

Methods of test for petroleum and its products —

**BS 2000-466: Liquid petroleum
products — Unleaded petrol —
Determination of organic oxygenate
compounds and total organically bound
oxygen content by gas chromatography
using column switching**

(Identical with IP 466/2001)

The European Standard EN 13132:2000 has the status of a
British Standard

ICS 75.160.20

National foreword

This British Standard is the official English language version of EN 13132:2000.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

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

The Institute of Petroleum publishes and sells all parts of BS 2000, and all BS EN petroleum test methods that would be part of BS 2000, both in its annual publication “Standard methods for analysis and testing of petroleum and related products and British Standard 2000 parts” and individually.

Further information is available from:

**The Institute of Petroleum, 61 New Cavendish Street, London W1M 8AR.
Tel: 020 7467 7100. Fax: 020 7255 1472.**

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled “International Standards Correspondence Index”, or by using the “Find” facility of the BSI Standards Electronic Catalogue.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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

Summary of pages

This document comprises a front cover, an inside front cover, the EN title page, pages 2 to 21 and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

This British Standard, having been prepared under the direction of the Sector Committee for Materials and Chemicals, was published under the authority of the Standards Committee and comes into effect on 15 August 2000

© The Institute of Petroleum and BSI 08-2000

ISBN 0 580 36216 7

Amendments issued since publication

Amd. No.	Date	Comments

English version

Liquid petroleum products - Unleaded petrol - Determination of organic oxygenate compounds and total organically bound oxygen content by gas chromatography using column switching

Produit pétroliers liquides - Essence sans plomb -
Détermination des composés oxygénés organiques et de la
teneur totale en oxygène organique par chromatographie
en phase gazeuse avec commutation de colonnes

This European Standard was approved by CEN on 14 February 2000.

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.

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 Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.



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

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

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 September 2000, and conflicting national standards shall be withdrawn at the latest by September 2000.

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.

In this standard, annex A is normative and annex B is informative.

1 Scope

This European Standard specifies a gas chromatographic method using column switching 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 3,7 % (m/m) in unleaded petrol having a final boiling point not greater than 220 °C.

NOTE 1 The final boiling point can be measured by using prEN ISO 3405:1998 ¹⁾.

NOTE 2 For the purposes of this European Standard, the terms “% (m/m)” and “% (V/V)” are used to represent respectively the mass fraction and the volume fraction.

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 Directives²⁾.

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 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 standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170:1988, including Amendment 1:1998).*

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling (ISO 3171:1988).*

EN ISO 3675, *Crude petroleum and liquid petroleum products - Laboratory determination of density - Hydrometer method (ISO 3675:1998).*

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987).*

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 (ISO 3838:1983).*

EN ISO 12185, *Crude petroleum and petroleum products - Determination of density - Oscillating U-tube method (ISO 12185:1996).*

¹⁾ prEN ISO 3405:1998: Petroleum products - Determination of distillation characteristics at atmosphere pressure (ISO/DIS 3405:1998).

²⁾ EU Directive 85/210/EEC, Council Directive on the approximation of the laws of the Member States concerning the lead content of petrol. EU Directive 85/536/EEC, Council Directive on crude-oil savings through the use of substitute fuel components in petrol.

3 Principle

Oxygen containing organic compounds are isolated from the sample using a first capillary column. In a second capillary column the oxygen containing organic compounds are separated, and detected individually using a flame ionization detector.

NOTE Guidance on the column switching technique is given in annex B.

4 Reagents and materials

Use only reagents of recognized analytical grade and water conforming to grade 3 of EN ISO 3696.

4.1 Carrier gas

Hydrogen, helium, or nitrogen, free of hydrocarbons.

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	$(\text{CH}_3)_2\text{CHOH}$	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	$(\text{CH}_3)_3\text{COH}$	<i>tert</i> -butyl alcohol; TBA;
2-methylpropan-1-ol	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	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;
<i>tert</i> -butyl methyl ether	$(\text{CH}_3)_3\text{CO CH}_3$	methyl tertiary butyl ether; MTBE;
methyl <i>tert</i> -pentyl ether	$(\text{CH}_3)_2\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}_3$	tertiary amyl methyl ether; TAME;
ethyl <i>tert</i> -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
<i>tert</i> -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, or n-heptane

Petrol which has been examined to ensure that it contains no organic oxygenate compounds detectable by this method, or n-heptane.

5 Apparatus

Usual laboratory apparatus and glassware, together with the following:

5.1 Gas chromatographic assembly

5.1.1 Gas chromatograph, provided with a means for column switching, equipped with a programmable oven temperature controller, or controllers in the case of dual oven gas chromatographs, and a flame ionization detector (FID).

NOTE It is recommended that a system constructed entirely of glass from the sample injection port up to the detector system is used since petrol may contain organic oxygenate compounds which can give rise to corrosion and changes of retention times in systems constructed using metals.

5.1.2 Two capillary columns

NOTE Recommended columns are described in annex B.

The columns shall be coated with a suitable phase so that the required resolution between the components and between the components and the matrix to be determined, shall be at least 1 after elution from the second column.

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:

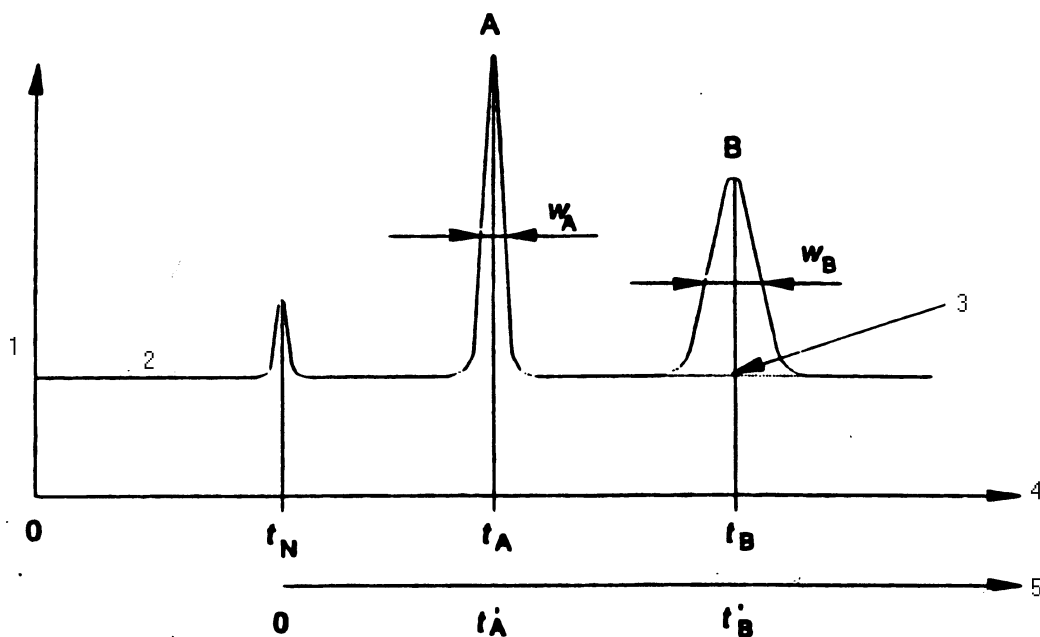
t'_A is the retention time of component A in s;

t'_B is the retention time of component B in s;

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

w_B is the peak width at half-height of component B in s;

1,18 is a factor originating from a peak resolution equation.



Key

- 1 Start
- 2 Zero line
- 3 Baseline
- 4 Time axis
- 5 Time axis

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.

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

5.1.3 Device for the control of the flow of carrier gas

5.1.4 Recorder and/or integrator

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

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).