SLOVENSKI STANDARD
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Utekočinjeni naftni plini - Določevanje raztopljenih ostankov - Metoda plinske kromatografije z visoko temperaturo

Liquefied petroleum gases - Determination of dissolved residues - High temperature Gas chromatographic method

Flüssiggas - Bestimmung der gelösten Rückstände - Hochtemperatur-Gaschromatographie-Verfahren

Gaz de pétrole liquéfié - Détermination des résidus dissous - Méthode par chromatographie en phase gazeuse, à haute température

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Liquefied petroleum gases - Determination of dissolved residues - High temperature Gas chromatographic method

Gaz de pétrole liquéfié - Détermination des résidus dissous - Méthode par chromatographie en phase gazeuse, à haute température

Flüssiggas - Bestimmung der gelösten Rückstände - Hochtemperatur-Gaschromatographie-Verfahren

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European foreword

This document (EN 15470:2017) has been prepared by Technical Committee CEN/TC 19 “Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 2018, and conflicting national standards shall be withdrawn at the latest by January 2018.

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

This document supersedes EN 15470:2007.

The main changes in this version being:

a) numerous changes of both technical and editorial nature have been made to add clarity to the text;

b) clarification that the use of a drying agent in the desiccator is not recommended;

c) the description of the equipment used has been improved;

d) Formula (1) has been corrected for an error;

e) small changes in the vent line (6.6) and the flasks (6.7) in order to improve the technical safety of the method;

f) information contained in Annex B that deemed to be obsolete has been removed.

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1 Scope

This European Standard specifies a method for determining the dissolved residual matter in liquefied petroleum gases (LPG), in the range of 40 mg/kg to 100 mg/kg. Higher concentrations can be determined by adjusting the sample size.

The dissolved residue is the amount of organic compounds which is detectable by gas chromatography after evaporation of the sample at ambient temperature and then in an oven at 105 °C.

This method is not suitable for detecting solid materials or for possibly high molar mass polymers (>1 000 g/mol).

From the analysis of a limited LPG sample size (50 g to 75 g) this method allows obtaining information on the potential origin of the residue (gasoil, lubricants, plasticizers, etc.).

The precision data of the method have been determined from 20 mg/kg to 100 mg/kg. For a higher content of residue, the precision has not been tested.

NOTE An alternative European Standard, EN 15471 [1], specifies a gravimetric method.

WARNING — The use of this standard can involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this standard to take appropriate measures to ensure the safety and health of personnel prior to application of the standard, and fulfil statutory and regulatory requirements for this purpose.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 4257, *Liquefied petroleum gases - Method of sampling (ISO 4257:2001)*

3 Terms and definitions

For the purposes of this document, the following term and definition applies.

3.1
liquefied petroleum gas
LPG
petroleum gas that can be stored and/or handled in the liquid phase under moderate conditions of pressure and at ambient temperature, consisting predominantly of propane and butanes, with small proportions of propene, butenes and pentanes/pentenes

4 Principle

A known mass of LPG, between 50 g and 75 g, is sampled and evaporated in a standard small flask. The residue is heated in an oven at 105 °C for 1 h. It is then diluted with a solvent and one internal standard is added. The mixture is then analysed by a capillary gas chromatography and quantified by the internal standard method.

5 Reagents

5.1 Propan-2-ol, analytical grade.

5.2 **Carbon dioxide**, solid for cooling.

5.3 Carbon disulfide, analytical grade (99,9 % minimum).

5.4 Normal Octane, analytical grade (99,9 % minimum), for use as internal standard.

5.5 Pentane, analytical grade (99,5 % minimum).

6 Apparatus

6.1 Sample cylinder, of a total mass compatible with the balance used; preferably made of stainless steel fitted with two stainless steel valves free of oily materials, conforming to EN ISO 4257.

6.2 Cooling bath, comprised of a 0,5l to 2l Dewar flask, filled with propan-2-ol (5.1) cooled by adding solid carbon dioxide (5.2), to achieve a temperature of approximately −77 °C.

6.3 Sampling set, according to Annex A.

6.4 Balance, for weighing the sample cylinder, maximum weight depending of the sample cylinder weight (for instance 16 kg or 30 kg), capable of weighing to the nearest 1 g.

6.5 Analytical balance, capable of weighing to the nearest 0,1 mg.

6.6 Vent line, according to Annex A. The vent line shall have a suitable internal diameter as not to restrict adequate venting of the evaporated LPG; 1/8 inch tubing has been found suitable for use.

6.7 Flasks, (100 ml to 150 ml), made of glass and capable of being sealed or closed. Flasks with screw open caps in conjunction with a septum (see 6.8) have been found suitable for use.

6.8 Septum, adapted to the flask, PTFE/silicon.

6.9 Gas chromatograph.

6.10 Capillary column, capable of being programmed up to 400 °C for which the following characteristics are suggested: weakly polar capillary column (phenyl polycarborane siloxane at 5 %), high temperature, type HT5, 0,53 mm id, 0,15 µm, 10 m.

6.11 Oven, of the static type (without fan assisted circulation), explosion-proof, capable of heating to (105 ± 5) °C.

6.12 Desiccator, (a drying agent is not recommended).

7 Sampling

Samples shall be taken as described in EN ISO 4257 and/or in accordance with the requirements of national standards or regulations for the sampling of automotive LPG.

8 Procedure

8.1 Safety

CAUTION — It is essential to work under an explosion-proof hood. In order to remove both the LPG and carbon disulfide vapours, take all the necessary safety measures and, in particular, earth the equipment in order to eliminate the risks associated with static electricity.

8.2 Sample transfer procedure

a) Put the sample cylinder (6.1) on the balance (6.4);

b) assemble the apparatus, using the set shown in Annex A and following Figure A.1, by connecting the liquid phase valve of the sample cylinder to the sampling line comprising:

— PTFE line;

— spindle-needle valve;

— 1/16” stainless steel injection tubing;

c) fix the PTFE line to a support in order that the sampling operations do not disturb the balance;

d) prepare a cooling bath (6.2) by filling a beaker or small Dewar with solid carbon dioxide and propan-2-ol;

e) clean a flask (6.7) with analytical pentane (5.5) and dry the flask;

f) place the cleaned and dry flask in the cooling bath for at least 1 min before starting the transfer of the sample;

NOTE This enables a better introduction of the sample into the glass container.

Figure A.1 provides one example of a set-up for transferring a quantity of material from the sample cylinder to the flask, which includes a screw open cap (6.7) and septum (6.8) with 2 small holes permitting passages for a sample introduction line and venting line (A.2).

g) close the needle valve;

h) open the sample cylinder cautiously and fill/purge the sampling line by opening the needle valve slightly and progressively;

i) close the needle valve when the LPG flows regularly;

j) introduce the injection end in the flask;

k) record the mass of the sample cylinder, m_1;

l) transfer the LPG sample slowly by opening the needle valve;

m) close the needle valve when approximately 75 g product has been transferred;

n) record the mass of the sample cylinder, m_2;

o) the mass *m* of the LPG sample in grams is given by the following formula:

$$m = m_1 - m_2 \quad (1)$$

8.3 Evaporation procedure

Disconnect the sampling line and leave the vaporized gas to exit through the venting line.

CAUTION — The lower end of the vent line, as shown in Figure A.1 shall never reach into the boiling liquid phase.

The evaporation of the sample starts as soon as the sample transfer begins; the flask is left at ambient temperature.

The gas is vented through the hood.

When the evaporation of the sample from the flask at ambient conditions is completed (no apparent liquid is in the flask), the flask is opened and the residue is further evaporated in the oven for 1 h at 105 °C. The flask is then cooled down in a desiccator for 30 min before it is closed with cap and septum.

CAUTION — Close the flask with the septum with the PTFE side downwards. Store the flask in the upright position.

8.4 Gas chromatography analysis of the residue

8.4.1 Preparation of the internal standard solution A

Accurately (at 0,1 mg) weight approx. 40 mg of normal Octane (5.4) and dilute to 100 g of CS_2 (5.3) at 0,1 g accurate.

A recommended scheme of operating conditions is reported in Table 1.

Table 1 — Recommended operation conditions

Carrier gas	type	helium
	flow	4 ml/min
Injector	type	direct inlet
	temperature	380 °C
Injection	volume	2 µl
Detector	type	FID
	temperature	400 °C
	hydrogen flow	30 ml/min
	air flow	350 ml/min
	make-up gas flow	30 ml/min
Oven	initial temperature	10 °C, constant for 1 min
	final temperature	400 °C
	rate	15 °C/min