BS EN 16423:2013

BSI Standards Publication

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

bsi.

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 16423:2013.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum Testing and Terminology.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Published by BSI Standards Limited 2013

ISBN 978 0 580 78988 5
ICS 75.160.20

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 31 October 2013.

Amendments/corrigenda issued since publication

Date	Text affected

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 16423

October 2013

ICS 75.160.20

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

This European Standard was approved by CEN on 31 August 2013.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

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

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 16423:2013: E

Contents

Page

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.

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

According to the CEN/CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

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.

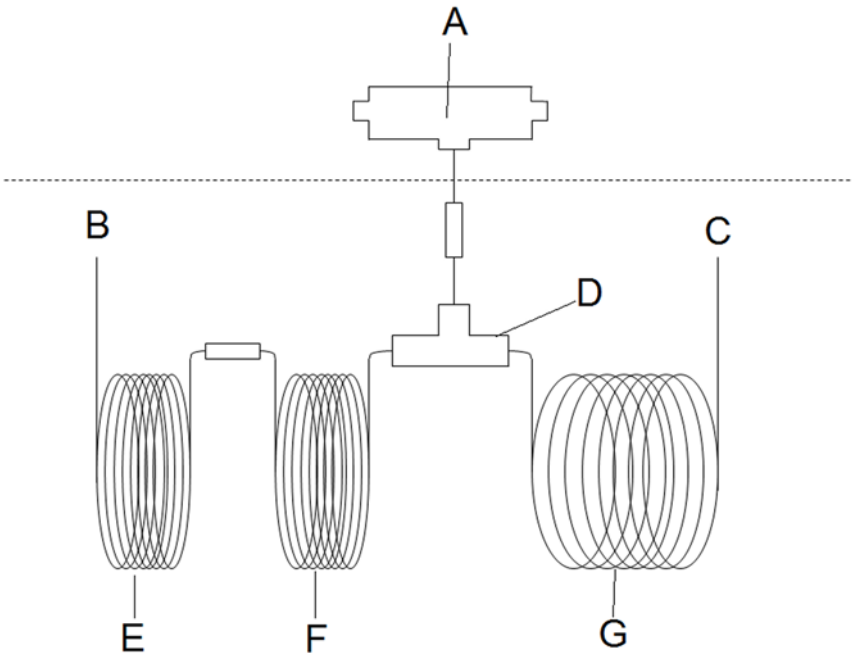
Table 1 — Typical column configuration

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.

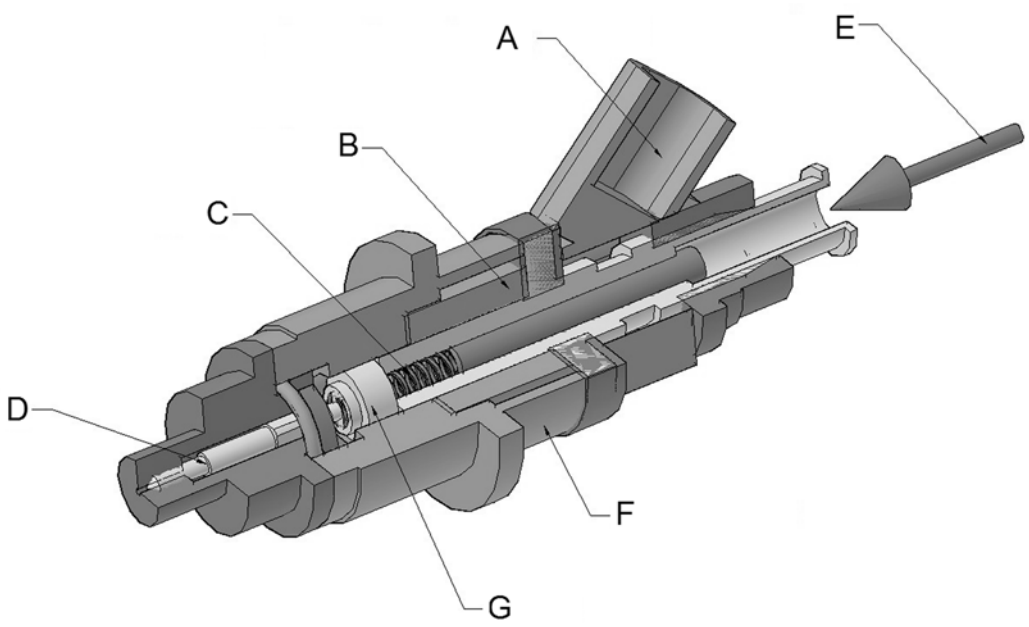


Key

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.

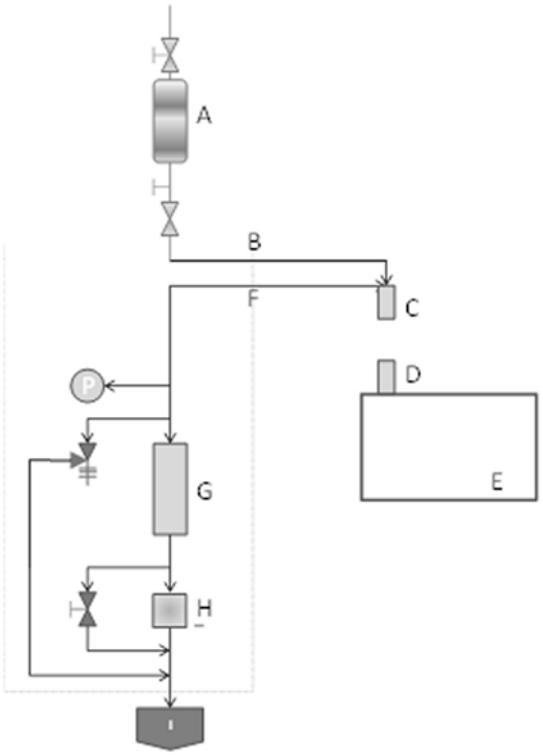


Key

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

Figure 2 — High pressure valve

6.9 Pressure station, ensuring a sample in liquid phase at a constant pressure, with a typical configuration as in Figure 3.



Key

A sample cylinder
B sample line in
C injection device
D cool on column inlet
E gas chromatograph
F sample line out
G rotometer
H vaporiser
I waste system

Figure 3 — Typical configuration of the pressure station

7 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 4257 and/or in accordance with the requirements of national regulations for the sampling of the product under test.

8 Preparation of apparatus

CAUTION —Take all the necessary safety measures and, in particular, earth the equipment in order to eliminate the risks associated with static electricity.

8.1 Gas chromatograph: install and verify performance in accordance with the manufacturer's instructions. Typical operating conditions are shown in Table 1.

8.2 Pressure station: install in accordance with the manufacturer's instructions. Purge sample and check carefully for leaks. Connect the outlet to a waste system.

8.3 High pressure liquefied gas injector: install in accordance with the manufacturer's instructions.

8.4 Column configuration: install the columns as shown in Figure 1, using low dead volume connections, and check for leaks.

9 Test procedure

9.1 Safety and hazards

9.1.1 There is a significant fire hazard from LPG, and since the boiling point of LPG can be as low as -41 °C, there is a risk of freezing "burns". Take appropriate safety precautions to prevent ignition or fire, and wear suitable protective equipment to protect against skin contact with LPG.

9.1.2 An appropriate laboratory ventilation system shall be used.

9.1.3 An appropriate waste line shall be installed. The pressure station and injector shall be connected to this line. The waste line shall exit outside the building. An appropriate waste facility shall be available for liquid (pentane).

9.1.4 The pressure station, cylinder, injector and controller shall be grounded appropriately.

9.2 Summary of the method

a) A sample cylinder of LPG is pressurised on the pressure station to 2 500 kPa using nitrogen or helium.

b) The injection system is flushed with LPG in liquid phase at room temperature. The end of the injection purge line is connected to a heated vaporiser which vaporises the LPG before transporting it to a waste disposal system.

c) After flushing, the injection device is routed to the GC injector port and LPG (25 ms activation time equivalent to 30 µl) is introduced via a high pressure valve and needle which is inserted into the Cool On Column inlet.

d) The gas chromatograph is equipped with a solvent vent which routes most of the LPG light components out of the analytical system and leaves behind the components of interest.

e) The dissolved residue to be determined is retained on the pre-column.

f) After venting, the light ends, the flow from the pre-column is switched to the analytical column and a temperature program is started.

g) Dissolved residue contaminants are separated and identified based on differences in boiling point temperature.

h) Total residue is quantified using area summation of components corresponding to the expected range of C_{10} to C_{40} (174 °C to 522 °C).

Provide guidance for determining heavy residue with a boiling range less than the C_{10} nominal boiling point 174 °C.

9.3 Calibration

This method uses a one point calibration performed at instrument installation, when the result of the validation sample falls outside acceptable limits and whenever there are changes in the application hardware and/or gas supply. Instrument preparation and the calibration procedure follow.

a) Cycle the GC several times through the method temperature program until the baseline is stable. A baseline is stable when the start and end signal of two consecutive blank runs are within 5 % in 10^{-9} A (pA, pico Ampere). An unstable baseline can be caused by a leak, detector gases or by high boiling point components or materials that have not yet eluted from the column. The signal height (in pA) at the end of an analysis of a calibration, validation or sample shall be equal or higher than the blank baseline. A signal higher than 5 % could indicate a poorly conditioned column or the elution of sample components with a boiling point higher than 522 °C. Refer to the datasheet of the column for instructions on conditioning the

column. Run a baseline correction or a blank run, without sample injection if baseline correction is to be used in the integration.

b) Analyse the *n*-alkane retention time standard (5.3), and establish the retention time for C_{10} and C_{40}. There should be baseline separation between the solvent (pentane) and the first normal alkane peak (C_{10}). If the separation is not sufficient, adjust the temperature program, re-establish the baseline, and then re-analyse the retention time standard. An example is shown in Figure 4.

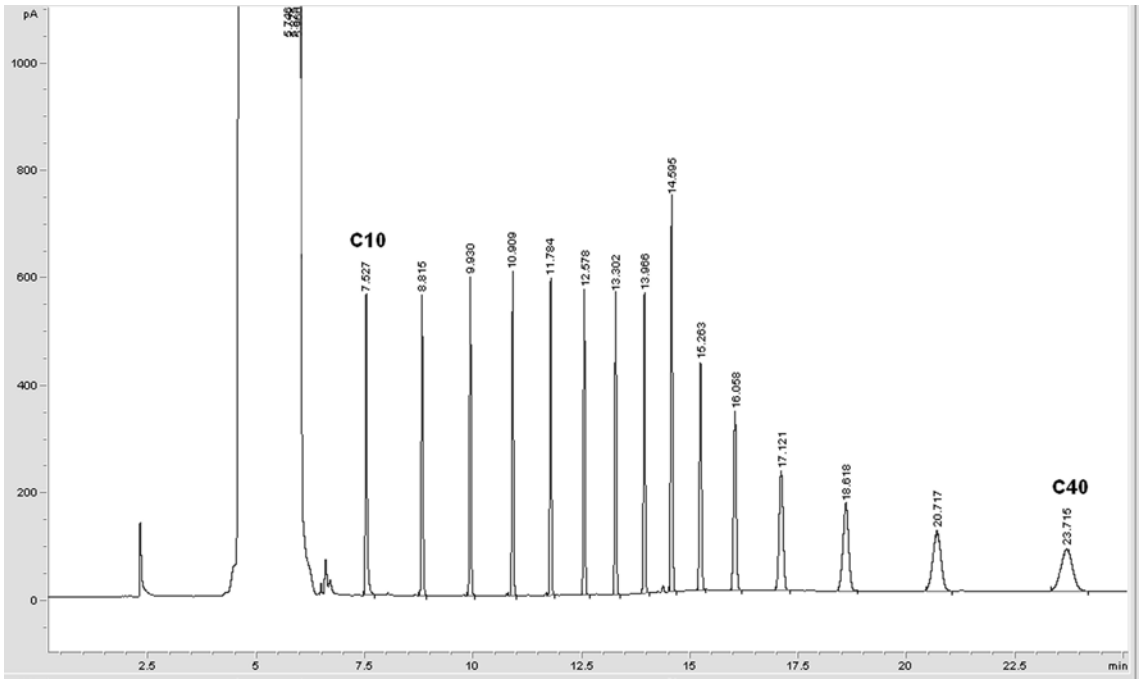


Figure 4 — Chromatogram of C_{10} through C_{40}

c) Analyse the calibration mixture. The calibration mixture uses either certified LPG (5.1) or GC grade pentane (5.2).

d) Integrate the dissolved residue by summing the area from C_{10} through C_{40}.

e) Determine the response factor by dividing the nominal concentration in the calibrant solution by the total area and use this for calculation of unknown sample concentrations under the assumption that all sample components have the same response factor. (See 10.4)

f) Analyse the validation sample. Analyse the validation sample daily or whenever samples are expected. Repeat the analysis when the result of the validation sample falls outside the acceptable SQC limits per Clause 11.

9.4 Procedure

a) Connect the calibration, validation or sample cylinder to the pressure station and pressurise to 2 500 kPa ± 200 kPa. It is important to maintain and reproduce this pressure as closely as possible to ensure sample size injection repeatability.

b) Open the cylinder at both sides and flush the sample for approximately 3 min with a flow rate of about 5 ml/min.

c) Inject sample (trigger pulse 25 ms at 2 500 kPa, equivalent to approximately 30 µl).

d) Analyse each sample in duplicate. If the difference between the results of the two analyses is > 5 %, perform an extra analysis and average the two closest results.

e) Close the sample cylinder after injection and repeat 9.4 b) for the next injection. When all analyses are finished, close the sample cylinder and release the system pressure. Remove the sample cylinder.

f) For each sample run, integrate that part of the chromatogram corresponding to the dissolved residue by summing the area from C_{10} through C_{40} as defined by the *n*-alkane standard (see 9.3 b).

g) Pentane based calibration, validation, and *n*-alkane samples, may be analysed by filling an appropriate high pressure sample cylinder with the solution using the same injection procedure as for LPG samples.

10 Calculations

10.1 Verify whether the separation between the matrix and C_{10} is sufficient for correct integration of the residue.

NOTE An example of a correct chromatogram of a 50 mg/kg mineral oil is shown in Figure 5.

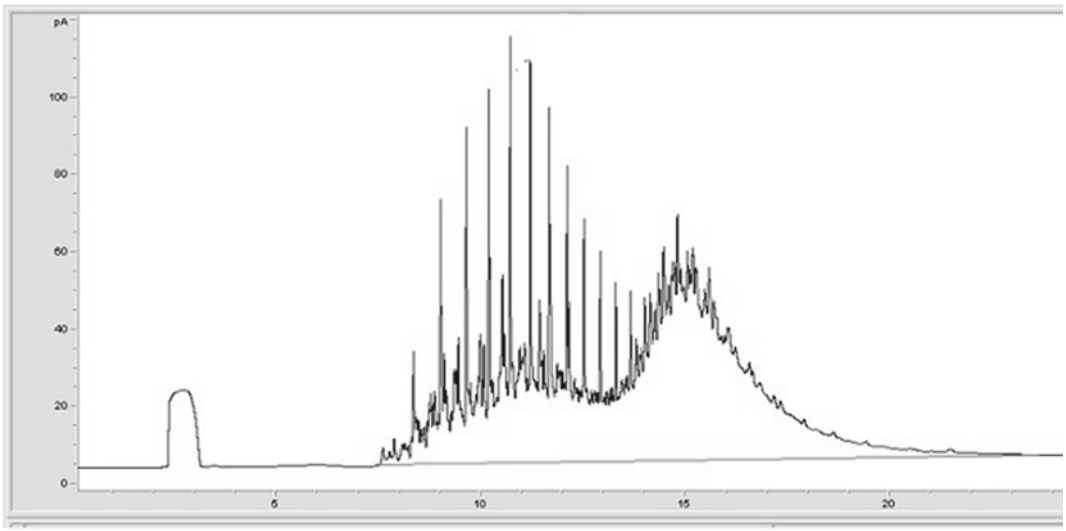


Figure 5 — Chromatogram example

10.2 Start the integration at the retention time of C_{10} or at the point where the slope of solvent peak goes from negative to positive (the valley). This point should not be higher than two times the value of the baseline in pA.

10.3 Calculation is based on a response factor and correction for the difference in density between the sample and the calibration mixture. Correction for the difference in density between the sample and the calibration standard is performed as in Annex A.

10.4 Calculation of the response factor, using the calibration mixture:

$$Rf = DR_{\mathrm{cm}} / S_{\mathrm{c}} \quad (1)$$

where

Rf is the response factor;

DR_{cm} is the nominal dissolved residue content in the LPG calibration standard or in the standard in pentane in mg/kg;

S_{c} is the summed area of the area of C_{10} to C_{40} in the LPG calibration standard or in the pentane standard *i* prepared in accordance with 5.2.

10.5 Calculation of a sample concentration; when the calibration mixture and the sample have the same density:

$$DR_s = S_s \times Rf \quad (2)$$

where

DR_s is the dissolved residue content in the sample in mg/kg;

S_s is the summed area of the area of C_{10} to C_{40} in the sample;

Rf is the response factor as calculated in 10.4.

10.6 Calculation of sample concentration with correction for the density; to be used when the density of the calibration mixture and the sample differ:

$$DR_s = S_s \times Rf \times \frac{\rho_c}{\rho_s} \quad (3)$$

where

ρ_c is the density of calibration standard at measurement temperature in g/ml;

ρ_s is the density of the sample solution at measurement temperature in g/ml.

11 Quality control

At a minimum, confirm the performance of the instrument or the test procedure by analysing validation samples (see 5.2) after each calibration and at least once whenever samples are to be analysed. .

Alternatively, use established test facility QC/(QA) protocols to confirm that the instrument is within the testing facility control limits.

Annex B may be used as guidance to aid in the establishment of a formal QC/QA system.

12 Expression of results

Report the content of dissolved residue (evaporation residue) to the nearest 0,1 mg/kg.

13 Precision

13.1 General

The following precision statement was derived from statistical analysis ([4], [5]) of the results of an interlaboratory study relating to LPG samples with dissolved residue contents between nominally 10 mg/kg and 600 mg/kg. The range of results applicable for *r* and *R* equations listed below are from 6,1 mg/kg to 640,8 mg/kg. Table 2 provides examples of *r* and *R* values at various levels.

NOTE This precision is based on the analysis of five samples using seven independent instrument installations and operators.

13.2 Repeatability

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 value calculated from the following formula only in one case in twenty:

$$r = 0{,}145\,3\,(X)^{0{,}829\,2} \quad (4)$$

where X is the average of the two results being compared, in mg/kg.

13.3 Reproducibility

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 value calculated from the following formula only in one case in twenty:

$$R = 0{,}792\,9\,(X)^{0{,}829\,2} \quad (5)$$

where X is the average of the two results being compared, in mg/kg.

Table 2 — Example of *r* and *R* values at various oil residue levels

Dissolved residue content mg/kg	***r*** mg/kg	***R*** mg/kg
10,0	0,98	5,35
50,0	3,73	20,32
100,0	6,62	36,11
250,0	14,15	77,20
600,0	29,24	159,54

14 Test report

The test report shall specify:

a) reference to this European Standard, i.e. EN 16423;

b) type and complete identification of the product tested;

c) result of the test (see Clause 12);

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

e) date of the test.

Annex A
(normative)

Density calculation of the LPG and correction of the result

A.1 General

The mass of the sample injected into the GC using the liquefied injector depends on the pressure of the sample, the time setting for the injection and the density of the sample.

An analytical method generally holds the pressure and the time setting constant. A variation in injected mass occurs when there is a difference in composition (and therefore density) between the LPG sample and the calibration material (for example calibration standards prepared in pentane (see 5.2).

In that case, the calculated residue result in mg/kg needs to be corrected for the difference in the injected mass (see 10.6). This requires the density of both the calibration matrix and the sample matrix.

When the sample density has not been determined by direct measurement, it shall be calculated according to EN ISO 8973 using the LPG composition analysis. The density equation given requires the sample composition to be in mass %.

The composition of an LPG sample is readily determined by GC methods which generally conform to EN 27941. This method suggests reporting results in mole % (*X*) of the major sample components. When available laboratory analytical results are expressed in mole % (*X*), the inter conversion procedures outlined in EN ISO 8973 may be used to give an equivalent mass % which may then be used to calculate the density of the analysed product.

A.2 Inter conversion to LPG mass fraction according to EN ISO 8973

Where applicable, inter conversion to mass fraction of each component of the mixture (μ_i) shall be according to the following formula (as in 6.2.1 of EN ISO 8973:1999):

$$\mu_i = \frac{X_i M_i}{\sum_i^n X_i M_i} \qquad \text{(A.1)}$$

where:

i is the number of the specific component;

n is the total number of components;

X_i is the mole fraction of component (*i*) in the mixture;

M_i is the relative molecular mass of component (*i*) taken from Table 1;

$\sum_i^n X_i M_i$ is the sum of the products of *X* and *M* for every component.

A.3 Density calculation according to EN ISO 8973

Where applicable, calculation of sample density shall be according to Formula (A.2):

$$\rho = \frac{1}{\sum_i^n \frac{\mu_i}{P_i}} \quad \text{(A.2)}$$

where

ρ is the calculated density of the LPG sample in kg/m^3;

μ_i is the mass fraction of component (*i*) in the mixture;

P_i is the density factor of component (*i*) taken from Table A.1 in kg/m^3, 15 °C;

$\sum_i^n \frac{\mu_i}{P_i}$ is the sum of μ_i / P_i for every component in the mixture.

Table A.1 — Calculation factors for common LPG components

Component	Relative molecular mass	Density factor *P*i kg/m3
Ethane	30,069 4	375,76
Ethene	28,053 6	369,00
Propane	44,097 2	507,30
Propene	42,081 4	521,33
i-Butane	58,123 0	562,98
Butane	58,123 0	584,06
1-Butene	56,107 2	601,15
i-Butene	56,107 2	600,50
cis-2-Butene	56,107 2	627,20
trans-2-Butene	56,107 2	610,00
1,2-Butadiene	54,091 4	658,00
1,3-Butadiene	54,091 4	627,30
i-Pentane	72,149 8	624,35
Pentane	72,149 8	631,00
1-Pentene	70,134 0	645,65

A.4 Example of a calculation

A sample calculation using the hypothetical EN 27941 LPG compositional analysis as presented in Table A.2 is used to present an example:

Table A.2 — Composition data used in the example

Component	mole %
ethane	0,05
propane	78,45
iso-butane	5,50
n-butane	16,00

Dissolved residue chromatogram area result equivalent to: **35,0 ppm mass/mass in pentane.**

Step 1: Inter conversion to mass percentage as in Formula (A.1) is shown in Table A.3:

Table A.3 — Calculation step 1

Component	Mole fraction	Multiply mole fraction by relative molecular weight factor	Product	Divide by total = mass fraction
ethane	0,000 5	30,069 4	0,015 034 7	0,000 3
propane	0,784 5	44,097 2	34,594 253 4	0,734 4
iso-butane	0,055 0	58,123 0	3,196 765	0,067 9
n-butane	0,160 0	58,123 0	9,299 680	0,197 4
Total	1,000 0		47,105 733 1	1,000 0

Step 2: Density calculation, ρ, in kilograms/m^3 at 15 ^{0}C, via Formula (A.2) is shown in Table A.4:

Table A.4 — Calculation step 2

Component	Mass fraction	Divide mass fraction by density factor	Quotient: 1/total (kg/m^3)
ethane	0,000 3	0,000 000 7	
propane	0,734 4	0,001 447 6	
iso-butane	0,067 9	0,000 120 6	
n-butane	0,197 4	0,000 337 9	
Total		0,001 906 8	524,43885

Step 3: Correcting for density difference between the LPG sample and calibrant pentane:

DR_s = (631,00/524,44) * 35,0 mg/kg = 42,1 mg/kg dissolved residue in the sample.

Annex B
(informative)

Quality control monitoring

B.1 Confirm the performance of the instrument or the test procedure by analysing quality control (QC) sample(s).

B.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. See [4] and [6].

B.3 Record the QC results and analyse by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process ([4], [6]). Investigate any out-of-control data for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

NOTE In the absence of explicit requirements given in the test method, B.4 provides guidance on QC testing frequency.

B.4 The frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample should be analysed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analysed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample testing precision should be periodically checked against this method's precision to ensure data quality. See [4] and [6].

B.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analysed. An ample supply of QC sample material should be available for the intended period of use, and shall be homogenous and stable under the anticipated storage conditions.

B.6 See [4] and [6] for further guidance on QC and control charting techniques.

Annex C
(informative)

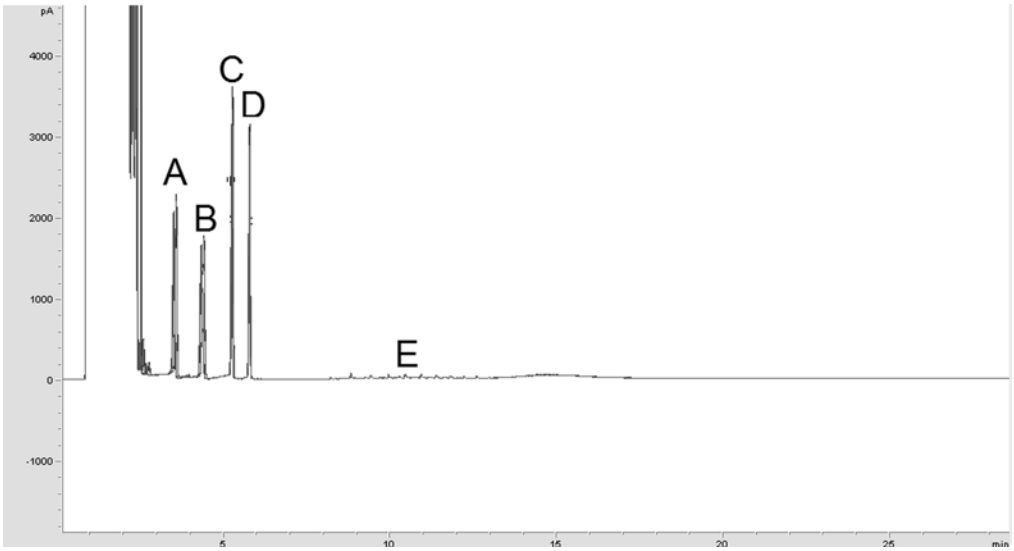
Analysis of benzene, toluene and hydrocarbons C_7 through C_{10}

This annex provides guidance for determining heavy residue with a boiling range less than the C_{10} nominal boiling point 174 °C. These fall outside the scope of this method.

The recovery of benzene nominal boiling point 80 °C has been tested successfully and the results are presented below.

This expansion of the analysis boiling range requires a shorter vent time for the matrix or solvent. A vent time of 6 s gave good recovery of 44,0 ppm benzene in a pentane matrix. Standard C_{10+} vent times of (50 to 60) s are the norm with the column system described in Clause 6 of this method.

Care should be taken to examine the degree of separation in the chromatogram between the components of interest and the matrix peak to ensure proper integration for quantitation. Figure C.1 shows an overlay of four chromatograms of a sample spiked with benzene, toluene, heptane and octane used for the setting the vent time.



Key

A benzene 44,0 ppm
B toluene 41,0 ppm
C nC_7 33,0 ppm
D nC_8 37,0 ppm
E mineral oil 51,0 ppm

Figure C.1 — Overlay of four chromatograms of a spiked sample

Calibration follows the procedure as in 9.3.

The total residue is calculated by summing the individual identified peaks shown with the unresolved C_{10} to C_{40} mineral oil area.

The recovery of 44 mg/kg benzene in comparison with 41 mg/kg toluene is 98 %, the repeatability over four analyses is according to Table C.1:

Table C.1 — Recovery figures

Component	**Nominal concentration** mg/kg	**Average** mg/kg	**Standard deviation**	**Relative standard deviation** %	**Recovery** **%**
benzene	44	40,7	1,38	3,4	98
toluene	41	38,8	1,31	3,4	100
n-heptane	33	31,7	0,62	1,9	102
n-octane	37	35,4	0,79	2,2	101

Annex D
(informative)

Analysis of di-iso-propanolamine

This annex has been added to the test method to provide guidance for the analysis of di-iso-propanolamine (DIPA) in LPG. See Figure D.1 for an example chromatogram of DIPA (4,0 mg/kg) and mineral oil (36,0 mg/kg).

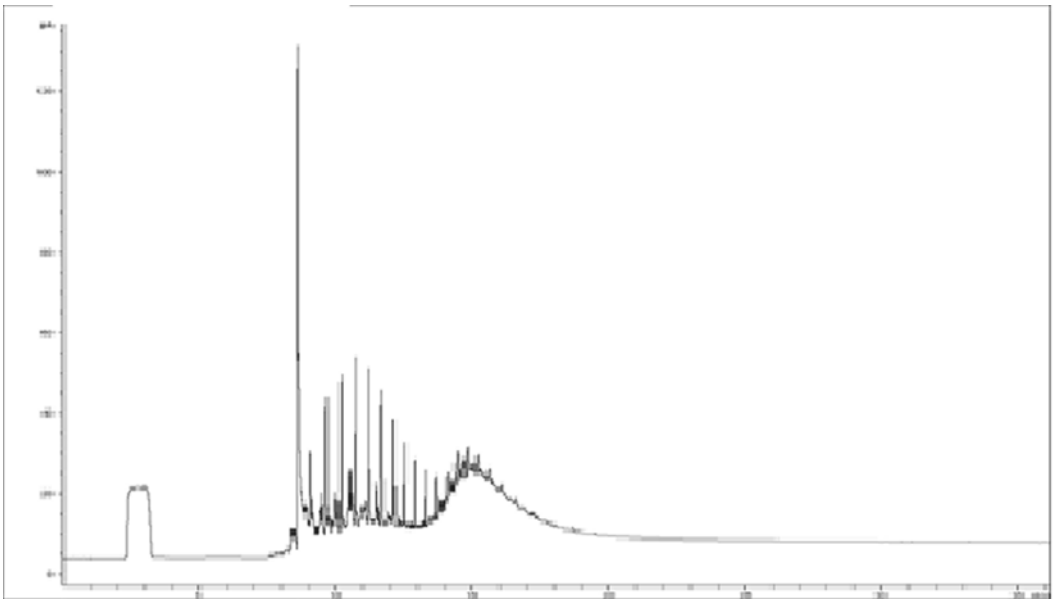


Figure D.1 — Chromatogram of DIPA and mineral oil

This application requires an amine treated column or a metal column to avoid adsorption of amine on the fused silica. Successfully used columns for this application are the RTX-amine column (30 m*0,32 mm*1,0 µm) or the MTX-5 column (30 m*0,32 mm*1,0 µm). Both columns are available from the company Restek (www.restek.com).

Typical conditions, other than the column, are described in Table 1.

Calibration follows the procedure as in 9.3.

The total residue is calculated by summing the individual identified peaks shown with the unresolved C_{10} to C_{40} mineral oil area. The total DIPA concentration is determined by integrating the DIPA peak.

Annex E
(informative)

FID linearity check

E.1 To verify system linearity over the range of expected sample residue, it is suggested that a range of standards which bracket this expected value be prepared and analysed after installation or major repair.

E.2 Prepare a mineral oil or site specific oil standard by weighing to the nearest mg and dissolving in ACS or better pentane or certified LPG. Choose the weighed sample amount and volume of diluent to give a residue concentration at twice the expected concentration in the routine samples.

E.3 Dilute the above prepared standard (E.2) 1:1 (vol/vol) in the diluent (ACS or better pentane or certified LPG) to give a standard roughly equivalent to the expected routine sample residue concentration.

E.4 Prepare a third standard at roughly half the expected routine sample residue by diluting the first standard (E.2) 1:3 (vol/vol) with the diluent (GC grade pentane for residue analysis or better or certified LPG).

The user may choose to prepare other residue standard concentrations to verify linearity over the range of interest.

E.5 Analyse a minimum of the three described standards according to the procedure described in the method.

E.6 Integrate the residue chromatogram and sum the area of range C_{10} to C_{40}.

E.7 Prepare a plot of area versus nominal concentration in mg/kg (ppm). This plot should give a straight line with a constant slope.

E.8 Any deviation from linearity indicates nonlinear behaviour of the application set up.

E.9 Non-linear behaviour can be caused by poor control of the injection volume (check the peak shape) or the detector (check the manufacturer manual for correct FID setting). Correct the issue and repeat the linearity check.

Bibliography

[1] ASTM D2158, *Standard Test Method for Residues in Liquefied Petroleum (LP) Gases*

[2] EN 15471, *Liquefied petroleum gases — Determination of dissolved residues — High temperature gravimetric method*

[3] EN 15470, *Liquefied petroleum gases — Determination of dissolved residues — High temperature Gas chromatographic method*

[4] EN ISO 4259, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259)*

[5] ASTM D6300, *Determination of Precision and Bias Data for Use in Test Methods for Petroleum Products and Lubricants*

[6] ASTM D6299, *Standard Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance*

[7] ASTM D6667, *Standard Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence.*

[8] EN 27941, *Commercial propane and butane — Analysis by gas chromatography (ISO 7941)*

This page deliberately left blank

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards -based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email bsmusales@bsigroup.com.

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Copyright

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

bsi.

...making excellence a habit.™