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Petroleum products — Determination of water — Potentiometric Karl Fischer titration method

Produits pétroliers — Dosage de l'eau — Méthode de titrage Karl Fischer par potentiométrie

Reference number
ISO 6296:2000(E)

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Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 6296 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 a normative part of this International Standard.

INTERNATIONAL STANDARD **ISO 6296:2000(E)**

Petroleum products — 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 method for the direct determination of water in petroleum products boiling below 390 °C. It covers the mass fraction range 0,003 % (*m/m*) to 0,100 % (*m/m*).

This International Standard may be applicable to petroleum products boiling above 390 °C and lubricating base oils. However, the precision has not been established for these materials.

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. In petroleum products, the most common interferences are hydrogen sulfide and mercaptan sulfur, however, concentrations of these below 0,003 % *(m/m)* as sulfur will not cause significant interference over the range 0,003 % *(m/m)* to 0,100 % *(m/m)* water. Other organic sulfur compounds commonly present such as sulfides, disulfides and thiophenes, do not interfere.

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 of a material respectively.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC 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*.

3 Principle

A sample is visually inspected (see 6.2.1). If clear and bright, and free from both water droplets and particulate matter on swirling, a weighed portion is injected into the titration vessel of a potentiometric Karl Fischer apparatus containing a mixed solvent. The water present is titrated to a potentiometric end-point using Karl Fischer reagent. If the sample is not clear and bright, or water droplets or particulate matter are observed on swirling, a portion of a solution of sodium dioctylsulfosuccinate is added prior to homogenizing with a mixer. A weighed portion is then treated as above.

4 Reagents and materials

4.1 Molecular sieve pellets, type 4A.

Activate in an oven at 200 °C to 250 °C for 4 h. Transfer immediately to a dry, sealable bottle or desiccator and allow to cool.

4.2 Xylene, reagent grade.

Dry by adding approximately 100 g of activated molecular sieve pellets (4.1) to 2 litres of xylene. Allow to stand overnight.

4.3 Karl Fischer reagents

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

4.3.1 Pyridine-containing Karl Fischer reagent, with a nominal water equivalence of 5 mg of water/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 tested as described in 7.1. The solvent specified in 4.8.1 shall be used with this reagent.

4.3.2 Pyridine-free Karl Fischer reagent, containing iodine, sulfur dioxide and an odourless amine, and with a nominal water equivalence of 5 mg/ml. The Karl Fischer reagent shall have a minimum water equivalence of 3 mg/ml when tested as described in 7.1. The solvent specified in 4.8.2. shall be used with this reagent.

4.3.3 Karl Fischer reagent specially formulated for ketones, of nominal water equivalence 5 mg/ml. This Karl Fischer reagent shall have a minimum water equivalence of 3 mg/ml when tested as described in 7.1. The solvent specified in 4.8.3 shall be used with this reagent.

4.4 Sodium dioctylsulfosuccinate, reagent grade.

NOTE 1 Sodium dioctylsulfosuccinate is also sold under the names dioctyl ester of sodium sulfosuccinic acid and dioctyl sulfosuccinate sodium salt.

NOTE 2 Other anionic surfactants may be used in place of sodium dioctylsulfosuccinate, provided they meet the requirements of annex A.

4.4.1 Sodium dioctylsulfosuccinate solution

Dry sodium dioctylsulfosuccinate (4.4) in an oven at 105 °C to 110 °C for 4 h. Transfer immediately to a dry sealable bottle or desiccator, and allow to cool. Once cool, dissolve 10 g of the dried sodium dioctylsulfosuccinate in dry xylene (4.2) and make up to 100 ml with dry xylene. The mass fraction of water in this solution shall be less than 0,010 % (*m/m*) when checked by the procedure given in 7.2.

4.5 Water, conforming to grade 3 of ISO 3696.

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

4.7 *N*-ethyl piperidine, reagent grade.

4.8 Titration solvent

Use the solvent specified in 4.8.1 with pyridine-containing Karl Fischer reagent (4.3.1), the solvent specified in 4.8.2 with pyridine-free Karl Fischer reagent (4.3.2), and the solvent specified in 4.8.3 with the Karl Fischer reagent specially formulated for ketones (4.3.3).

4.8.1 Titration solvent for pyridine-containing Karl Fischer reagent

Mix 40 ml of *N*-ethyl piperidine (4.7), 20 ml of methanol (4.6) and 40 ml of pyridine-containing Karl Fischer reagent (4.3.1), in a sealable glass vessel. Allow this mixture to stand overnight before adding 200 ml of dry xylene (4.2). Add additional methanol, if required, to ensure a single-phase solution.

4.8.2 Titration solvent for pyridine-free Karl Fischer reagent

Mix one part by volume of commercially available pyridine-free solvent, containing sulfur dioxide and an odourless amine in methanol, with one part by volume of dry xylene (4.2). Store in a sealable glass vessel.

4.8.3 Titration solvent for Karl Fischer reagent specially formulated for ketones

Mix four parts by volume of solvent for Karl Fischer titrations of ketones with four parts by volume of dry xylene (4.2) and two parts by volume of *N*-ethyl piperidine (4.7). Store in a sealable glass vessel.

5 Apparatus

5.1 Karl Fischer titrator, using potentiometric end-point.

NOTE Karl Fischer titrators are commercially available and some of them automatically stop the titration at the end-point. Instructions for operation of these devices are provided by the manufacturer and are not described here.

5.2 Non-aerating mixer, capable of meeting the homogenization requirements given in clause A.3.

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

5.3 Syringes, of glass, with 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 a fixed needle for periodic checking of the titrator performance,

b) 5 ml for petroleum product samples, and

c) 10 ml for addition of the sodium dioctylsulfosuccinate solution to petroleum product samples which are not clear and bright, or which contain free water or particulate matter.

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

5.5 Volumetric flask, of 100 ml capacity.

5.6 Sealable bottles or desiccators, to hold activated molecular sieve and dried sodium dioctylsulfosuccinate.

5.7 Ovens, capable of maintaining temperatures of 105 °C to 110 °C and 200 °C to 250 °C.

5.8 Cooling bath, if required, capable of meeting the requirements of 6.2.8.

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

6 Sampling and sample preparation (see annex A)

6.1 Sampling

Samples shall be drawn in accordance with ISO 3170, ISO 3171, or an equivalent National Standard.

If sampling is carried out manually, use a clear borosilicate glass bottle. If an automatic technique is employed, either collect a separate sample for water determination, or treat the whole sample collected in accordance with 6.2.4.

6.2 Sample preparation

6.2.1 If the sample is not in a container suitable for visual inspection, or is opaque, then it should be treated as if it were not clear and bright (see 6.2.4). It should not be transferred to another container.

6.2.2 Immediately prior to analysis, shake the sample vigorously by hand for 30 s and then, when free from bubbles, visually inspect it. Hold the sample up to the light and examine it for haze or lack of clarity and then swirl the sample to produce a vortex and examine both the bottom of the vortex and the bottom of the sample container for water droplets and particulate matter. Record the visual clarity as clear and bright or not clear and bright. Record whether water droplets or particulate matter were, or were not, observed on swirling.

6.2.3 If the sample is both clear and bright, free from water droplets and particulate matter, proceed in accordance with 7.2.

6.2.4 If the sample is not clear and bright, or if water droplets or particulate matter were observed on swirling, proceed in accordance with 6.2.5 to 6.2.8.

NOTE The precision of this method for samples which are not clear and bright is critically dependent upon the effectiveness of the homogenization stage which is proved periodically, see normative annex A.

6.2.5 Use a clean, dry 10 ml syringe (5.3) to add a volume of sodium dioctylsulfosuccinate solution (4.4.1) as established by the procedure specified in annex A.

NOTE Correction of the sample water content for the water content of the sodium dioctylsulfosuccinate solution is not required because the latter is negligible.

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

6.2.7 To ensure homogeneity, mix the sample in the original container immediately prior to analysis. The mixing time, mixing power (speed) and mixer position relative to the bottom of the container, shall be that found to be satisfactory for the material and sample size as established by the procedure given in clause A.3. The sample volume and water content of the sample shall not exceed the maxima validated in clause A.3.

6.2.8 Record the temperature of the laboratory sample in degrees Celsius immediately after mixing. The rise in temperature between this reading and the reading in 6.2.6 shall not exceed 2 °C, otherwise loss of sample light ends or loss of water may occur. If this criterion cannot be met, the sample shall be placed in a cooling bath (5.8) prior to carrying out the procedure in 6.2.6.

7 Procedure

7.1 Standardization of the Karl Fischer reagent

7.1.1 The Karl Fischer reagent shall be standardized daily before use. Follow the same standardization procedure for the pyridine-containing titrant/solvent system, the pyridine-free titrant/solvent system and the titrant/solvent system specially formulated for ketones.

7.1.2 Add enough of the appropriate titration solvent (4.8), either pyridine-containing, pyridine-free or specially formulated for ketones, to the clean, dry titration vessel (5.1) to cover the electrodes. 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 its inside walls. Add more Karl Fischer reagent if needed until a steady end-point is reached and maintained for at least 15 s. Repeat these swirling and titration steps until the vessel walls are dry.

7.1.3 Fill a 10 µl syringe (5.3) with water, 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 its 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 15 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.

7.1.4 Calculate the water equivalence of the Karl Fischer reagent using the following equation:

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

where

F is the water equivalence of the Karl Fischer reagent, expressed in milligrams per millilitre (mg/ml);

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

T is the titre, expressed in millilitres (ml).

7.1.5 Repeat the procedure specified in 7.1.3 and 7.1.4 to give a duplicate value. If the variation between the two titrations is greater than 2 % relative, discard the contents of the titration vessel. Introduce a further portion of appropriate titration solvent into the vessel and repeat the standardization procedure starting from 7.1.2. 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 starting from 7.1.2.

7.1.6 Determine and record the mean water equivalence value.

7.2 Test portion

7.2.1 Mix the laboratory sample as specified in clause 6.

7.2.2 Add fresh titration solvent, either pyridine-containing, pyridine-free or specially formulated for ketones, as appropriate, to the titration vessel and titrate the solvent to the end-point condition as described in 7.1.2. Although all three titrant/solvent combinations can be used for most samples, use only the combination specially formulated for ketones for oxygenated gasolines.

7.2.3 Dry a 5 ml syringe (5.3) 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 is maintained for at least 15 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 15 s (alternatively, oven-dried syringes, cooled in a desiccator, may be used).

7.2.4 Immediately after mixing, use the dry syringe to withdraw at least three portions of the sample and discard as waste.

7.2.5 Immediately withdraw a 4 ml to 5 ml 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 to the nearest 0,1 mg and record the mass of the test portion taken.

7.2.6 Titrate to the end-point state which shall be stable for at least 15 s. Do not shake the cell after addition of the sample. Record the titre to the nearest 0,01 ml.

The solvent should be changed when the test portion content exceeds 2 g of sample 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 mass fraction of water, w, expressed as a percentage, using the following equation:

$$w = \frac{FT}{10\,m}$$

where

F is the water equivalence of the Karl Fischer reagent, expressed in milligrams per millilitre (mg/ml);

T is the sample titre, expressed in millilitres (ml);

m is the mass of test portion used, expressed in grams (g).

NOTE If the result is additionally required in terms of percentage by volume, it can be calculated using the following equation:

$$\varphi = \frac{w \times p}{1000}$$

where

φ is the volume fraction of water, expressed as a percentage;

w is the mass fraction of water, expressed as a percentage;

ρ is the density of the sample, expressed in kilograms per cubic metre (kg/m^3) at 15 °C.

9 Expression of results

Report the mass fraction of water in the sample to the nearest 0,001 %.

10 Precision

10.1 Repeatability, r

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the long run, in the normal and correct operation of the test method, exceed the following value in only one case in twenty.

r = 0,001 7

10.2 Reproducibility, R

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

R = 0,007 7

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) whether the sample was, or was not, clear and bright, and whether water droplets or particulate matter were observed on swirling.

d) if the sample was not clear and bright, or if water droplets or particulate matter were observed on swirling:

- the type, concentration and quantity of emulsifier used (see clause 6);
- the type of mixer, mixing time, mixing speed and the approximate position of the mixer relative to the bottom of the sample container;
- the temperature of the sample before and after mixing;

e) the result of the test (see clause 9);

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 are 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 test methods 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 should 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.1.6 Manual samples of light and middle distillates shall be taken in clear borosilicate glass containers.

A.2 Homogenization of samples

A.2.1 Introduction

Samples which are clear and bright and which contain no water droplets or particulate matter on swirling do not require mixing.

Procedures are specified for the homogenization of samples that are not clear and bright, or which contain water droplets or particulate matter on swirling, 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 manually agitate samples of petroleum products containing free water and sediment enough to disperse the water and sediment within the sample. Addition of a portion of a suitable emulsifier solution followed by vigorous mechanical or hydraulic mixing is necessary in order to homogenize the sample prior to transfer or sub-sampling.

A.2.2 Homogenization by a high-shear non-aerating insertion mixer

Add a portion of a suitable emulsifier solution as determined in clause A.3. Insert the mixer into the sample container so that the tip of the shaft reaches to within the distance of the bottom verified in clause A.3. Mix the sample using the mixing time and speed verified in clause A.3.

In order to minimize loss of light ends from samples containing volatile compounds, it is preferable to operate the mixer through a gland in the closure of the sample container. Avoid a rise in temperature during mixing that exceeds 2 °C. To meet this requirement, it may be necessary to hold the sample container in a cooling bath during the mixing operation.

Thoroughly wash the shaft of the mixer with solvent, and dry it between test runs with different samples.

A.2.3 Homogenization by non-aerating circulating mixing system

Add a portion of a suitable emulsifier solution as determined in clause A.3 and 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. Follow the manufacturer's instructions for the operation of the specific pump design and capacity chosen.

Use the circulating flow rate, mixing time and position of suction and discharge ports as verified in clause A.3. When the whole sample is thoroughly mixed, run off the required quantity of subsample 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. Dry the system by blowing dry compressed air or nitrogen through it to remove all traces of the cleaning solvent.

A.3 Verification of mixing conditions

A.3.1 Whatever means are chosen for obtaining a subsample from a non-homogeneous mixture, verify the suitability of the mixing technique and the time required to obtain a suitably mixed sample.

A.3.2 Fill a preweighed sample container to 80 % capacity with a sample of the petroleum product under test, which is clear and bright and free from water droplets and particulate matter on swirling. Determine the blank mass fraction of water in accordance with the procedure given in 7.2. Calculate the mean blank mass fraction of water.

NOTE It will not be necessary to mix this sample prior to determination of the mass fraction of water.

A.3.3 Reweigh the sample container to the nearest 0,1 g to determine the mass of sample within it. Record the temperature of the sample to the nearest 1 °C. Add sufficient water to increase the mass fraction of water to 0,100 %. Record the mass of this water to the nearest 0,1 mg.

A.3.4 Add a portion of a suitable emulsifier solution from a 10 ml syringe. If the product under test is gasoline, kerosine or gas oil, the addition of 1 ml of sodium dioctylsulfosuccinate solution in xylene (4.4.1) per 100 ml of sample, is often sufficient. However, if the product under test is naphtha, the addition of 2 ml of sodium dioctylsulfosuccinate solution in xylene (4.4.1) per 100 ml of sample, is often required.

A.3.5 Mix the sample. For a high-shear mixer, record the mixing speed, mixing time and approximate distance between the tip of the shaft and the bottom of the container; 15 000 r/min, 60 s and 20 mm respectively, are often suitable. For a circulating mixer, record the circulation time and rate and the approximate position of suction and discharge ports. A time of 15 min with a flow rate that circulates the entire contents at least once per minute and the suction port as near the bottom of the container as possible, are often suitable.

A.3.6 After mixing, withdraw two portions of the sample and test them in accordance with the procedure specified in 7.2. The time after mixing that the second portion is injected into the titration cell defines the verified maximum period of stability. 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), record the mixing conditions as adequate.

If the results do not show good agreement, within the repeatability of the method, then discard them. Revert to the beginning of this procedure, and use more severe mixing conditions.

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