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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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Foreword

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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 $\text{l}\cdot\text{d}^{-1}$ of drinking water for one year that results in an effective dose of 0,1 $\text{mSv}\cdot\text{a}^{-1}$ 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.

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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}
$C_{A,59\mathrm{Ni}}$	^{59}Ni activity concentration	Bq·l^{-1}
$C_{A,63\mathrm{Ni}}$	^{63}Ni activity concentration	Bq·l^{-1}
$C_{\mathrm{S},59\mathrm{Ni}}$	^{59}Ni calibration standard solution activity concentration	Bq·g^{-1}
$C_{\mathrm{S},63\mathrm{Ni}}$	^{63}Ni calibration standard solution activity concentration	Bq·g^{-1}
$C_{\mathrm{c,Ni}}$	Mass concentration of stable nickel carrier	g·g^{-1}
$C_{\mathrm{m,Ni}}$	Mass concentration of stable nickel in the measurement solution	g·g^{-1}
$C_{\mathrm{y,Ni}}$	Mass concentration of stable nickel in the yield solution	g·g^{-1}
$C_{\mathrm{g,Ni}}$	Mass concentration of natural nickel in the sample	g·g^{-1}
$\varepsilon_{59\mathrm{Ni}}$	Response of the ICP-MS to ^{59}Ni at $\frac{m}{z} = 59$	s^{-1}·g^{-1}
$\varepsilon_{63\mathrm{Ni}}$	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	—
$m_{\mathrm{a},59\mathrm{Ni}}$	Atomic mass of ^{59}Ni 58,934 346 7	g·mol^{-1}
$m_{\mathrm{a},63\mathrm{Ni}}$	Atomic mass of ^{63}Ni 62,929 669 4	g·mol^{-1}
$m_{\mathrm{c,Ni}}$	Mass of stable nickel carrier used	g

Table 1 *(continued)*

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

Table 1 *(continued)*

Symbol	Description	Unit
U	Expanded uncertainty	—
u_{rel}	Relative uncertainty NOTE $u_{\mathrm{rel}}(x) = u(x)/x$.	—
V_{g}	Sample volume	l
$w_{\mathrm{net,59}}$	Net response of an ICP-MS system to a given mass concentration of ^{59}Ni	s^{-1}
$w_{\mathrm{net,63}}$	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, $c_{\mathrm{C6H14N2O7}} = 1\ \mathrm{mol{\cdot}l^{-1}}$

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, $c_{\mathrm{C6H14N2O7}} = 0{,}2\ \mathrm{mol{\cdot}l^{-1}}$

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, $c_{\mathrm{NH4OH}} = 6\ \mathrm{mol{\cdot}l^{-1}}$

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

5.4.4 Dimethylglyoxime solution, 1 %, $c_{\mathrm{C4H8N2O2}} = 0{,}086\ \mathrm{mol{\cdot}l^{-1}}$

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

5.4.5 Hydrochloric acid solution, $c_{\mathrm{HCl}} = 6\ \mathrm{mol{\cdot}l^{-1}}$

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

5.4.6 Hydrochloric acid solution, $c_{\mathrm{HCl}} = 1\ \mathrm{mol{\cdot}l^{-1}}$

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

5.4.7 Iron chloride solution, $c_{\mathrm{FeCl3}} = 0{,}02\ \mathrm{mol{\cdot}l^{-1}}$

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, $c_{\mathrm{HNO3}} = 16\ \mathrm{mol{\cdot}l^{-1}}$

Use a concentrated nitric acid solution.

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

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

5.4.10 Nitric acid solution, $c_{\mathrm{HNO3}} = 2\ \mathrm{mol{\cdot}l^{-1}}$

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