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

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

Reference number
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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.

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.

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.

5 Apparatus

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:
a) 10 µl with fixed needle for periodic addition of water to check the titrator performance;
b) 250 µl and 1 ml for crude petroleum samples.

5.4 Balance, capable of weighing to ±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.

7 Procedure

7.1 Preparation of the apparatus

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

7.1.2 Add the anolyte 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 anolyte.

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:

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

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

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:

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

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.

Table 2 — Precision Intervals

Water content %(*m*/*m*)	**Repeatability** *r*	**Reproducibility** *R*
0,020	0,003	0,008
0,050	0,005	0,014
0,100	0,009	0,023
0,300	0,018	0,047
0,500	0,025	0,066
0,700	0,032	0,083
1,00	0,04	0,11
1,50	0,05	0,14
2,00	0,06	0,17
2,50	0,07	0,19
3,00	0,08	0,22
3,50	0,09	0,24
4,00	0,10	0,26
4,50	0,11	0,29
5,00	0,12	0,31

Annex A
(normative)

Sample handling

A.1 General

A.1.1 The methods of handling samples between the point at which they are extracted or drawn, and the laboratory test bench or sample storage are devised to ensure that the nature and integrity of the sample be maintained.

A.1.2 The method of handling a sample will depend on the purpose for which it has been taken. The laboratory analytical procedure to be used will often require a special handling procedure to be associated with it. For this reason, consult the appropriate methods of test so that any necessary instructions as to sample handling can be given to the person drawing the sample. If the analytical procedures to be applied have conflicting requirements, then draw separate samples and apply the appropriate procedure to each sample.

A.1.3 Take particular care in respect of the following:

a) liquids containing volatile material, since loss by evaporation can occur;

b) liquids containing water and/or sediment, since separation tends to occur in the sample container;

c) liquids with potential wax deposition, since deposition can occur if a sufficient temperature is not maintained.

A.1.4 When making up composite samples, take great care not to lose light ends from volatile liquids and not to alter water and sediment content. This is a very difficult operation and shall be avoided if at all possible.

A.1.5 Do not transfer samples of volatile liquids to other containers at the sampling location but transport them to the laboratory in the original sample container, cooled and inverted, if necessary. Great care is necessary if a sample contains both volatile components and free water.

A.2 Homogenization of samples

A.2.1 Introduction

Procedures are specified for the homogenization of samples that may contain water and sediment, or are in any other way non-uniform, before transfer from the sample container to smaller containers or into laboratory test apparatus. Procedures for verifying that the sample is satisfactorily mixed before transfer are given in clause A.3.

It is not possible to agitate manually samples of liquids containing water and sediment enough to disperse the water and sediment within the sample. Vigorous mechanical or hydraulic mixing is necessary in order to homogenize the sample prior to transfer or sub-sampling.

Homogenization may be accomplished by various methods. Whichever method is used, it is recommended that the homogenizing system produces water droplets below 50 µm, but not less than 1 µm. Water droplets below 1 µm will give a stable emulsion and the water content cannot then be determined by centrifuge methods.

A.2.2 Homogenization by high-shear non-aerating mechanical mixer

Insert a high-shear mechanical mixer into the sample container so that the tip of the shaft reaches to within 30 mm of the bottom. A mixer operating at 15 000 min^{-1} is usually suitable. Other designs may be used if the performance is satisfactory.

In order to minimize loss of light ends from crude petroleum or other samples containing volatile compounds, operate the stirrer through a gland in the closure of the sample container. A mixing time of 3 min is sometimes sufficient to ensure that the sample is completely homogenized, but the size of the container and the type of crude petroleum affect the homogenization time. Verify that the sample has become homogeneous (see A.3).

NOTE — High shear mixers frequently produce stable emulsions such that water contents after mixing cannot be determined by centrifuge methods.

Avoid any rise in temperature greater than 10 °C during mixing.

A.2.3 Circulation with non-aerating circulating mixing system

Circulate by means of a small pump the contents of either permanently sited or portable containers through a static mixer installed externally in small bore piping. For portable containers, use a quick-disconnect coupling. Follow the manufacturer’s instructions for the operation of the specific pump design and capacity chosen.

Use a circulating flow rate sufficient to circulate the contents at least once per minute.

NOTE — A typical mixing time is 15 min, but this will vary according to the water content, the type of hydrocarbon and the design of the system.

When the whole sample is thoroughly mixed, run off the required quantity of sub-sample from a valve in the circulating line, whilst the pump is running. Then empty the container and thoroughly clean the entire system by pumping solvent round until all traces of the hydrocarbon have been removed.

A.3 Verification of mixing time

A.3.1 If the sample remains homogeneous and stable after mixing (e.g. where completely miscible components such as lubricant additives have been blended), continue the mixing procedure until sucessive samples drawn from the main bulk of the sample give identical results. This establishes the minimum mixing time.

NOTE — As the sample is homogeneous after this time, and will remain so, transfers from the main bulk can be made without further mixing.

A.3.2 If the sample does not remain homogeneous for more than a short period of time after mixing (e.g. if water and sediment are part of the mixture) use the special method for the verification of mixing time described in A.3.3.

NOTE — It may be necessary, owing to the characteristics of the crude petroleum, to sub-sample whilst mixing is still in progress.

A.3.3 Ensure the sample as drawn fills the pre-weighed container to approximately three quarters full, and homogenize the sample. Record the mixing time, mixer speed and the mixer position relative to the bottom of the container. After mixing take duplicate test portions and determine their water content immediately by a standard method (see A.3.4). If the test results give good agreement, within the repeatability of the method, record the mean value obtained as the blank water content. If the test results do not give a good agreement repeat this procedure with a longer mixing time or faster mixing speed.

Reweigh the sample container and calculate the mass of crude petroleum. Add an accurately measured quantity of water to raise the water content to approximately 2 %(*m/m*). Homogenize using the same mixing time, mixer speed and position relative to the bottom of the container as was used for the blank. After mixing take duplicate test portions and determine their water content immediately by the standard method. If there is good agreement, within the repeatability of the method, between the water contents determined and the total quantity of water known to be present (added water plus that found in the blank) then record the mixing conditions as adequate. The time between the end of mixing and taking the second test portion is the period for which the sample is known to be homogeneous and stable.

If the results do not show good agreement within the repeatability of the method, then discard them. Revert to the beginning of A.3.3 and use a longer period of mixing and/or faster mixing speed.

A.3.4 Do not determine water content by the centrifuge method (ISO 3734) or by the distillation method (ISO 3733) for this verification of the mixing system, as these methods do not determine total water content.

A.4 Transfer of samples

A.4.1 If the sample container is not portable, or if it is inconvenient to take samples directly from the container into laboratory test apparatus, transfer a representative sample into a portable container for transport to the laboratory.

A.4.2 At every stage of transfer of a sample, it is essential to homogenize the contents of the container from which the sample is being taken using one of the methods specified in clause A.2.

A.4.3 Verify the mixing time for each combination of container and mixer by one of the methods specified in clause A.3.

A.4.4 Complete any transfer of sample within the period during which the mixture is known to be homogeneous and stable. This period is short; do not take longer than 20 min to complete any transfer.

Annex B
(informative)

Alternative test method using volumetric measurement of test portion size

B.1 General

This alternative test method covers the determination of water in crude petroleum as described in this International Standard with the exception that a volumetric measure is used for the test portion of the crude petroleum injected into the titration vessel. The limitations under which this alternative may be used are as follows:

— the prior agreement of both parties has been obtained;

— the vapor pressure and viscosity of the crude petroleum permit an accurate determination of the volume of the test portion.

B.2 Principle

The principle is identical to that described in clause 3 except that the test portion is measured by volume rather than by mass. The procedures described in this International Standard are followed except as described below.

B.3 Additional interferences

The presence of gas bubbles in the syringe can be a source of interference leading to low results. The tendency of the crude petroleum to form gas bubbles is a function of crude petroleum type, condition, and corresponding vapor pressure.

Viscous crude petroleums may prove to be difficult to measure with a precision syringe.

B.4 Apparatus

Syringes, 250 µl, 500 µl and 1 ml capacities, accurate to the nearest 2 µl, 2 µl and 0,01 ml (10 µl) respectively.

B.5 Procedure

Add a test portion of the crude petroleum to the titration cell immediately after the mixing steps, described in 6.3.1 to 6.3.3, using the following method.

Using a clean, dry syringe of suitable capacity (see table B.1 and note following table B.1) 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 record the volume in the syringe to the nearest 2 µl or 10 µl as appropriate (see clause B.4). 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 sample. After the end point is reached, record the water titrated from the readout displayed on the instrument.

Table B.1 — Test portion size based on expected water content

Expected water content %(*V*/*V*)	**Test portion** ml	**Water titrated** µg
0,02 - 0,1	1	200 - 1 000
0,1 - 0,5	0,5	500 - 2 500
0,5 - 5	0,25	1 250 - 12 500