SLOVENSKI STANDARD
SIST EN 16423:2013

01-december-2013

Utekočinjeni naftni plini - Določevanje raztopljenega ostanka - Metoda plinske kromatografije z injiciranjem tekočine v kolono

Liquefied petroleum gases - Determination of dissolved residue - Gas chromatographic method using liquid, on-column injection

Flüssiggas - Bestimmung gelöstes Residuals - Gaschromatografisches Prüfverfahren mit benützung von flüssigem, on-column Injektion

Gaz de pétrole liquéfié - Détermination des résidus dissous - Méthode par chromatographie en phase gazeuse avec injection liquide sur colonne

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English Version

Liquefied petroleum gases - Determination of dissolved residue - Gas chromatographic method using liquid, on-column injection

Gaz de pétrole liquéfié - Détermination des résidus dissous - Méthode par chromatographie en phase gazeuse avec injection liquide on-column

Flüssiggas - Bestimmung gelöster Rückstände - Gaschromatographisches Prüfverfahren durch Direkteinspritzung von Flüssigkeit auf die Säule

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

This document (EN 16423:2013) 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of an identical text or by endorsement, at the latest by April 2014 and conflicting national standards shall be withdrawn at the latest by April 2014.

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Introduction

Control over the residue content as specified in EN 589 is of considerable importance in end-use applications of Liquefied Petroleum Gas (LPG). Dissolved residual matter, also known as evaporation residue, in LPG is contamination which can occur during production, transportation or storage.

This standard has been developed as a potential replacement of the commonly used methods, as this method of determination:

– is quicker and much more sensitive than manual methods, such as ASTM D2158 [1] or EN 15471 [2], which are based on evaporation of (large) sample volumes followed by visual or gravimetric estimation of residue content;

– provides enhanced sensitivity in measurements of heavier (evaporation) residues compared to EN 15470 [3], with a quantification limit of 10 mg/kg total residue;

– gives both quantitative results and information about contaminant composition such as boiling point range and fingerprint, which can be very useful in tracing the source of a particular contaminant.

1 Scope

This European Standard specifies a method for the determination of the dissolved residual matter, also known as evaporation residue, in liquefied petroleum gases (LPG), by gas chromatography in the range of (10 to 600) mg/kg (ppm mass).

This test method quantifies soluble organic compounds (hydrocarbon materials), sometimes called 'evaporation residue', which can be present in liquefied petroleum gases and which are substantially less volatile than the LPG product, i.e. with a boiling point between 174 °C and 522 °C (C_{10} to C_{40}). Higher boiling materials, or materials that adhere permanently to the chromatographic column, will not be detected.

WARNING — This standard does not purport to address all of the safety concerns, if any, 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.

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 589, *Automotive fuels — LPG — Requirements and test methods*

EN ISO 4257, *Liquefied petroleum gases — Method of sampling (ISO 4257)*

EN ISO 8973:1999, *Liquefied petroleum gases — Calculation method for density and vapour pressure (ISO 8973:1997)*

ISO 1998-1, *Petroleum industry — Terminology — Part 1: Raw materials and products*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 589, ISO 1998-1, and the following apply.

3.1
high pressure liquefied gas injector
sample introduction device which injects liquefied gas samples under pressure and at room temperature directly onto the chromatographic column thereby maintaining the sample in liquid phase during the injection process

3.2
pressure station
device that supplies high pressure inert gas to a suitable sample cylinder and therefore maintains sample in the liquid phase during the injection procedure

4 Principle

A small quantity of LPG is directly transferred in liquid phase from the sample cylinder on to a GC column using a high pressure liquefied gas injector. The mixture is then analysed by capillary gas chromatography and the dissolved residue content is quantified by the external standard method.

5 Reagents and materials

IMPORTANT — Standards that are prepared in pentane, normally liquid at room temperature, shall be stored under refrigeration and transferred to sample cylinders prior to use. Alternatively, they can be stored in air tight cylinders.

5.1 Mineral oil in LPG calibration mixture.

One of the following mixtures shall be selected for calibration:

5.1.1 Mineral oil in LPG calibration mixture, certified calibration mixture with about 50 mg/kg mineral oil in LPG.

5.1.2 Mineral oil in pentane calibration mixture.

Prepare a calibration standard of mineral oil in pentane. Record the exact weighed value to the nearest mg of mineral oil and calculate the concentration in mg/kg. The concentration of the mineral oil shall be close to the expected concentration of the contamination in the LPG sample.

5.1.3 Mineral oil or local hydrocarbon fraction, boiling point range approximately C_{10} to C_{40}.

Alternatively, a well characterised local hydrocarbon fraction, within the range C_{10} to C_{40}, can be used to provide quantitative and qualitative comparison to the contaminant in the sample. Care should be taken to ensure no significant fraction falls outside the C_{10} to C_{40} range.

5.2 Validation standard, mineral oil in pentane.

Prepare a validation standard of mineral oil in pentane. Record the exact weighed value to the nearest mg of mineral oil and calculate the concentration in mg/kg. The concentration of the mineral oil shall be close to the expected concentration of the contamination in the LPG sample.

5.3 *n*-Alkane retention time standard, mixture containing at least C_{10} and C_{40} in a concentration of (nominally) 5 mg/l each, dissolved in pentane or heptane.

5.4 Solvent, GC grade pentane.

6 Apparatus

NOTE Successfully used columns and conditions are given in Table 1.

6.1 Gas chromatograph, equipped with a Large Volume Cold on Column Injector (LVOCI), linear temperature programmable column oven, and a flame ionisation detector (FID), with data acquisition and processing system.

For checking the linearity of the FID one may use Annex E.

6.2 Solvent vent, controlled to allow venting the major part of the matrix.

6.3 Retention gap, uncoated stainless steel capillary.

6.4 Retaining pre-column, a column with a polydimethylsiloxane stationary phase.

6.5 Analytical column, a column with a polydimethylsiloxane stationary phase.

6.6 Column coupler, coupling device suitable for leak free coupling of the retention gap to the retaining pre-column.

See Figure 1 for a schematic overview of the couplings inside the GC oven and the couplings to the solvent vent valve.

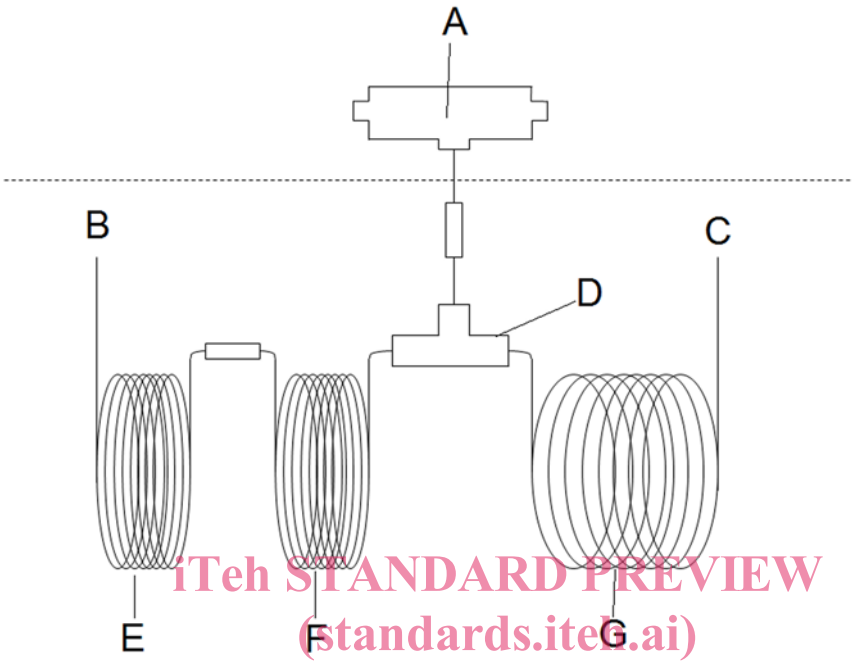
Table 1 — Typical column configuration

Equipment part	Typical operation conditions
Oven program	35 °C for 3 min, 35 °C to 340 °C at 25 °C/min, 340 °C for 10 min
Inlet program	Type: cool on-column Temp: 55 °C for 3 min, 55 °C to 340 °C at 25 °C/min, 340 °C for 9 min
Detector settings	Air flow: 400 ml/min Hydrogen flow: 40 ml/min Make up gas flow: 20 ml/min Temperature: 350 °C Data rate: 20 Hz
Column	Retention gap: Sulfinert® [1)] stainless steel capillary with inner diameter 0,53 mm and length of 5 m Retaining pre-column: 3 m HP-1, 0,53 mm, 2,65 µm Analytical column: HP-1, 30 m, 0,32 mm, 0,25 µm
Pressure station	Sample flow: 2 ml/min Nitrogen pressure: 2 500 kPa Nitrogen purge pressure: 500 kPa
Liquefied gas injector	Injection: 25 ms

1) Sulfinert ® is a stainless steel treatment system from Restek Co., 110 Benner Circle, Bellefonte, PA 16823, USA. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6.7 Column splitter, suitable for leak-free coupling of the retaining pre-column to one side of the analytical column and the deactivated capillary on the other side.

See Figure 1 for a schematic overview of the couplings inside the GC oven and the couplings to the solvent vent valve.

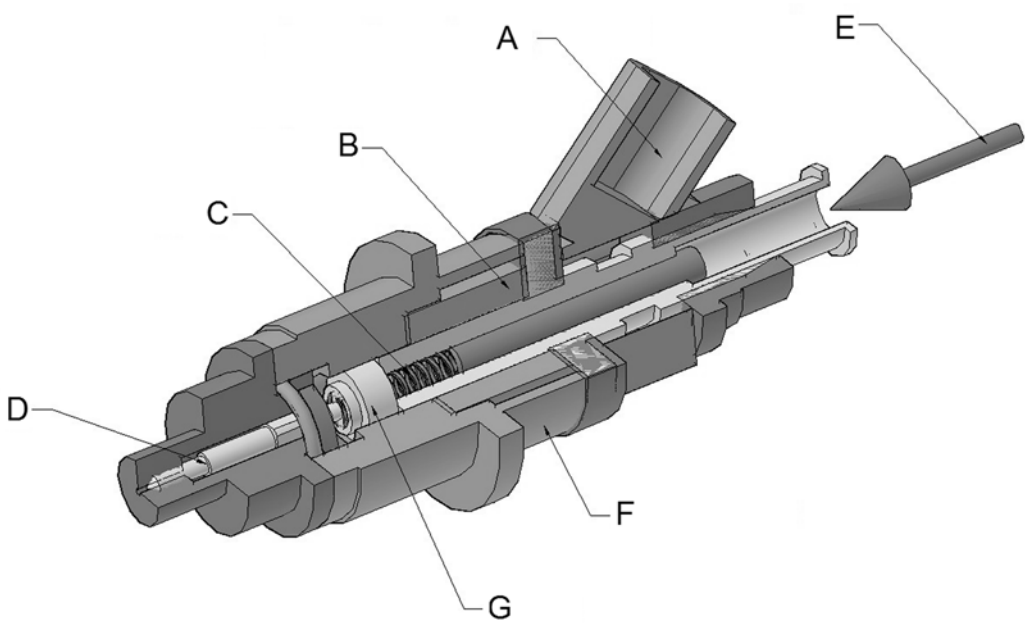


Key

A solvent vent valve
B cool on-column inlet
C detector
D column splitter
E retention gap
F retaining pre-column
G analytical column

Figure 1 — Column overview

6.8 High pressure liquefied gas injector, a high pressure valve as in Figure 2, directly connected to a needle which is inserted in the injection port of the GC, after which the valve is triggered in order to introduce a representative aliquot into the GC system without sample discrimination.



Key

A	electrical attachment	E	pressurised fuel injection
B	solenoid on	F	injector casing
C	valve spring	G	plunger
D	spray tip		

Figure 2 — High pressure valve