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

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

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 10336 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.

Crude petroleum — Determination of water — Potentiometric 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 potentiometric Karl Fischer titration method for the direct determination of water in crude petroleum. It covers the range 0,05 % (*m/m*) to 2,00 % *(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 0,02 % *(m/m)* to 2,00 % *(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. At levels less than 0,05 % *(m/m)* as sulfur the interference is insignificant when determining water in the range 0,05 % *(m/m)* to 2,00 % *(m/m)*.

NOTE 2 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 petroleum with a mixer, a weighed test portion is injected into the titration vessel of a volumetric Karl Fischer apparatus containing a mixed solvent. The water present is titrated to a potentiometric end point using Karl Fischer reagent.

4 Reagents

4.1 Karl Fischer reagents

Use commercially available reagents that meet the performance requirements described below.

4.1.1 Pyridine-containing Karl Fischer reagent, nominal water equivalence 5 milligrams of water per millilitre of reagent (5 mg/ml). This shall be based on either methanol or ethylene glycol monomethyl ether. The Karl Fischer reagent shall have a minimum water equivalence of 3 mg/ml when standardized as described in 7.2. The solvent specified in 4.6.1 shall be used with this reagent.

4.1.2 Pyridine-free Karl Fischer reagent, containing iodine, sulfur dioxide and an odourless amine. Nominal water equivalence of 5 mg/ml. This shall be used either undiluted or diluted by adding three parts of the pyridine-free Karl Fischer reagent to one part of xylene. In both cases the Karl Fischer reagent shall have a minimum water equivalence of 3 mg/ml when standardized as described in 7.2. The solvent specified in 4.6.2 shall be used with this reagent.

4.2 Xylene, reagent grade.

4.3 Methanol, specially dried for Karl Fischer analysis, containing less than 0,05 % (*m/m*) water.

4.4 *N*-ethyl piperidine, reagent grade.

4.5 Solvent for pyridine-free Karl Fischer titrations

Use commercially available solvent containing sulfur dioxide and an odourless amine dissolved in methanol.

4.6 Titration solvents

Use 4.6.1 with pyridine-containing Karl Fischer reagent and 4.6.2 with pyridine-free Karl Fischer reagent.

4.6.1 Titration solvent for pyridine-containing Karl Fischer reagent

Mix 40 ml of *N*-ethyl piperidine, 20 ml of methanol and 40 ml of Karl Fischer reagent (4.1.1) in a sealable glass vessel. Seal the vessel and allow to stand overnight before adding 200 ml of xylene.

NOTE — Additional methanol may be required in some cases to ensure a single-phase solution.

4.6.2 Titration solvent for pyridine-free Karl Fischer reagent

Mix one part xylene with one part pyridine-free solvent (4.5) and store in a sealed glass vessel. An alternative solvent is three parts chloroform to one part pyridine-free solvent.

WARNING – Chloroform should be handled as a carcinogenic substance.

4.7 Water, conforming to grade 3 of ISO 3696.

5 Apparatus

5.1 Karl Fischer titrator, using a potentiometric end point.

NOTE — There are presently available on the market commercial Karl Fischer titrators, some of which automatically stop the titration at the end point. Instructions for operation of these devices are provided by the manufacturer and are not described herein.

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

5.3 Syringes

Test portions are most easily added 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 titration solvent when inserted through the inlet port. 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 addition of water during the standardization procedure (7.2);
b) 500 µl, 1 ml, 2 ml and 5 ml for crude petroleum samples.

5.4 Balance, capable of weighing to ± 0,1 mg.

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

6 Sampling and sample preparation (see annex A)

6.1 General

Sampling is defined as all 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 tested using 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 laboratory 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

Set up the apparatus in accordance with the manufacturer’s instructions.

7.2 Standardization of the Karl Fischer reagent

7.2.1 The Karl Fischer reagent shall be standardized daily before use. The same standardization procedure is followed for the pyridine-containing titrant/solvent system and the pyridine-free titrant/solvent system.

7.2.2 Add enough of the appropriate titration solvent, either pyridine-containing or pyridine-free, to the clean, dry titration vessel to cover the electrodes. The volume of the solvent depends on the size of the titration vessel. Seal all openings to the vessel, start the magnetic stirrer and adjust for smooth stirring action. Turn on the indication circuit and add Karl Fischer titrant from the burette until the end point is reached. Swirl the titration vessel to dry the inside walls of the titration vessel. Add more Karl Fischer reagent if needed until a steady end point is reached and maintained for at least 30 s. Repeat these swirling and titration steps until the vessel walls are dry.

7.2.3 Fill a 10 µl syringe with water (4.7) taking care to eliminate air bubbles. Wipe the needle with a tissue to remove any residual water from its surface. Add the contents of the syringe to the titration solvent in the vessel which has been adjusted to the end point, ensuring that the tip of the needle is below the surface of the titration solvent. Reseal the vessel immediately. Titrate the water with Karl Fischer reagent until a steady end point is reached and maintained for at least 30 s. After adding water do not shake the vessel. Record to the nearest 0,01 ml the volume of titrant needed to reach the end point.

7.2.4 Calculate the water equivalence of the Karl Fischer reagent as follows:

$$F = \frac{V}{T}$$

where

F is the water equivalence of the Karl Fischer reagent in milligrams per millilitre;

V is the volume of water added in microlitres (assuming that 1 µl of water weighs 1 mg);

T is the titre in millilitres.

7.2.5 Repeat the above procedure from 7.2.3 to give a duplicate value. Duplicate values of water equivalence shall agree to within 2 % relative. If the variation between the two titrations is greater than this, discard the contents of the titration vessel. Introduce a further portion of appropriate titration solvent into the vessel and repeat the standardization procedure from 7.2.2. If the titrations for two further portions of water still vary by more than 2 % relative, it is likely that either the Karl Fischer reagent and/or the titration solvent have aged. Replace these with fresh reagents and repeat the procedure from 7.2.2.

7.2.6 Determine and record the mean water equivalence value.

7.3 Test portion

Mix the laboratory sample exactly as specified in 6.3.1 to 6.3.3.

7.3.1 Add fresh sample solvent, pyridine-containing or pyridine-free as appropriate, to the titration vessel and titrate the solvent to the end point condition as described in 7.2.2.

7.3.2 Dry a suitable syringe (see table 1) by drawing the titration solvent up into the syringe and discharging back into the vessel. If the vessel contents become wet, add Karl Fischer reagent until the end point state is maintained for at least 30 s without further addition of titrant. Repeat this drying procedure until no further addition of Karl Fischer reagent is necessary to maintain the end point state for at least 30 s. (Alternatively, oven-dried syringes cooled in a desiccator may be used.)

Table 1 — Test portion size based on expected water content

Expected water content % (*m*/*m*)	**Burette volume** ml	**Volume of titration solvent** ml	**Portion size** g
0,02 to 0,3	5	< 20	2
	5, 10 or 20	> 20	5
0,3 to 1	5	< 20	1
	5, 10 or 20	> 20	2
1 to 2	5	< 20	0,5
	5, 10 or 20	> 20	1

7.3.3 Immediately after mixing use the dry syringe to withdraw at least 3 portions of the sample and discard to waste.

7.3.4 Immediately withdraw a test portion of the sample, clean the needle with a paper tissue and weigh the syringe and contents to the nearest 0,1 mg. Insert the syringe into the titration vessel such that the needle is below the surface of the titration solvent and discharge its contents. Withdraw the syringe, reseal the vessel, wipe the needle with a clean tissue, reweigh the syringe to the nearest 0,1 mg and record the mass of the test portion taken.

7.3.5 Titrate to the end point state which shall be stable for at least 30 s. Do not shake the cell after addition of the sample. Record the titre to the nearest 0,01 ml.

7.3.6 Repeat the above procedure from 7.3.4 to give a duplicate determination. Duplicates shall be drawn and injected within the period for which the sample is known to be homogeneous and stable as determined in A.3.3. Duplicates shall agree to within the repeatability limit of 10.1.1.

NOTE — The solvent should be changed when the test portion content exceeds 2 g of crude petroleum per 15 ml of solvent or when 4 ml of titrant per 15 ml of solvent has been added to the titration vessel.

8 Calculation

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

$$w = \frac{F \times T}{10 \times m}$$

where

F is the water equivalence of the Karl Fischer reagent in milligrams per millilitre;

T is the test portion titre in millilitres;

m is the mass of the test portion in grams.

If the result is additionally required in terms of percentage (volume/volume), calculate it 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 metre at 15 °C.

9 Expression of results

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 only in one case in twenty:

Pyridine-containing Karl Fischer reagent, $r = 0{,}034X^{1/3}$

Pyridine-free Karl Fischer reagent, $r = 0{,}032X^{1/3}$

where X is the mean of the results being compared in the range from 0,02 *% (m/m)* to 2,00 *% (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:

Pyridine-containing Karl Fischer reagent, $R = 0{,}111X^{1/3}$

Pyridine-free Karl Fischer reagent, $R = 0{,}095X^{1/3}$

where X is the mean of the results being compared in the range from 0,02 *% (m/m)* to 2,00 *% (m/m).*

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 mixer position relative to the bottom of the sample 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.

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 small 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.