

BRITISH STANDARD

**BS EN 1601 :
1997
BS 2000 :
Part 408 : 1997**

Methods of test for

Petroleum and its products

**Part 408. Liquid petroleum products -
Unleaded petrol - Determination of organic
oxygenate compounds and total organically
bound oxygen content by gas chromatography
(O-FID)**

(Identical with IP 408/98)

The European Standard EN 1601 : 1997 has the status of a
British Standard

National foreword

This British Standard was published under the authority of the Materials and Chemicals Sector Board and comes into effect on 9 December 1997. It is the English language version of EN 1601 : 1997 Liquid petroleum products - Unleaded petrol - Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography, published by the European Committee for Standardization (CEN).

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of 'IP Standard methods for analysis and testing of petroleum and related products' which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as Parts of BS 2000.

The numbering of the Parts of BS 2000 follows that of the corresponding methods published in 'IP Standard methods for analysis and testing of petroleum and related products'. Under the terms of the agreement between BSI and the Institute of Petroleum, BS 2000 : Part 408/BS EN 1601 will be published by the IP (in 'Standard methods for analysis and testing of petroleum and related products and British Standard 2000 Parts' and as a separate publication). BS 2000 : Part 408 : 1997 is thus identical with IP 408/98.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

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The following BSI references
relate to the work of this
standard:

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Descriptors: petroleum products, liquid fuels, gasoline, chemical analysis, determination of content, organic compounds, oxygen, gas chromatography

English version

**Liquid petroleum products - Unleaded petrol -
Determination of organic oxygenate compounds
and total organically bound oxygen content by gas
chromatography (O-FID)**

Produits pétroliers liquides - Essence sans plomb - Détermination des composés oxygénés organiques et de la teneur totale en oxygène organiquement lié par chromatographie en phase gazeuse (O-FID)

Flüssige Mineralölerzeugnisse - Unverbleite Ottokraftstoffe - Bestimmung sauerstoffhaltiger organischer Verbindungen und des Gesamtgehalts an organisch gebundenem Sauerstoff mittels Gaschromatographie (O-FID)

This European Standard was approved by CEN on 1997-02-28. 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 Central Secretariat or to any CEN member.

The European Standards exist 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 Central Secretariat has the same status as the official versions.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Contents	Page
Foreword	3
1 Scope	4
2 Normative References	4
3 Principle	5
4 Reagents and materials	5
5 Apparatus	6
6 Sampling	7
7 Procedure	8
8 Calculation of results	9
9 Expression of results	11
10 Precision	11
11 Test report	12
Annex A (normative) Densities at 15° C of organic oxygen containing compounds	13
Annex B (informative) Guidance on the oxygen selective detection (O-FID) technique	20

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products", the secretariat of which is held by NNI.

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 December 1997, and conflicting national standards shall be withdrawn at the latest by December 1997.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a gas chromatographic method for the quantitative determination of individual organic oxygenate compounds in the range 0,17 % (m/m) to 15 % (m/m) and total organically bound oxygen up to 3,7 % (m/m) in unleaded petrol having a final boiling point not greater than 220 °C.

This European Standard is applicable to the determination of oxygen-containing compounds and total organically bound oxygen in unleaded petrol in line with the relevant EU Directive¹⁾.

WARNING : The use of this standard may 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 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

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 3675	Crude petroleum and liquid petroleum products - Laboratory determination of density or relative density - Hydrometer method
EN ISO 3838	Crude petroleum and liquid or solid petroleum products - Determination of density or relative density - Capillary-stoppered pycnometer and graduated bicapillary pycnometer methods
EN ISO 12185	Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method
ISO 3170	Petroleum liquids - Manual sampling
ISO 3171	Petroleum liquids - Automatic pipeline sampling

3 Principle

After separation of the sample using a capillary column, the organic oxygenate compounds are selectively converted to carbon monoxide, hydrogen and carbon in a pyrolytic cracking reactor. In a hydrogenation reactor, carbon monoxide is then converted to methane and subsequently detected using a flame ionization detector (O-FID).

1) EU Directive 85/536/EEC, Council Directive on crude-oil savings through the use of substitute fuel components in petrol.

NOTE : Guidance on the oxygen selective detection (O-FID) technique is given in annex B.

4 Reagents and materials

Use only reagents of recognized analytical grade.

4.1 Gases

4.1.1 Carrier gas

Helium, or nitrogen, free of hydrocarbons, oxygen and water as impurities.

Hydrogen shall not be used as a carrier gas because it will interfere with the cracking reaction.

4.1.2 Reactor and detector gases

Hydrogen, and air or oxygen.

WARNING : Hydrogen is explosive when mixed with air at concentrations ranging approximately from 4 % (V/V) to 75 % (V/V). All joints and lines carrying hydrogen shall be made gas tight to prevent leakage of hydrogen into a confined space.

4.2 Reagents for the preparation of calibration samples

Reagents shall be not less than 99,0 % (m/m) pure.

Calibration samples may be combinations of the following reagents:

methanol (CH_3OH) (methyl alcohol; MeOH);

ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) (ethyl alcohol; EtOH);

propan-1-ol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) (propyl alcohol; NPA);

propan-2-ol [$(\text{CH}_3)_2\text{CH OH}$] (iso-propyl alcohol; IPA);

butan-1-ol ($\text{CH}_3[\text{CH}_2]_3\text{OH}$) (butyl alcohol; NBA);

butan-2-ol ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3$) (*sec*-butyl alcohol; SBA);

2-methylpropan-2-ol [$(\text{CH}_3)_3\text{COH}$] (*tert*-butyl alcohol; TBA);

2-methylpropan-1-ol [$(\text{CH}_3)_2\text{CH CH}_2\text{OH}$] (iso-butyl alcohol; IBA);

pentan-2-ol [$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_3$] (*sec*-amyl alcohol; SAA);

tert-butyl methyl ether [$(\text{CH}_3)_3\text{CO CH}_3$] (methyl tertiary butyl ether; MTBE);

methyl *tert*-pentyl ether [$(\text{CH}_3)_2\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}_3$] (tertiary amyl methyl ether; TAME);

ethyl *tert*-pentyl ether $[(\text{CH}_3)_2\text{C}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}_3]$ (ethyl tertiary amyl ether; ETAE);

acetone $[(\text{CH}_3)_2\text{CO}]$;

butanone $(\text{CH}_3\text{CH}_2\text{COCH}_3)$ (methyl ethyl ketone; MEK);

tert-butyl ethyl ether $[(\text{CH}_3)_3\text{CO CH}_2\text{CH}_3]$ (ethyl tertiary butyl ether; ETBE).

4.3 Internal standards

Use one of the reagents listed in 4.2. If all of these reagents are likely to be present in the sample under test, use a different organic oxygenate compound of the same purity and similar volatility.

4.4 Petrol containing no organic oxygenate compounds

Petrol which has been examined to ensure that it contains no organic oxygenate compounds detectable by this method.

5 Apparatus

Usual laboratory apparatus and glassware, together with the following.

5.1 Gas chromatographic assembly

5.1.1 Gas chromatograph, equipped with an oxygen selective flame ionization detection system.

5.1.2 Columns

The separation column shall consist of a capillary column, coated with a suitable phase for achieving the required resolution.

NOTE : Polyethylene glycol and methyl silicone have been found to be suitable.

The resolution between the compounds to be determined, and between water and oxygen, shall be at least 1.

The resolution, R , between peaks A and B (see figure 1) shall be calculated as follows:

$$R = 1,18 \frac{t'_B - t'_A}{w_A + w_B}$$

where:

t'_A is the retention time of component A;

t'_B is the retention time of component B;

w_A is the peak width at half-height of component A;

w_B is the peak width at half-height of component B.

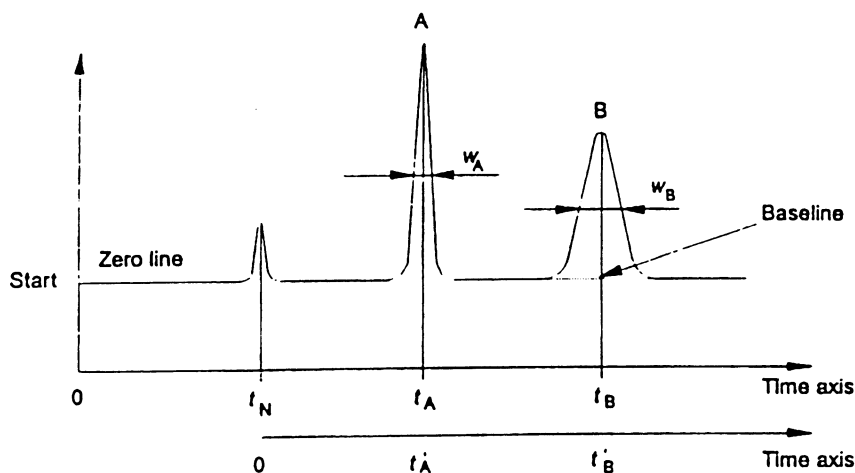


Figure 1 : Calculation of the resolution between peaks A and B

NOTE : t_N is the hold-up time zero of the column, i.e. the time taken for an inert component, such as methane, to travel through the column without chromatography taking place.

5.1.3 Devices for the control of the flow of carrier, reactor and detector gases

5.1.4 Recorder and/or integrator

An amplifier and potentiometric recording device, or an integrator or data processor system, giving area values corresponding to the peak area in square millimetres.

5.2 Injection device

5.3 Test sample container, normally with a capacity of between 10 ml and 100 ml, fitted with a self-sealing rubber septum coated with polytetrafluoroethylene (PTFE).

6 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in ISO 3170 or ISO 3171 and/or in accordance with the requirements of national standards or regulations for the sampling of petrol.