
**Reactor technology — Power reactor
analyses and measurements —
Determination of heavy water isotopic
purity by Fourier transform infrared
spectroscopy**

*Technologie du réacteur — Analyses et mesurages relatifs aux
réacteurs de puissance — Détermination de la pureté isotopique de
l'eau lourde par spectroscopie infrarouge à transformée de Fourier*
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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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Reactor technology — Power reactor analyses and measurements — Determination of heavy water isotopic purity by Fourier transform infrared spectroscopy

1 Scope

This document specifies an analytical method for determining heavy water isotopic purity by Fourier transform infrared spectroscopy (FTIR). It is applicable to the determination of the whole range of heavy water concentration. The method is devoted to process controls at the different steps of the process systems in heavy water reactor power plant or any other related areas.

The method can be applied for heavy water isotopic purity measurements in a heavy water reactor power plant or research reactor, heavy water production factory and heavy water related areas.

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*

3 Terms and definitions

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For the purposes of this document, the following terms and definitions are applied.

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

- ISO Online browsing platform: available at <https://www.iso.org/obp>
- IEC Electropedia: available at <https://www.electropedia.org/>

3.1

heavy water

water which contains a higher than normal proportion of the heavy isotopes of hydrogen in combination with oxygen

Note 1 to entry: HDO exists whenever there is water with hydrogen-1 and deuterium in the mix. HDO is formed when hydrogen and deuterium atoms are rapidly exchanged between light water and heavy water molecules.

Note 2 to entry: Heavy water here does not mean “heavy water” which is enriched in the heavier oxygen isotopes ^{17}O and ^{18}O .

Note 3 to entry: The ice point of heavy water is as high as 3,8 °C, care should be taken to avoid heavy water from freezing.

[SOURCE: ISO 6107:2021, 3.272, modified — Notes 1 to 3 to entry were added.]

3.2

light water

water that contains natural abundance of protium and deuterium

3.3
Fourier transform infrared spectroscopy
FTIR

method in which a sample is subjected to excitation of molecular bonds by pulsed, broad-band infra-red radiation and the Fourier transform mathematical method is used to obtain an absorption spectrum

[SOURCE: ISO/TS 80004-6:2021, 5.8]

3.4
D₂O
molecular formula of deuterium oxide

3.5
heavy water isotopic purity

c_{atom}
percentage of deuterium atoms in the total number of all hydrogen atoms including deuterium, protium and tritium atoms

Note 1 to entry: Expressed as atom%.

3.6
D₂O concentration

c_{mass}
percentage of the mass of D₂O in total water mass, assuming that all of the deuterium exist in the form of D₂O

Note 1 to entry: Expressed as mass fraction.

Note 2 to entry: The mass percentage of D₂O is deduced from heavy water isotopic purity which does not precisely mean the mass percentage of D₂O in water because deuterium exists both in the form of HDO and D₂O.

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3.7
precision

closeness of agreement between independent test results/measurement results obtained under stipulated conditions

[SOURCE: ISO 3534-2:2006, 3.3.4]

4 Principle

HDO, D₂O and H₂O co-exist in heavy water, with [Formula \(1\)](#):



The O-H bond and the O-D bond have each different infrared spectroscopy. Heavy water isotopic purity is proportional to the absorption strength of characteristic region in infrared spectrum within certain range of heavy water concentration.

Almost all protium in high isotopic purity heavy water, like a mass fraction from 98,500 to 100,000 in %, exists in the form of HDO, in which O-H has the biggest absorption at infrared wave number about 3 400 cm⁻¹ (λ is 2,94 μm). The absorption strength of this specified infrared wave number is proportional to protium isotopic purity and proportional inversely to the deuterium isotopic purity in heavy water. Almost all deuterium in low concentration of heavy water, like a mass fraction from 0,05 to 2,00 in %, exists in the form of HDO, in which O-D has the biggest absorption at infrared wave number about 2 500 cm⁻¹ (λ is 4,00 μm). The absorption strength of this specified infrared wave number is proportional to deuterium isotopic purity and proportional to heavy water concentration.

For heavy water concentration in the range of a mass fraction from 2,00 to 98,50 in %, different ranges could be subdivided according to different interested regions of the spectra respectively.

5 Reagents and materials

Use only reagents of recognized analytical grade, unless otherwise specified.

- 5.1 **Demineralised light water**, in accordance with the requirements of grade 1 as defined in ISO 3696.
- 5.2 **High isotopic purity heavy water reference standards**, a series of heavy water standards with precisely characterized D₂O concentration, acquired from a certified laboratory and are free from impurities and organic matters. Their conductivity should be less than 2 µS/cm.
- 5.3 **Acetone or absolute ethyl alcohol**.
- 5.4 **Helium**, with a purity of 99,999 % in volume.
- 5.5 **Dry nitrogen or compressed air**, with a dew point less than -30 °C.

6 Apparatus

The usual laboratory apparatus and, in particular, the following:

- 6.1 **FTIR spectrometer**, with a resolution of 4 cm⁻¹ and a spectral range of 1 000 cm⁻¹ to 6 000 cm⁻¹.
 - 6.2 **Infrared liquid cell**, super-sealed liquid cells with Luer-Lock fittings for syringe filling of the samples and shall have precise and reproducible path length. Two plugs are attached with each cell. Different path lengths of cells like 0,5 mm, 0,3 mm, 0,2 mm, 0,1 mm, 0,05 mm may be prepared for the method.
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- NOTE Liquid cells without temperature control are used in this standard method. A temperature controlled liquid cell can be used for this method if necessary.
- 6.3 **Hypodermic glass syringes**, with Luer-Lock tips, clean and dry, always kept in a desiccator (6.9).
 - 6.4 **Disposable syringes**.
 - 6.5 **Needles**, with slip tips and suitable outer diameter.
 - 6.6 **Polyethylene or Polypropylene bottles**, clean and dry, with tight caps.
 - 6.7 **Fume hood**, with the inlet air flow in the range of (0,3 to 0,6) m/s.
 - 6.8 **Oven**, with a temperature control model; the oven can heat up to 120 °C.
 - 6.9 **Desiccator**.
 - 6.10 **Electrical analytical balance**, which can be read to the nearest 0,1 mg.
 - 6.11 **Syringe filter**, with the pore size of 0,45 µm.
 - 6.12 **Tissue paper**, lint-free tissue paper for cleaning the cell window.

7 Heavy water reference standard preparation

7.1 General requirements

High isotopic purity heavy water reference standards (5.2) should be procured from a certified laboratory. Heavy water reference standards of lower concentration may be prepared by mixing a high isotopic purity heavy water standard and demineralized light water (5.1) in the laboratory according to 7.3.

7.2 Storage of high isotopic purity heavy water reference standard

7.2.1 Ampoule bottle

High isotopic purity heavy water degrades easily. The reference standards shall be enclosed in sealed ampoule bottles and each shall be used only once.

7.2.2 Specially designed stainless steel container

Specially designed stainless steel container is recommended for the storage of high purity heavy water reference standard, which is able to hold a relatively big amount of heavy water and prevent the heavy water from degradation for a long time by covering the heavy water surface with pure helium (5.4). The heavy water in the container can be extracted through a sampling port with rubber diaphragm. See Annex A for reference.

If a container has not been sampled for several weeks, successive samples should be withdrawn and analysed until two consecutive samples deviate within a mass fraction of 0,005 in %.

7.3 Lower D₂O concentration reference standard preparation

The relative humidity should be controlled under 40 %, preferably as low as possible, in the standard preparation area of the laboratory. The bottles, pipettes or any other apparatus which will be used for the standard preparation should be dry and of constant weight before the standard preparation.

Lower D₂O concentration of heavy water reference standards can be prepared in a clean and dry bottle by mixing appropriate volume of a high purity heavy water reference standard with appropriate volume of demineralized light water (5.1). The masses of the heavy water reference standard and the light water need to be accurate to 0,1 mg weighted by the electrical analytical balance (6.10). D₂O concentration of the prepared heavy water reference standard can be referred to Formula (2):

$$c_r = \frac{c_D \times w_D + w_H \times c_H}{w_D + w_H} \quad (2)$$

where

c_r is the target D₂O concentration of the lower reference standard, expressed as mass fraction in %;

c_D is the D₂O concentration of the high purity heavy water reference standard expressed as mass fraction in %;

w_D is the mass of the high purity heavy water reference standard, expressed in grams;

w_H is the mass of the light water (5.1) added, expressed in grams;

c_H is the D₂O concentration of the light water (5.1), expressed as mass fraction in %;

NOTE c_H , the D₂O concentration of light water (5.1) which is approximately a mass fraction of 0,0173 in %, while it varies in different areas around the world. This value can be measured through mass spectrometers by a qualified institute.

The maximum duration is 3 weeks when the lower D₂O concentration heavy water reference standards stored in a polyethylene or polypropylene bottle with a tight cap. The reference standards should be re-prepared once introduction of light water is suspected.

8 Sampling

8.1 General requirements

WARNING — Heavy water is not radioactive. However, heavy water in nuclear power plant may contain a large amount of tritium and other radionuclides. Proper protection measures shall be taken when sampling and analysing heavy water samples in nuclear facilities. All syringes and cell filling of the test should be carried out in a fume hood (6.7).

Heavy water degrades easily when open to atmosphere. It is very important to keep the sample sealed after sampling.

8.2 Sampling with syringes

Hypodermic glass syringes (6.3) with Luer-Lock tips and matched needles (6.5) are widely used for heavy water sampling in industry. Specially designed syringe sampling station is provided in heavy water reactor power plants. The sampling station is a stainless steel pot with the diaphragm of a polychloroprene disc, and the connections are welded to the sample tubing. A small isolation valve is provided on each side of the sample pot for normal isolation and for diaphragm changing. A bypass is provided to permit continuous flow during isolation of the hypodermic pots.

To take a heavy water sample from the station, a flow through the station shall be established. Dry syringe (6.3) and dry needle (6.5) are used to extract the sample through the rubber diaphragm after the flow has been established for more than 2 min.

8.3 Sampling with bottles

Once syringe sampling is not applicable, clean and dry bottles (6.6) should be used for sampling. Immediately tighten the bottle cap after sampling.

9 Preparation of calibration curves of the method

9.1 General

Table 1 gives 5 typical calibration curves of different D₂O concentration ranges of heavy water with different test conditions based on the test of a CaF₂ infrared liquid cell (6.2) with a same path length of 0,2 mm. The spectra with regions of interest of different D₂O concentration ranges are given in Annex B.

Table 1 — Calibration curves for different D₂O concentration range

Curve number	D ₂ O concentration range ^a mass fraction in %	Cell material ^b	Background	Region of interest suggested cm ⁻¹	Baseline suggested ^c cm ⁻¹	Linear coefficient
1	98,500 to 100,000	CaF ₂	Air	3 200 to 3 600	around 3 100	≥99,99 %
2	80,0 to 98,5	CaF ₂	Air	2 850 to 3 050	around 3 850 or 4 500	≥99,9 %
3	20,0 to 80,0	CaF ₂	Air	2 000 to 2 100	around 3 850 or 4 500	≥99 %
4	2,0 to 20,0	CaF ₂	Air	5 050 to 5 300	around 5 500	≥99,9 %
5	0,05 to 2,00	CaF ₂	demineralized light water (5.1)/Air	2 530 to 2 600	around 2 800	≥99,99 %

^a D₂O concentration range can be changed according to the choice of different path lengths of cells.

^b The window material of the cell could be ZnSe for all the curves. SiO₂ could be used for curve 1 only.

^c A baseline shall be specified to draw the curves. For curve 1, 4 and 5 which are plotted by peak area integration, a one-point baseline is suggested, which means a horizontal baseline will be drawn through the specified point of each spectrum where all spectra have a minimum absorbance. A two-point baseline may be selected for curve 1, 4 and 5, in which case the baseline will be drawn through both points. For curve 2 and 3, which are plotted by peak height integration, a fixed x-axis location where all spectra have a minimum absorbance shall be selected for the baseline integration.

Both curve 1 and curve 5 have a linear coefficient above 99,99 % and show good repeatability and reproducibility.

Curve 2, curve 3, and curve 4 for mid-range concentration heavy water (mass fraction from 2,0 to 98,5 in %) measurement do not have as good repeatability as curve 1 or curve 5, although their linear coefficient can reach above 99 %. There are maybe some other acceptable regions of interest that could be used for D₂O concentration analysis of the mid-range concentration heavy water. These 3 curves are suitable for rapid and routine analysis and meet the process control requirements of the heavy water reactor power plant. For more precise results, subdivide the curves into several narrower ranges to get better results or dilute the samples to the range of curve 1 or curve 5 according to the preliminary test results of curve 2, curve 3 and curve 4.

Different optical path length of the infrared cell like 0,5 mm, 0,3 mm, 0,1 mm or less can also be used for the method; in which case the D₂O concentration range of each curve will be changed according to the difference of the absorption strength of the spectra.

EXAMPLE To measure D₂O concentration of the high isotopic purity heavy water more precisely, curve 1 can be further split into 2 curves with one using a 0,3 mm cell (6.2) for higher part of this range (e.g. higher than a mass fraction of 99,200 in %) and one with a 0,1 mm cell (6.2) for lower part of this range (from a mass fraction of 98,100 to 99,200 in %). Curve 5 can be further split into 2 curves in a similar way.

9.2 Preparation of the apparatus

9.2.1 FTIR spectrometer

The temperature of the laboratory should be in the range of 18 °C to 25 °C and maintained at a constant operating room temperature within ±1 °C. For example, the temperature is kept at (22 ± 1) °C.

The non-condensing relative humidity of the laboratory should be in the range of 30 % to 60 %, preferably as low as possible.

Make sure the humidity indication of the instrument is in normal status.

Turn on the instrument and wait for the instrument stabilization according to the instrument instructions.

9.2.2 Infrared liquid cell

The cell should be clean and dry. If the cell is kept filled with heavy water sample, make sure to rinse the cell thoroughly with the next sample.

Once the cell is contaminated with oil or any other solvents, use acetone or absolute ethyl alcohol (5.3) to clean the cell (6.2) in the fume hood (6.7), and flush the cell with demineralised light water (5.1). Then purge with dry nitrogen or compressed air (5.5) and keep it dry.

9.3 Editing of the method

According to Table 1, edit the parameters of the curves through the instrument software.

Choose the integration region and the baseline point in the suggested baseline region according to Table 1. Integrate the interested region by area for curve 1, curve 4 and curve 5 and integrate by height for curve 2 and curve 3. Normally 16 scan times are set for one spectrum.

NOTE Integration by area has the priority for the test method. If the interested region is only the absorbance strength of a characteristic wavelength, integrate the height of the characteristic wavelength with a selected baseline point in the suggested area which is recommended in Table 1.

9.4 Background spectrum

Scan air or demineralised light water (5.1) for background spectrum according to Table 1.

9.5 Heavy water reference standard spectra

Make sure the temperature of the heavy water reference standards reach the constant operating room temperature.

Extract heavy water reference standard using clean and dry syringe (6.3). Inject the reference standard into the infrared liquid cell (6.2) in an amount at least 5 times that of the cell volume to make sure that the cell is thoroughly rinsed, and insert the cell outlet with a plug and remove the syringe (6.3), then insert another plug into the cell inlet. Make sure there are no air bubbles or suspended dirt in the cell and the outside of the cell window is free of lint.

Place the cell (6.2) in the sample chamber of the Fourier transform infrared spectrometer (6.1). Scan the reference standard immediately after it has been put into the instrument chamber and get the spectrum. Repeat the above steps and get all the spectra of the reference standards.

Each curve should have 5 or more spectra.

9.6 Draw the calibration curves for different D₂O concentration ranges

Choose the spectra of the standards, draw the curves respectively.

The linear coefficient of the curves shall meet the requirements in Table 1.