INTERNATIONAL
STANDARD

ISO
3734

Second edition
1997-08-01

Petroleum products — Determination of water and sediment in residual fuel oils — Centrifuge method

Produits pétroliers — Détermination de la teneur en eau et en sédiments dans les fuel-oils résiduels — Méthode par centrifugation

Reference number
ISO 3734:1997(E)

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 3734 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 6, *Bulk cargo transfer, accountability, inspection and reconciliation.*

This second edition cancels and replaces the first edition (ISO 3734:1976), which has been technically revised.

Annexes A and B form an integral part of this International Standard.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central
Printed in Switzerland

Petroleum products — Determination of water and sediment in residual fuel oils — Centrifuge method

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address any 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 laboratory determination of the sum of water and sediment in residual fuel oils using the centrifuge method. With some oils it is difficult to obtain water or sediment contents using this method. When this situation is encountered, ISO 3733 and ISO 3735 should be used.

NOTE — It has been observed that centrifugal methods of determination of water and sediment may, in many cases, give erroneous results. This is especially so when use of a high-speed mixer has been employed to obtain a representative sample. The method is therefore not entirely satisfactory and the amount of water determined is almost always lower than the actual water content.

Significant quantities of water and sediment can cause operational problems in handling equipment and in engines and burners, particularly when the water present contains mineral salts. Design of residual fuel oil treatment facilities, such as filters or centrifuges, is based on a maximum quantity of material to be removed before combustion. Residual fuel oils destined for further refinery processing also require low levels of water and sediment to minimize corrosion problems.

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 3733:—[1], *Petroleum products and bituminous materials — Determination of water — Distillation method.*

---

[1] To be published. (Revision of ISO 3733:1976)

ISO 3735:—[2], *Crude petroleum and fuel oils — Determination of sediment — Extraction method.*

ISO 4787:1984, *Laboratory glassware — Volumetric glassware — Methods for use and testing of capacity.*

ISO 5272:1979, *Toluene for industrial use — Specifications.*

ISO 12937:—[3], *Petroleum products — Determination of water — Coulometric Karl Fischer method.*

3 Principle

Equal volumes of fuel oil and water-saturated toluene are placed in a cone-shaped centrifuge tube. After centrifuging, the volume of the higher-density water and sediment layer at the bottom of the tube is read.

4 Reagents and materials

4.1 Toluene, conforming with the requirements for grade 1 toluene as specified in ISO 5272.

The solvent shall be water-saturated at the test temperature, 50 °C ± 1 °C or 60 °C ± 1 °C, as appropriate, but shall be free of suspended water (see annex B for the solvent/water saturation procedure).

4.2 Demulsifier, to promote the separation of water from the test portion and to prevent its clinging to the walls of the centrifuge tube. The type of demulsifier, and the concentration and quantity used, shall be agreed between the parties. The recommended stock solution is 25 % (*V/V*) demulsifier to 75 % (*V/V*) toluene. For some fuel oils a different ratio of demulsifier may be required.

Demulsifiers used in the concentration and quantity recommended will not add to the water and sediment volume determined. Store the solution in a tightly-stoppered brown glass bottle.

NOTE — For the purposes of this International Standard, the expression % (*V/V*) is used to represent volume fractions.

5 Apparatus

5.1 Centrifuge

The centrifuge shall be capable of spinning two or more filled, cone-shaped 200 mm centrifuge tubes (5.2) at a speed that can be controlled to give a relative centrifugal force (rcf) of between 500 and 850 at the tip of the tubes.

---

[2] To be published. (Revision of ISO 3735:1975)

[3] To be published.

The revolving head, trunnion rings and trunnion cups, including the cushions, shall be soundly constructed to withstand the maximum centrifugal force capable of being delivered by the power source. The trunnion cups and cushions shall firmly support the tubes when the centrifuge is in motion. The centrifuge shall be enclosed by a metal shield or case strong enough to eliminate danger if any breakage occurs. The centrifuge shall be controlled thermostatically to avoid unsafe conditions. It shall be capable of maintaining the sample temperature during the entire run at 50 °C ± 3 °C.

The speed of the rotating head in revolutions per minute (r/min) is calculated as follows:

$$\mathrm{r/min} = 1\,335\sqrt{\mathrm{rcf}/d}$$

where

rcf is the relative centrifugal force;

d is the diameter of swing measured between the tips of opposite tubes when in the rotating position, in millimetres.

5.2 Centrifuge tubes

Each centrifuge tube shall be a cone-shaped tube, nominally 200 mm in height, with a maximum height of 203 mm, conforming to the dimensions given in figure 1 and made of thoroughly annealed glass with a straight sides taper. The graduations, numbered as shown in figure 1, shall be clear and distinct, and the mouth shall be constricted in shape for closure with a cork. Scale-error tolerances and the smallest graduations between various calibration marks are given in table 1 and apply to calibrations made with air-free water at 20 °C when reading the bottom of the shaded meniscus. The accuracy of the graduations on the centrifuge tube shall be volumetrically verified, in accordance with ISO 4787, before use of the tube.

The verification shall include calibration at each mark up through the 0,5 ml mark and at the 1,0 ml, 1,5 ml, 2,0 ml, 50,0 ml and 100 ml marks. The tube shall not be used if the scale error at any mark exceeds the applicable tolerance from table 1.

Table 1 — Centrifuge tube calibration tolerances for 200 mm tube

Range ml	Subdivision ml	Volume tolerance ml
0 to 0,1	0,05	±0,02
Above 0,1 to 0,3	0,05	±0,03
Above 0,3 to 0,5	0,05	±0,05
Above 0,5 to 1,0	0,10	±0,05
Above 1,0 to 2,0	0,10	±0,10
Above 2,0 to 3,0	0,20	±0,10
Above 3,0 to 5,0	0,50	±0,20
Above 5,0 to 10	1,00	±0,50
Above 10 to 25	5,00	±1,00
Above 25 to 100	25,00	±1,00

Dimensions in millimetres

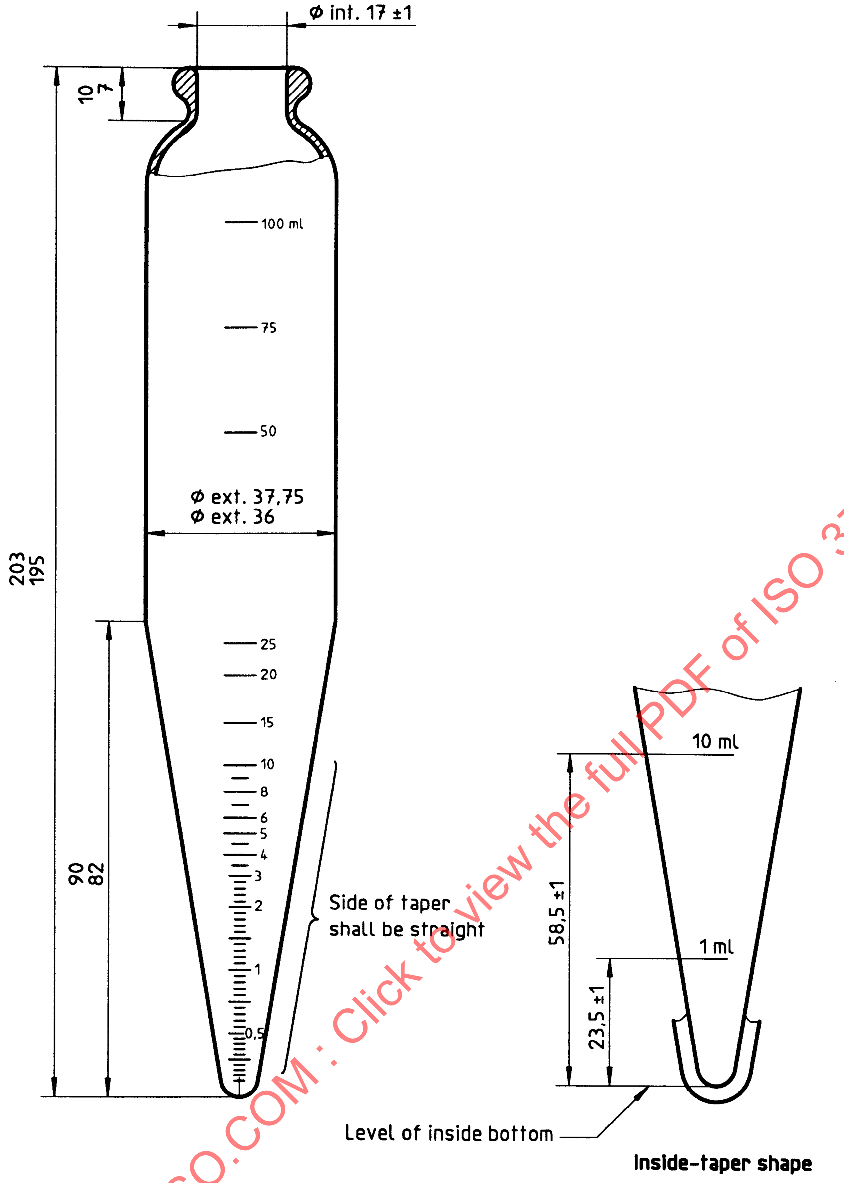

Figure 1 — 200 mm centrifuge tube

5.3 Heating bath

The bath shall be either a solid metal block bath or a liquid bath of sufficient depth for immersing the centrifuge tube in the vertical position to the 100 ml mark. Means shall be provided for maintaining the temperature at 50 °C ± 1 °C or 60 °C ± 1 °C.

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

6 Sampling (see annex A)

6.1 General

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

6.2 Laboratory sample

Only representative samples obtained as specified in ISO 3170 and ISO 3171 shall be used in this International Standard. Before taking a test portion from the sample received by the laboratory, homogenize the sample using the procedure described in annex A.

7 Procedure

7.1 Fill each of two centrifuge tubes (5.2) to the 50 ml mark with toluene which has been water saturated at 50 °C; then immediately pour the laboratory sample directly from the sample container into the centrifuge tubes until the total volume in each tube is 100 ml. Read the top of the meniscus at both the 50 ml and 100 ml marks. Add 0,2 ml of demulsifier solution (4.2) to each tube, using a 0,2 ml pipette or an automatic pipettor. Stopper the tubes tightly and shake vigorously until the contents are thoroughly mixed. Immerse the tubes to the 100 ml mark for 10 min in the bath maintained at 50 °C ± 1 °C.

7.2 If wax contributes to the volume of water and sediment observed (see 7.5) preheat the oil-solvent mixture to 60 °C before each spinning; the final temperature of the mixture shall not drop below 47 °C.

7.3 Invert the tubes to assure that the oil and solvent are uniformly mixed and shake cautiously.

7.4 Place the tubes in the trunnion cups on opposite sides of the centrifuge (5.1) to establish a balanced condition, and spin for 10 min at a relative centrifugal force of between 500 and 850 at the tip of the spinning tubes, as calculated using the equation given in 5.1 (see table 2 for the relationship between diameter of swing, relative centrifugal force and revolutions per minute).

Table 2 — Rotation speeds applicable for centrifuges of various diameters of swing

Diameter of swing[1)] mm	Revolutions per minute at 500 rcf	Revolutions per minute at 800 rcf
432	1 440	1 820
457	1 400	1 770
483	1 360	1 720
508	1 330	1 680
533	1 300	1 640
559	1 270	1 600
584	1 240	1 560
610	1 210	1 530

1) Measured in millimetres between the tips of opposite tubes when in the rotating position.

7.5 Immediately after the centrifuge comes to rest following the spin, read and record the combined volume of water and sediment (see 7.2) at the bottom of each tube to the nearest 0,05 ml from 0,1 to 1 ml graduations. Below 0,1 ml, estimate the reading to the nearest 0,025 ml (see figure 2). Return the tubes without agitation to the centrifuge and spin for another 10 min at the same rate.

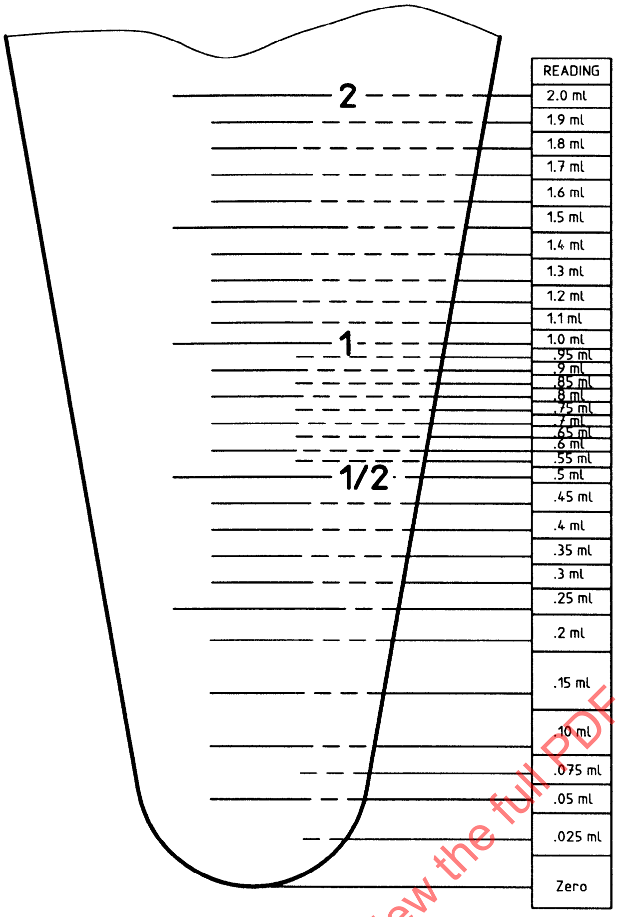

Figure 2 — Procedure for reading water and sediment at low levels

7.6 Repeat this operation until the combined volume of water and sediment remains constant for two consecutive readings. In general, not more than two spinnings are required.

8 Expression of results

Record the final volume of water and sediment in each tube and report the sum of these two readings rounded according to 7.5 as the percentage volume of sediment and water. Report results lower that 0,05 % either as 0 or 0,05, whichever is closer.

9 Precision

The criteria described in 9.1 and 9.2 shall be used for judging the acceptability of results (95 % probability).

9.1 Repeatability

The difference between successive test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the values in figure 3 in only one case in twenty.

9.2 Reproducibility

The difference between two single and independent test results, obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the values in figure 3 in only one case in twenty.

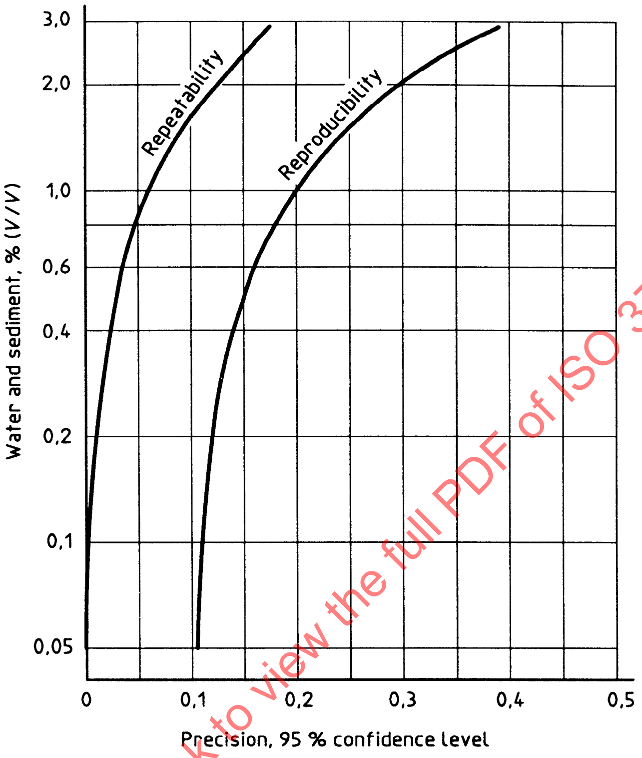

Figure 3 — Precision data

10 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 results of the test (see clause 8);

d) the name and amount of demulsifier used;

e) the heating bath temperature;

f) any deviation, by agreement or otherwise, from the standard procedures specified;

g) the date of the test.

Annex A
(normative)

Sample handling

NOTE — This annex reproduces the instructions on sample handling from ISO 3170:1988 and ISO 3171:1988 and is essentially identical with the corresponding clauses therein.

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 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.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 manually agitate 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 produce water droplets below 50 µm, but not less than 1 µm. Water droplets of 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 mechanical mixer

Insert a high-shear mechanical mixer into the sample container so that the rotating element reaches to within 30 mm of the bottom. A mixer with counter-rotating blades operating at approximately 3 000 r/min (50 s^{-1}) is usually suitable. Other designs may be used if the performance is satisfactory.

Record the temperature of the sample before mixing. In order to minimize loss of light ends from crude oils or other samples containing volatile compounds, operate the stirrer through a gland in the closure of the sample container. Mix until the sample is completely homogenized.

NOTE 1 A mixing time of 5 min is sometimes sufficient, but the size of the container and the nature of the sample affect the homogenization time.

Record the temperature of the sample immediately after mixing. If the rise in temperature during mixing exceeds 10 °C, cool the sample and repeat the mixing at a lower energy input.

NOTE 2 A rise in temperature of greater than 10 °C may result in a decrease in viscosity sufficient for the sediment to settle.

Verify that the sample has become homogeneous (see clause A.3).

NOTE 3 High-shear mixers frequently produce stable emulsions and water contents after stirring that cannot be determined by centrifuge methods.

A.2.3 Circulation with external mixer

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 successive samples drawn from the main bulk of the sample give identical results. This establishes the minimum mixing time.

NOTE — As the sample is, by this time, homogenous 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 hydrocarbon, to sub-sample while mixing is still in progress.

A.3.3 Ensure the sample as drawn fills the container to approximately three-quarters full, and homogenize the sample for a known period of time, which shall be recorded. During this period draw off small portions at regular intervals and test each immediately for water content in accordance with ISO 6296-2 (in preparation) or ISO 12937. When the test results are consistent record the value obtained as the blank water content.

Add an accurately measured quantity of water, between 1 % and 2 %, and homogenize for the same period of time as for the blank and take samples as before. If there is good agreement between the water content determined, taking account of the blank water content, and the quantity of water added then repeat by adding a further accurately measured quantity of water, again between 1 % and 2 %. If the results continue to give good agreement then assume that the mixing time is adequate.

If the results do not show good agreement (within the repeatability of the method), then discard them. Revert to the beginning of the procedure, and use a longer period of mixing.

A.3.4 Do not determine water content by the centrifuge method 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.