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Liquefied petroleum gases — Determination of oily residues — High-temperature method

Gaz de pétrole liquéfiés — Détermination des résidus huileux — Méthode à haute température

Reference number
ISO 13757:1996(E)

Foreword

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International Standard ISO 13757 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Annex A of this International Standard is for information only.

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Liquefied petroleum gases — Determination of oily residues — High-temperature 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 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 determination of the residual matter in liquefied petroleum gases (LPG) that remains after evaporation at 105 °C. This material, termed "oily residues", represents those products that are deposited in vaporizers that are subject to a heat input greater than that of ambient evaporation.

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

ISO 4257:1988, *Liquefied petroleum gases — Method of sampling.*

3 Definition

For the purposes of this International Standard, the following definition applies.

3.1 liquefied petroleum gas: Hydrocarbon gas that can be stored and/or handled in the liquid phase under moderate conditions of pressure and at ambient temperature. It consists essentially of C_3 and C_4 alkanes or alkenes, or a mixture of these, contains generally less than 5 % by liquid volume of material of higher carbon number, and has a gauge vapour pressure not exceeding approximately 1 600 kPa at 40 °C.

4 Principle

A known mass of filtered LPG sample is concentrated by evaporation. The concentrate is transferred into an evaporation flask using dichloromethane (methylene chloride) and then evaporated by means of a rotary evaporator. The oily residue remaining after this evaporation is placed in an oven at 105 °C for 1 h, then cooled and weighed.

5 Reagents

5.1 Acetone, analytical grade.

5.2 Ammonium peroxodisulfate, $(NH_4)_2S_2O_8$, in sulfuric acid solution.

Prepare the necessary volume of solution by dissolving the appropriate quantity (8 g/dm^3) of ammonium peroxodisulfate in concentrated sulfuric acid (98 % minimum purity).

CAUTION — Sulfuric acid and ammonium peroxodisulfate are strong oxidizing agents and therefore contact with organic materials should be avoided. Wear goggles, gloves and safety apron, all made from appropriate materials, during all handling operations.

5.3 Solid carbon dioxide, for the cooling bath.

5.4 Dichloromethane, analytical grade, containing less than 4 mg/kg oily residue after evaporation at 105 °C.

NOTE 1 If the use of dichloromethane poses problems in terms of health and any regulations, it may be possible to replace it by pentane of the same quality (containing less than 4 mg/kg of residues at 105 °C). In this case the procedure is unchanged.

CAUTION — Dichloromethane is an irritant and poses risks to health if handled incorrectly. Extract the vapours while working under a fume cupboard.

5.5 Laboratory detergent, see annex A, reference [6].

5.6 Water, conforming to grade 3 of ISO 3696.

6 Apparatus

6.1 Sample cylinder, stainless steel, fitted with two stainless steel valves, the upper one fitted with a dip tube, maximum service pressure 3 MPa, minimum capacity 3,75 dm^3, containing the LPG whose oily residues are to be determined.

6.2 In-line filter support, stainless steel, for high pressure (see annex A, reference [1]).

6.3 Filter discs, plain white membrane, diameter 47 mm, made of a blend of cellulose esters, nominal pore dimension 0,8 µm (see annex A, reference [2]).

6.4 Cooling coil, stainless steel, made by coiling 5 m of tube of external diameter 3 mm and internal diameter 2 mm onto a mandrel of diameter approximately 50 mm and fitted with the necessary connections (see annex A, reference [3]).

6.5 Cooling bath, comprising a 3-dm^3 Dewar flask, three-quarters filled with an appropriate liquid, e.g. acetone cooled with solid carbon dioxide, to achieve a temperature below − 60 °C.

To obtain quickly a cooling bath at the correct temperature, introduce approximately 1 kg of solid carbon dioxide into a 3-dm^3 beaker and slowly pour in acetone. Transfer the cooled acetone into the Dewar flask containing approximately 200 g of solid carbon dioxide. Repeat the operation until the desired volume is obtained.

NOTE 2 Such a bath can maintain a temperature below − 60 °C for several hours.

6.6 Thermometer, capable of measuring a temperature of − 60 °C ± 1 °C.

6.7 Sampling lines, stainless steel, conforming to the specification given in 6.4. The capacity of the sampling unit (filter, cooling coil, lines) shall be less than 25 cm^3.

6.8 Needle valves

6.8.1 One stainless steel spindle-needle valve with 3-mm fittings, permitting regulation of the flow (equipment of chromatographic quality) (see annex A, reference [4]).

6.8.2 One stainless steel V-needle valve with 3-mm fittings (see annex A, reference [4]).

6.9 Beaker, glass, graduated, of capacity 5 dm^3, shallow form.

6.10 Water bath, comprising a metal tank measuring approximately 300 mm × 300 mm × 300 mm, with water inlet and outlet, capable of being maintained at a temperature of 15 °C ± 5 °C; or a **steam bath** fitted with an orifice of diameter between 58 mm and 62 mm.

6.11 Rotary evaporator, any model enabling the evaporation of at least 200 cm^3 of solvent, over a bath of softened water regulated at 65 °C ± 5 °C, from a ground-necked evaporation flask.

NOTE 3 A double-coil water condenser may suffice for apparatus located in a fume cupboard; otherwise, a solid carbon dioxide/acetone coolant is necessary (see annex A, reference [5]).

6.12 Evaporation flask, 200-cm^3 glass round-bottom flask with a ground neck and fitted with a glass stopper, tare less than 130 g (including stopper).

6.13 Oven, capable of maintaining a temperature of 105 °C ± 5 °C.

6.14 Balances

6.14.1 For the sample cylinder, balance with a range of 10 kg minimum, accurate to within ± 1 g or better.

6.14.2 For the evaporation flask, balance with a range of 160 g minimum, accurate to within ± 0,1 mg or better.

6.15 Laboratory gloves, of fine PVC, resistant to dichloromethane and talc-free.

6.16 Desiccator, without desiccating agent.

7 Preparation of equipment

7.1 New glassware

Clean new glassware by immersing it in detergent (5.5) for a minimum of 12 h before use. In case of dispute or when abnormal results have been obtained, immerse the glassware in a solution of ammonium peroxodisulfate/sulfuric acid (5.2) for 12 h.

After cleaning with detergent or ammonium peroxodisulfate/sulfuric acid solution, remove the glassware and rinse it in tap water and then in grade 3 water (5.6), using gloves (6.15) or tongs. Continue to wear gloves when handling the glassware throughout the remainder of the test procedure. Dry the glassware in the oven (6.13) for 30 min. Leave to cool in a desiccator (6.16) for at least 2 h before use (take care that the stopper does not become stuck during cooling).

After cleaning the apparatus, carry out the tare by weighing the evaporation flask (with stopper) to the nearest 0,1 mg after having unstoppered it for 30 s.

7.2 Previously used glassware

Remove any traces of organic products from used glassware by washing it carefully with dichloromethane (5.4) using gloves. Rinse with acetone (5.1) and dry in the oven (6.13) for 30 min. Continue to wear gloves when handling the glassware throughout the remainder of the test procedure. Carefully remove the solvent vapours from the evaporation flask, either by inverting the flask for approximately 10 s or by blowing nitrogen into it. Place the flask, fitted with its stopper, and the rest of the glassware in a desiccator (6.16) for at least 2 h before use (take care that the stopper does not become stuck during cooling).

If the glassware is not clean enough, or in case of dispute or when abnormal results have been obtained, clean the glassware as described in 7.1, using gloves, having first removed any organic products by rinsing with dichloromethane (5.4) followed by acetone (5.1).

After cleaning the apparatus, carry out the tare by weighing the evaporation flask (with stopper) to the nearest 0,1 mg after having unstoppered it for 30 s.

7.3 Sampling line

The sampling line shall be rinsed first with dichloromethane (5.4), and then with the LPG to be tested.

8 Test procedure

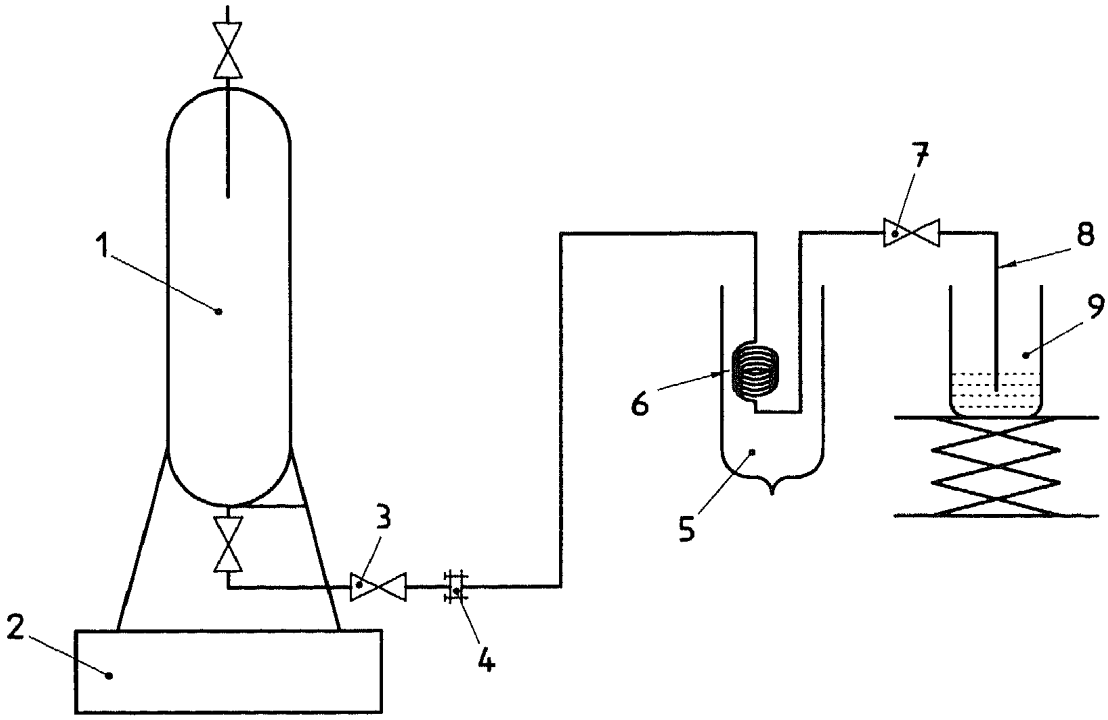
CAUTION — It is essential to work under an explosion-proof hood or in the open, taking all the necessary safety measures, in particular the need to earth equipment to eliminate the risks associated with static electricity.

8.1 Sampling procedure

Slowly shake the sample cylinder containing the LPG to be analysed in order to mix the contents, and then remove a mass of 800 g to 1 200 g of product, weighed to within ± 1 g, into a 5-dm^3 shallow-form beaker in accordance with the procedure defined in 8.1.1 and 8.1.2.

8.1.1 Assemble the apparatus, as shown in figure 1, by connecting the lower valve of the sample cylinder to the sampling line comprising:

- the V-needle valve (3);
- the in-line filter (4);
- the cooling coil (6) immersed in the bath (5), the temperature of which (below − 60 °C) has been checked with a thermometer;
- the spindle-needle valve (7);
- a nozzle in the form of a flexible polytetrafluoroethylene (PTFE) tube (8) or, if not available, a stainless steel tube, enabling flow into the beaker (9).



Key

1	Sample cylinder, as defined in 6.1
2	Balance accurate to 1 g (see 6.14.1)
3	V-needle valve admitting LPG into the circuit (see 6.8.2)
4	In-line filter support (see 6.2 and 6.3)
5	Dewar flask filled as stipulated in 6.5
6	Stainless steel cooling coil (see 6.4)
7	Spindle-needle valve (see 6.8.1)
8	PTFE tube, length 20 cm
9	Shallow-form 5-dm^3 beaker (6.9) containing 50 cm^3 of dichloromethane (5.4)

Figure 1 — Sampling assembly

8.1.2 Having connected the sampling line [valves (3) and (7) closed] to the sample cylinder, open the lower valve of the cylinder and:

- purge and fill the line with the LPG to be analysed by opening valve (7) and then, progressively, valve (3), so as not to damage filter (4);
- close valves (7) and (3) in turn and then the lower valve of the sample cylinder;
- disconnect the sampling line from the sample cylinder and weigh the latter to obtain its mass T in grams;
- reconnect the purged and filled sampling line to the sample cylinder;
- position the beaker (9) containing 50 cm^3 dichloromethane (5.4) such that the PTFE tube is immersed in the dichloromethane;
- open the lower valve of the sample cylinder and regulate needle valves (7) and (3) to obtain a steady flow of LPG sample into the beaker, until a mass of about 1 000 g ± 200 g is obtained;
- close valves (7) and (3) and the lower valve of the sample cylinder;
- disconnect the sampling line from the sample cylinder and weigh the sample cylinder once more to obtain the postsampling cylinder mass P, in grams.

8.1.3 The test sample mass, m_1, in grams, is determined by subtraction:

$$m_1 = T - P$$

NOTE 4 When the balance available is close to where test manipulations are performed, the cylinder and sampling line may be weighed together after the latter has been filled and again after the sample has been taken.

8.2 Evaporation of the LPG

Either immerse the beaker to a depth of 10 mm in a water bath (6.10) at 15 °C ± 5 °C (the temperature of which is regulated by water circulation) or place the beaker on a steam bath (6.10).

Leave to evaporate until the volume of liquid remaining in the beaker is close to the volume of the dichloromethane (5.4) introduced at the start (50 cm^3).

8.3 Evaporation of the dichloromethane

Rinse the walls of the beaker very carefully with approximately 25 cm^3 dichloromethane (5.4) and transfer the contents into a cleaned and previously prepared (7.2) evaporation flask (6.12). Rerinse the beaker with 25 cm^3 dichloromethane (5.4) and transfer this into the flask. Connect the flask to the rotary evaporator and partially immerse it in a bath of softened water regulated to 65 °C ± 5 °C and evaporate the contents until only a few cubic centimetres remain in the flask. Remove the flask from the rotary evaporator. Again carefully rinse the beaker with 50 cm^3 dichloromethane (5.4) and transfer this volume to the evaporation flask. Repeat this operation with another 50 cm^3 dichloromethane (5.4) and collect this volume in the evaporation flask as well. Replace the flask on the rotary evaporator and evaporate the contents until only the oily residue remains.

IMPORTANT — Do not put the evaporator under vacuum during these evaporations.

8.4 Oven drying and weighing

Remove the flask from the rotary evaporator. Rinse the outer walls with acetone (5.1). Place the flask with the neck horizontal in an oven (6.13) for 1 h. (Check the temperature of the oven with a thermometer.)

Because dichloromethane vapours are heavier than air, ensure they are carefully eliminated from the evaporation flask by inverting the flask for approximately 10 s or by blowing nitrogen into the flask.

Then place the flask fitted with its stopper (take care that the stopper does not become stuck during cooling) in a desiccator (6.16) for at least 2 h, and finally weigh the flask (with the stopper) to the nearest 0,1 mg after having unstoppered it for 30 s. The difference between this mass and the tare mass of the flask gives the mass m_2 of the oily residue obtained during the test.

8.5 Blank test

Carry out a blank measurement following the procedure described in 8.3 and 8.4, taking 200 cm^3 of the same batch of dichloromethane (5.4) as used during the test, but this time without the sample.

The mass of oily residue obtained during the blank test is m_3.

9 Calculation

Calculate the oily residue of the sample, E, after evaporation, in milligrams per kilogram LPG, using the following equation:

$$E = \frac{(m_2 - m_3) \times 1\,000}{m_1}$$

where

m_1 is the mass of the LPG sample, in grams (see 8.1.3);

m_2 is the mass of oily residue obtained during the test, in milligrams (see 8.4);

m_3 is the mass of oily residue obtained during the blank test, in milligrams (see 8.5).

10 Expression of results

Report the result to the nearest 1 mg/kg.

11 Precision

The precision of this method, established during interlaboratory tests relating to LPG samples with oily residue contents between 70 mg/kg and 100 mg/kg, using dichloromethane as solvent, and determined on the basis of statistical examination of interlaboratory test results, is as follows:

11.1 Repeatability, r

The difference between two test results obtained by the same operator with the same apparatus under constant operating conditions on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value below in only one case in 20.

$r = 15$ mg/kg

11.2 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 value below in only one case in 20.

$R = 50$ mg/kg

12 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 solvent used;

d) the result of the test, in milligrams oily residue per kilogram LPG sample (see clause 10);

e) any deviation, by agreement or otherwise, from the procedure specified;

f) the date of the test.

Annex A
(informative)

Commercially available equipment suitable for the test procedure

The tradenames given hereafter are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

[1] Filter support, No. XX 45 047 00
Millipore Corp., Ashby Road, Bedford,
MA 01730, USA

[2] Filter membranes, No. AAWP 047 00
Millipore Corp., Ashby Road, Bedford,
MA 01730, USA

[3] Stainless steel (type 304) tube, ref. 30203
Altech Europe, Begoniastraat 6, B-9731,
Nazareth (Eke), Belgium

[4] Stainless spindle-needle valve, valve type SS-SS 2
Whitey Co., 15635 Saranac Road, Cleveland,
OH 44110, USA

[4] Stainless V-needle valve, valve type SS-OVS 2
Whitey Co., 15635 Saranac Road, Cleveland,
OH 44110, USA

[5] Rotary evaporator
Buchi model EL 130

[6] Laboratory detergents

- Extram Flüssig
  E. Merck, 6100 Darmstadt 1,
  PO Box 4119, Germany
- Decontamin
  ICI Ltd., Imperial Chemical House,
  Millbank, London SW1, England
- Decon 90
  Prolabo
  12, rue Pelée, 75011 Paris, France

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Descriptors: petroleum products, liquefied petroleum gases, tests, determination of content, evaporation residue, evaporation analysis.

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