1}}$ from a suitable supplier; alternatively prepare and calibrate a tracer solution in-house from, for example, $\mathrm{Ni(NO_3)_2{\cdot}6H_2O}$.

6 Equipment

6.1 Laboratory equipment for direct evaporation

Use typical laboratory apparatus to store and prepare the sample as specified in ISO 5667-3, such as a hot plate, an automatic evaporator or any other appropriate apparatus.

6.2 Mass spectrometry vials

The vials shall be plastic.

6.3 Measurement equipment: Inductively coupled plasma mass spectrometry

Both ^{59}Ni and ^{63}Ni can be measured with a commercial ICP-MS.

7 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; hydrochloric acid shall be avoided.

8 ICP-MS setup and calibration

8.1 Background

Measure the background at mass 59 (p_{b59}) and 63 (p_{b63}) by running an instrument blank solution containing 0,5 $\mathrm{mol{\cdot}l^{-1}}$ $\mathrm{HNO_3}$.

Measurements with increasing concentrations of stable Ni and measuring the signal at *m/z* 58 and 59 can be used to determine the $^{58}\mathrm{Ni}^{1}\mathrm{H}$ formation rate and the concentration at which tailing from ^{58}Ni occurs. The NiH/Ni formation should be constant at all concentrations and a steady increase in this ratio is indicative of ^{58}Ni tailing. The concentration at which tailing occurs indicates the maximum stable Ni concentration that can be tolerated in the final sample.

The approach described above can also be applied to *m/z* 62 and 63 to determine the $^{62}\mathrm{Ni}^{1}\mathrm{H}$ formation rate. Tailing from ^{62}Ni is unlikely because of the low isotopic abundance (3,63 %).

Increasing concentrations of Na, Ca and Ti can be measured on the instrument and the background is monitored at mass 59 and 63. An increase in background at *m/z* 59 indicates an interference from $^{43}\mathrm{Ca}^{16}\mathrm{O}$, and an increase in background at *m/z* 63 indicates an interference from $^{23}\mathrm{Na}^{40}\mathrm{Ar}$ and/or $^{47}\mathrm{Ti}^{16}\mathrm{O}$. The concentration at which the background increases indicates the maximum concentration of the interfering element that can be tolerated in the final sample. These interferences can be removed by the chemical separation procedure.

8.2 Calibration

Prepare suitable calibration standards of ^{59}Ni and ^{63}Ni in 0,5 mol·l^{-1} HNO$_3$, and measure the instrument response at $\frac{m}{z}=59$ and $\frac{m}{z}=63$ to generate a calibration plot of activity concentration (Bq·g^{-1}) against instrument response (counts per second). For ^{59}Ni, this calibration plot has the form:

$$r_{s,59\text{Ni}} = w_{\text{net},59} + p_{\text{b},59}$$

where the measured output, $r_{\text{s},59\text{Ni}}$, of the ICP-MS is response of the ICP-MS measurement system, $w_{\text{net},59}$, to ^{59}Ni including some blank signal, $p_{\text{b},59}$.

The net response ($w_{\text{net},59}$) is linked to an activity of ^{59}Ni by an efficiency term that can be derived from the measurement of a standard ^{59}Ni solution:

$$\varepsilon_{59\text{Ni}} = \frac{w_{\text{net},59}}{C_{\text{S},59\text{Ni}} \cdot m_{\text{s},59\text{Ni}}}$$

and for ^{63}Ni:

$$r_{\text{s},63\text{Ni}} = w_{\text{net},63} + p_{\text{b},63}$$

and

$$\varepsilon_{63\text{Ni}} = \frac{w_{\text{net},63}}{C_{\text{S},63\text{Ni}} \cdot m_{s,63\text{Ni}}}$$

NOTE For the same activity concentration of ^{59}Ni and ^{63}Ni, the instrument response is lower for ^{63}Ni because of the shorter half-life.

8.3 Mass bias

The mass bias is a fundamental notion in mass spectrometry and the user shall take it into account during calculations to obtain an accurate result. This is a systematic deviation produced by the instrument between the analyte of interest and the tracer.

The mass bias, b_{59}, for ^{59}Ni (relative to ^{58}Ni), is estimated by measuring with the ICP-MS the count rate obtained for ^{59}Ni ($r_{\text{s},59\text{Ni}} - p_{\text{b},59}$) and for the tracer, ^{58}Ni, ($r_{\text{s},58\text{Ni}} - p_{\text{b},58}$) using a solution containing a known quantity of ^{59}Ni, $m_{\text{s},59\text{Ni}}$ and ^{58}Ni, $m_{\text{c,Ni}}$:

$$b_{59} = \left[\frac{r_{\text{s},59\text{Ni}} - p_{\text{b},59}}{r_{\text{s},58\text{Ni}} - p_{\text{b},58}}\right] \cdot \left[\frac{A_{59\text{Ni}} \cdot m_{\text{a},59\text{Ni}} \cdot T_{59\text{Ni}} \cdot m_{\text{s},59\text{Ni}}}{L_A \cdot \ln 2}\right] \cdot \left[\frac{1}{C_{\text{c,Ni}} \cdot m_{\text{c,Ni}} \cdot I_{58}}\right]$$

The mass bias b_{63}, for ^{63}Ni (relative to ^{58}Ni), is given by Formula (1):

$$b_{63} = \left[\frac{r_{\text{s},63\text{Ni}} - p_{\text{b},63}}{r_{\text{s},58\text{Ni}} - p_{\text{b},58}}\right] \cdot \left[\frac{A_{63\text{Ni}} \cdot m_{\text{a},63\text{Ni}} \cdot T_{63\text{Ni}} \cdot m_{\text{s},63\text{Ni}}}{L_A \cdot \ln 2}\right] \cdot \left[\frac{1}{C_{\text{c,Ni}} \cdot m_{\text{c,Ni}} \cdot I_{58}}\right] \tag{1}$$

8.4 Background signal

In order to calculate the decision threshold and detection limit, the reagent blank uncertainty is required. This is simply derived from a suitable number of repeat measurements at $\frac{m}{z}=59$ leading to $u\left(p_{\text{b},59}\right)$ and at $\frac{m}{z}=63$ leading to $u\left(p_{\text{b},63}\right)$.

9 Procedure

9.1 Preliminary

9.1.1 Stable element interferences content[12]

Stable calcium, cobalt, copper, sodium and titanium can interfere with the measurement of ^{59}Ni and ^{63}Ni as ^{59}Co, $^{43}Ca^{16}O$, ^{63}Cu, $^{47}Ti^{16}O$ and $^{23}Na^{40}Ar$ signals overlap with ^{59}Ni and ^{63}Ni. Therefore, stable calcium, cobalt, copper, sodium and titanium shall be chemically separated.

Measure the nickel $\left(C_{g,Ni}\right)$ concentrations in the sample according to ICP-MS described in ISO 17294-2.

9.1.2 Iron and nickel separation

Take a suitable aliquot of sample $\left(V_g\right)$ and add a known mass of calibrated nickel $\left(C_{c,Ni} \text{ and } m_{c,Ni}\right)$ carrier (5.4.12). Uncalibrated holdback carriers such as antimony, caesium, calcium, cerium, chromium, cobalt, iron, manganese, ruthenium, silver, strontium and zinc can be added depending on sample composition.

The addition of stable nickel carrier results in an increased background for ICP-MS measurement on the ^{59}Ni signal as a result of peak tailing and $^{58}Ni^{1}H$ formation. The amount of nickel added should be large enough to accurately calculate the nickel recovery, but not so large that measurements are compromised.

The addition of stable cobalt carrier is not advised for ICP-MS, as the signal from ^{59}Co overlaps with ^{59}Ni if not completely removed by chemical separation.

Add sodium hydroxide solution (5.4.11) to the sample, until the solution pH is greater than 10. Warm the solution to coagulate the precipitate.

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

Centrifuge the solution at a suitable rate to give effective separation of 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.

Redissolve the solid with nitric acid solution (5.4.9), warming if necessary. The temperature should not exceed 80 °C. Adjust the acid concentration to between 7 $mol \cdot l^{-1}$ to 8 $mol \cdot l^{-1}$ with respect to nitric acid in order to maximize uptake of uranium and thorium.

Purify the nickel fraction according to steps A.1.1 to A.1.7 or A.2.1 to A.2.7 as appropriate.

9.2 Nickel measurement solution preparation

Take the solution from step A.1.8 or A.2.8 as appropriate. Evaporate the separated Ni fraction to near-dryness, and redissolve in 0,5 $mol \cdot l^{-1}$ HNO_3 for ICP-MS measurement. Record the mass of solution added, and transfer the solution to a suitable vial for measurement.

The sample should be redissolved in the lowest possible volume of 0,5 $mol \cdot l^{-1} HNO_3$ to minimize sample dilution.

Record the measurement 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 hydrochloric acid (5.4.6), recording the mass, $m_{Ni,3}$ of this 'Nickel yield solution'.

Prepare each sample consistently with regards to carrier volume.

There should be a suitable rinse protocol in place to prevent cross-contamination between samples, and running of an instrument blank between each unknown sample to monitor this.

Measure the count rates at $\frac{m}{z}=59$ and $\frac{m}{z}=63$ for ^{59}Ni and ^{63}Ni respectively in the sample according to various protocols already described in ISO 17294-2.

The uncertainty in the measurement of each sample shall be recorded.

10 Quality control

Periodically check the measurement performance of the ICP-MS using material containing stable nickel and, if available, ^{59}Ni and ^{63}Ni. The results of such checks should be plotted on a Shewhart control chart and analysed using ISO 7870-2[13].

11 Expression of results

11.1 Nickel recovery

Using the "nickel yield solution" (see 9.2), measure the nickel concentration in the solution used to prepare the measurement sources, as in 9.1.1 $C_{y,\mathrm{Ni}}$.

The concentration of stable nickel in the measurement solution is:

$$C_{m,\mathrm{Ni}} = \frac{C_{y,\mathrm{Ni}} \cdot m_{\mathrm{Ni},3}}{m_{\mathrm{Ni},2}}$$

Thus, the total amount of nickel recovered is:

$$m_{r,\mathrm{Ni}} = \frac{C_{y,\mathrm{Ni}} \cdot m_{\mathrm{Ni},3}}{m_{\mathrm{Ni},2}} \cdot m_{\mathrm{Ni},1}$$

The total amount of nickel in the sample is:

$$m_{t,\mathrm{Ni}} = C_{g,\mathrm{Ni}} \cdot V_g + C_{c,\mathrm{Ni}} \cdot m_{c,\mathrm{Ni}}$$

Thus, the recovery of nickel, R_{Ni}, is:

$$R_{\mathrm{Ni}} = \frac{m_{r,\mathrm{Ni}}}{m_{t,\mathrm{Ni}}} = \frac{\left[\frac{C_{y,\mathrm{Ni}} \cdot m_{\mathrm{Ni},3}}{m_{\mathrm{Ni},2}} \cdot m_{\mathrm{Ni},1}\right]}{\left[C_{g,\mathrm{Ni}} \cdot V_g + C_{c,\mathrm{Ni}} \cdot m_{c,\mathrm{Ni}}\right]}$$

11.2 Nickel-59 activity calculation

Calculate the net count rate at $\frac{m}{z}=59$:

$$r_{\text{net},59} = r_{59} - p_{\text{b},59}$$

The mass concentration can be calculated as:

$$C_{\text{m},59\text{Ni}} = \frac{r_{\text{net},59} \cdot m_{\text{Ni},1}}{\varepsilon_{59\text{Ni}} \cdot R_{\text{Ni}} \cdot b_{59} \cdot V_{\text{g}}}$$

and the activity concentration:

$$C_{A,59\text{Ni}} = \frac{C_{\text{m},59\text{Ni}} \cdot L_A \cdot \ln 2}{m_{\text{a},59\text{Ni}} \cdot T_{59\text{Ni}}} = \left[\frac{r_{\text{net},59} \cdot m_{\text{Ni},1}}{\varepsilon_{59\text{Ni}} \cdot R_{\text{Ni}} \cdot b_{59} \cdot V_{\text{g}}}\right] \cdot \left[\frac{L_A \cdot \ln 2}{m_{\text{a},59\text{Ni}} \cdot T_{59\text{Ni}}}\right]$$

11.3 Nickel-63 activity calculation

Calculate the net count rate at $\frac{m}{z}=63$.

$$r_{\text{net},63} = r_{63} - p_{\text{b},63}$$

The mass concentration can be calculated as:

$$C_{\text{m},63\text{Ni}} = \frac{r_{\text{net},63} \cdot m_{\text{Ni},1}}{\varepsilon_{63\text{Ni}} \cdot R_{\text{Ni}} \cdot b_{63} \cdot V_{\text{g}}}$$

and the activity concentration can be calculated as:

$$C_{A,63\text{Ni}} = \frac{C_{\text{m},63\text{Ni}} \cdot L_A \cdot \ln 2}{m_{\text{a},63\text{Ni}} \cdot T_{63\text{Ni}}} = \left[\frac{r_{\text{net},63} \cdot m_{\text{Ni},1}}{\varepsilon_{63\text{Ni}} \cdot R_{\text{Ni}} \cdot b_{63} \cdot V_{\text{g}}}\right] \cdot \left[\frac{L_A \cdot \ln 2}{m_{\text{a},63\text{Ni}} \cdot T_{63\text{Ni}}}\right]$$

11.4 Uncertainties and characteristic limits[14]

11.4.1 Nickel-59 measurements

11.4.1.1 Nickel-59 uncertainty

The uncertainty in the count rate is:

$$u_{\text{rel}}\left(r_{\text{net},59}\right) = \frac{\sqrt{u^2\left(r_{59}\right) + u^2\left(p_{\text{b},59}\right) + u^2\left(r_{\text{net},0,59}\right)}}{r_{\text{net},59}}$$

Uncertainties are calculated thus:

$$u_{\text{rel}}\left(C_{A,59\text{Ni}}\right) = \sqrt{u_{\text{rel}}^2\left(r_{\text{net},59}\right) + u_{\text{rel}}^2\left(m_{\text{Ni},1}\right) + u_{\text{rel}}^2\left(\varepsilon_{59\text{Ni}}\right) + u_{\text{rel}}^2\left(R_{\text{Ni}}\right) + u_{\text{rel}}^2\left(V_{\text{g}}\right) + u_{\text{rel}}^2\left(b_{59}\right) + \text{u}_{\text{rel}}^2\left(T_{59\text{Ni}}\right)}$$

11.4.1.2 Nickel-59 decision threshold and detection limit

The detection limit (L_{D}) corresponds to the equivalent concentration of three times the standard deviation of the measurement of 10 test portions of a blank sample. The blank sample shall have passed through all steps of the method. The standard deviation of the measured counts per second can be converted to grams per kilograms of sample using Formula (2):

$$L_{\mathrm{D59}}=\left[3\cdot S_{r_{0,59,10}}\right]\cdot\left[\frac{m_{\mathrm{Ni},1}}{\varepsilon_{\mathrm{59Ni}}\cdot R_{\mathrm{Ni}}\cdot b_{59}\cdot V_{\mathrm{g}}}\right]\cdot\left[\frac{L_A\cdot\ln 2}{m_{\mathrm{a,59Ni}}\cdot T_{\mathrm{59Ni}}}\right] \qquad (2)$$

The limit of quantification (L_{Q}) is 10 times the standard deviation of the measurement of 10 test portions of the blank. This can be calculated using Formula (2):

$$L_{\mathrm{Q59}}=\left[10\cdot S_{r_{0,59}}\right]\cdot\left[\frac{m_{\mathrm{Ni},1}}{\varepsilon_{\mathrm{59Ni}}\cdot R_{\mathrm{Ni}}\cdot b_{59}\cdot V_{\mathrm{g}}}\right]\cdot\left[\frac{L_A\cdot\ln 2}{m_{\mathrm{a,59Ni}}\cdot T_{\mathrm{59Ni}}}\right]$$

11.4.2 Nickel-63 measurements

11.4.2.1 Nickel-63 uncertainty

The uncertainty in the count rate is:

$$u_{\mathrm{rel}}\left(r_{\mathrm{net},63}\right)=\frac{\sqrt{u^2\left(r_{63}\right)+u^2\left(p_{\mathrm{b},63}\right)+u^2\left(r_{0,63}\right)}}{r_{\mathrm{net},63}}$$

Uncertainties are calculated thus:

$$u_{\mathrm{rel}}\left(C_{\mathrm{A,63Ni}}\right)=\sqrt{u_{\mathrm{rel}}^2\left(r_{\mathrm{net},63}\right)+u_{\mathrm{rel}}^2\left(m_{\mathrm{Ni},1}\right)+u_{rel}^2\left(\varepsilon_{\mathrm{63Ni}}\right)+u_{\mathrm{rel}}^2\left(R_{\mathrm{Ni}}\right)+u_{\mathrm{rel}}^2\left(V_{\mathrm{g}}\right)+u_{\mathrm{rel}}^2\left(b_{63}\right)+u_{\mathrm{rel}}^2\left(T_{\mathrm{63Ni}}\right)}$$

11.4.2.2 Nickel-63 decision threshold and detection limit

The detection limit (L_{D}) corresponds to the equivalent concentration of three times the standard deviation of the measurement of 10 test portions of a blank sample. The blank sample shall have passed through all steps of the method. The standard deviation of the measured counts per second can be converted to grams per kilograms of the sample using Formula (3):

$$L_{\mathrm{D63}}=3\cdot S_{r_{0,63}}\cdot\left[\frac{m_{\mathrm{Ni},1}}{\varepsilon_{\mathrm{63Ni}}\cdot R_{\mathrm{Ni}}\cdot b_{63}\cdot V_{\mathrm{g}}}\right]\cdot\left[\frac{L_A\cdot\ln 2}{m_{\mathrm{a,63Ni}}\cdot T_{\mathrm{63Ni}}}\right] \qquad (3)$$

The limit of quantification (L_{Q}) is 10 times the standard deviation of the measurement of 10 test portions of the blank. This can be calculated using Formula (4):

$$L_{\mathrm{Q63}}=10\cdot S_{r_{0,63}}\cdot\left[\frac{m_{\mathrm{Ni},1}}{\varepsilon_{\mathrm{63Ni}}\cdot R_{\mathrm{Ni}}\cdot b_{63}\cdot V_{\mathrm{g}}}\right]\cdot\left[\frac{L_A\cdot\ln 2}{m_{\mathrm{a,63Ni}}\cdot T_{\mathrm{63Ni}}}\right] \qquad (4)$$

12 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 23655-2:2022);

b) identification of the sample;

c) units in which the results are expressed;