
**Crude petroleum — Determination of
water — Coulometric Karl Fischer titration
method**

*Pétrole brut — Dosage de l'eau — Méthode de Karl Fischer par titrage
coulométrique*

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X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 10337 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 6, *Bulk cargo transfer, accountability, inspection and reconciliation*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

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Crude petroleum — Determination of water — Coulometric Karl Fischer titration method

WARNING – The use of this International Standard may involve hazardous materials, operations, and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a coulometric Karl Fischer titration method for the direct determination of water in crude petroleum. It covers the range 0,050 % (m/m) to 5,00 % (m/m) water in crude petroleum containing less than 0,05 % (m/m) but more than 0,005 % (m/m) of either mercaptan sulfur or sulfide ion sulfur or both. It covers the range 0,020 % (m/m) to 5,00 % (m/m) water in crude petroleum containing less than 0,005 % (m/m) of either mercaptan sulfur or sulfide ion sulfur or both.

NOTE 1 A number of substances and classes of compounds associated with condensation or oxidation-reduction reactions interfere in the determination of water by Karl Fischer titration. However, the only likely interfering substances present in crude petroleum are mercaptans and ionic sulfides and providing that they are present at levels less than 0,05 % (m/m), the interference is insignificant when determining water in the range 0,050 % (m/m) to 5,00 % (m/m).

NOTE 2 An alternative procedure is provided in annex B for the direct determination of water over the range 0,05 % (V/V) to 5,00 % (V/V) in crude petroleum containing less than 0,05 % (V/V) of either mercaptan sulfur or ionic sulfide sulfur or both. The limitations under which this alternative volume measurement may be used are listed in annex B. The volume measurement may also be used to determine water in the range 0,02 % (V/V) to 5,00 % (V/V) if the above interfering substances are present at levels of less than 0,005 % (V/V) as either mercaptan sulfur or ionic sulfide sulfur or both.

NOTE 3 For the purposes of this International Standard, the terms "% (m/m)" and "% (V/V)" are used to represent the mass and volume fractions respectively.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 3170:1988, *Petroleum liquids – Manual sampling*.

ISO 3171:1988, *Petroleum liquids – Automatic pipeline sampling*.

ISO 3696:1987, *Water for analytical laboratory use – Specification and test methods*.

ISO 3733:1976, *Petroleum products and bituminous materials – Determination of water – Distillation method*.

ISO 3734:1997, *Petroleum products – Determination of water and sediment in residual fuel oils – Centrifuge method*.

3 Principle

After homogenizing the crude oil with a mixer, a weighed portion is injected into the titration vessel of a coulometric Karl Fischer apparatus in which iodine for the Karl Fischer reaction is generated coulometrically at the anode. When all the water has been titrated, excess iodine is detected by an electrometric end point detector and the titration is terminated. Based on the stoichiometry of the reaction, one mole of iodine reacts with one mole of water. Thus the quantity of water is proportional to the total integrated current according to Faraday's Law.

4 Reagents

4.1 Xylene, reagent grade.

4.2 Karl Fischer reagents

Use commercially available reagents that meet the performance requirements described in 7.3.

4.2.1 Anode electrolyte solution (anolyte)

Mix 6 parts by volume of commercial Karl Fischer anode solution with 4 parts by volume of reagent grade xylene. Other proportions of Karl Fischer anode solution and xylene may be used providing they meet the performance criteria of 7.3.

4.2.2 Cathode electrolyte solution (catholyte)

Use commercially available Karl Fischer cathode solution.

4.3 Water, conforming to grade 3 of ISO 3696.

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5 Apparatus

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5.1 Automatic coulometric Karl Fischer titrator

NOTE — There are presently available a number of commercial instruments. Instructions for operating these devices are provided by the manufacturers and are not described herein.

5.2 Non-aerating mixer, capable of meeting the homogenization efficiency requirements given in annex A.

NOTE — Both insertion mixers and circulating external mixers, such as those used with automatic crude petroleum sampling systems, are acceptable providing they comply with the principles of annex A.

5.3 Syringes

Add test portions to the titration vessel by means of glass syringes with Luer fittings and hypodermic needles of suitable length such that the tip can reach under the surface of the anolyte when inserted through the inlet port septum. The bores of the needles used shall be kept as small as possible, but large enough to avoid problems arising from back pressure or blocking whilst sampling.

NOTE 1 Needles with bores between 0,5 mm and 0,8 mm have been found suitable.

NOTE 2 Recommended syringe sizes are:

- 10 μ l with fixed needle for periodic addition of water to check the titrator performance;
- 250 μ l and 1 ml for crude petroleum samples.

5.4 Balance, capable of weighing to $\pm 0,1$ mg.

5.5 Thermometer, capable of measuring the sample temperature to the nearest 1 °C.

6 Sampling and sample preparation

6.1 General

Sampling is defined as all the steps necessary to obtain a representative sample of the contents of any pipe, tank or other system and to place the sample into the laboratory test container.

6.2 Laboratory sample

Only representative samples obtained as specified in ISO 3170 or ISO 3171 shall be used for this International Standard.

6.3 Preparation of the laboratory sample

The following sample handling procedure shall apply in addition to 6.2.

6.3.1 Record the temperature of the sample in degrees Celsius immediately before mixing.

6.3.2 Mix the laboratory sample immediately before analysis to ensure complete homogeneity. Mix the laboratory sample in the original container with the mixing time, mixing power (speed) and mixer position relative to the bottom of the container found to be satisfactory for the crude petroleum being analyzed as established by the procedure given in clause A.3.3. The volume and water content of the crude petroleum shall not exceed the maxima validated in clause A.3.3.

6.3.3 Record the temperature of the laboratory sample in degrees Celsius immediately after mixing. The rise in temperature between this reading and the reading in 6.3.1 shall not exceed 10 °C otherwise loss of water may occur or the emulsion may be destabilized.

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7 Procedure

7.1 Preparation of the apparatus

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7.1.1 Follow the manufacturer's directions for preparation and operation of the titration apparatus.

7.1.2 Add the analyte to the outer compartment of the titration cell to the level recommended by the manufacturer.

7.1.3 Add the catholyte to the inner compartment of the titration cell to a level 2 mm to 3 mm below the level of the analyte.

7.1.4 Seal all joints and connections to the titration cell to prevent atmospheric moisture from entering.

7.1.5 Turn on the titrator and stirrer. Allow the residual moisture in the titration cell to be titrated until the end point is reached. Do not proceed beyond this stage until the background current (or background titration rate) is constant and less than the maximum recommended by the manufacturer of the instrument.

NOTE — High background current for a prolonged period may be attributable to moisture on the inside walls of the titration cell. Gentle shaking of the cell (or more vigorous stirring action) will wash the inside with electrolyte. Also check all fittings to ensure atmospheric moisture does not enter the cell. It is recommended that the titrator be permanently switched on to stabilize to a low background current.

7.2 Test portion

Mix the sample as specified in 6.3.1 to 6.3.3.

7.2.1 Immediately after mixing use a clean, dry syringe of suitable capacity (see table 1 and the note following table 1) to withdraw at least 3 portions of the laboratory sample and discard to waste. Immediately withdraw a test portion of sample, clean the needle with a paper tissue and weigh the syringe and contents to the nearest 0,1 mg. Insert the needle through the inlet port septum, start the titration and, with the tip of the needle just below the liquid surface, inject the entire test portion. Withdraw the syringe, wipe the needle with a clean tissue and reweigh the syringe, to the nearest 0,1 mg. After the end point is reached, record the water titrated from the display on the titrator.

Table 1 — Test portion size based on expected water content

Expected water content % (m/m)	Test portion size g	Water titrated µg
0,02 to 0,1	1	200 to 1 000
0,10 to 0,5	0,5	500 to 2 500
0,50 to 5	0,25	1 250 to 12 500

NOTE — If the concentration of water in the laboratory sample is completely unknown it is advisable to start with a small trial test portion to avoid excessive titration time and depletion of the reagents. Further adjustment of the portion size may be made as necessary.

7.2.2 When the background current or titration rate returns to a stable reading as outlined in 7.1.5 an additional test portion shall be taken to give a duplicate determination. Duplicates shall be taken and injected within the period for which the sample is known to be homogeneous and stable as determined in clause A.3.3 Duplicates shall agree to within the repeatability limit of 10.1.1.

7.3 Check test

The water titrated is a direct function of the coulombs of electricity consumed. However, reagent performance deteriorates with use and shall be regularly monitored by accurately injecting 10 µl of water. Suggested intervals are initially with fresh reagents and then after every 10 test portion injections. Replace the anolyte and catholyte solutions whenever one of the following occurs:

- the result from a 10 µl injection of water is outside 10 000 µg ± 200 µg;
- persistently high or unstable background current;
- phase separation in the outer compartment or crude oil coating the electrodes;
- the total crude oil content of the titration cell exceeds one third of the volume of the anolyte;
- the titrator displays error messages which suggest replacement of the electrolytes (see manufacturer's instructions).

Thoroughly clean the anode and cathode compartments with xylene if the vessel becomes contaminated with crude oil. Never use acetone or other ketones. Blocking of the frit separating the vessel compartments will also cause instrument malfunction.

8 Calculation

Calculate the water content, w , as a percentage (mass/mass) by:

$$w = \frac{m_2}{10^6 \times m_1} \times 100$$

$$= \frac{m_2}{10^4 \times m_1}$$

where

- w is the water content in percentage (mass/mass);
- m_1 is the mass of the test portion in grams;
- m_2 is the mass of water displayed by the titrator in micrograms.

If the result is additionally required in terms of percentage (volume/volume), calculate using the following equation:

$$w_V = w_m \times \rho$$

where

w_V is the water content in percentage (volume/volume);

w_m is the water content in percentage (mass/mass);

ρ is the density of the sample of crude petroleum in kilograms per cubic meter at 15 °C.

9 Expression of results

If the water content is less than 1,00 % (m/m), report the water content of the sample as a percentage (mass/mass) to the nearest 0,001 % (m/m).

If the water content is between 1,00 % (m/m) and 5,00 % (m/m) report the water content of the sample as a percentage (mass/mass) to the nearest 0,01 % (m/m).

10 Precision

10.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

10.1.1 Repeatability, r

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions would, in the long run, in the normal and correct operation of the test method, exceed the following values in one case in twenty:

$$r = 0,040X^{2/3}$$

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where X is the mean of the results being compared in the range from 0,020 % (m/m) to 5,00 % (m/m).

10.1.2 Reproducibility, R

The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty:

$$R = 0,105X^{2/3}$$

where X is the mean of the results being compared in the range from 0,020 % (m/m) to 5,00 % (m/m).

NOTE — See table 2 for examples.

11 Test report

The test report shall contain at least the following information:

- a) a reference to this International Standard;
- b) the type and complete identification of the product tested;
- c) the result of the test (see clause 9);
- d) the mixer type, mixer speed, mixing time and mixing position relative to the bottom of the container;
- e) the temperature of the sample before and after mixing;
- f) any deviation, by agreement or otherwise, from the procedure specified;
- g) the date of the test.