



DRAFT INTERNATIONAL STANDARD ISO/DIS 22854

ISO/TC 28

Secretariat: ANSI

Voting begins on
2012-06-21

Voting terminates on
2012-11-21

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Liquid petroleum products — Determination of hydrocarbon types and oxygenates in automotive-motor gasoline — Multidimensional gas chromatography method

Produits pétroliers liquides — Détermination des groupes d'hydrocarbures et de la teneur en composés oxygénés de l'essence automobile pour moteurs — Méthode par chromatographie multidimensionnelle en phase gazeuse

[Revision of first edition (ISO 22854:2008)]

ICS 75.080

ISO/CEN PARALLEL PROCESSING

This draft has been developed within the European Committee for Standardization (CEN), and processed under the **CEN-lead** mode of collaboration as defined in the Vienna Agreement.

This draft is hereby submitted to the ISO member bodies and to the CEN member bodies for a parallel five-month enquiry.

Should this draft be accepted, a final draft, established on the basis of comments received, will be submitted to a parallel two-month approval vote in ISO and formal vote in CEN.

To expedite distribution, this document is circulated as received from the committee secretariat. ISO Central Secretariat work of editing and text composition will be undertaken at publication stage.

Pour accélérer la distribution, le présent document est distribué tel qu'il est parvenu du secrétariat du comité. Le travail de rédaction et de composition de texte sera effectué au Secrétariat central de l'ISO au stade de publication.

THIS DOCUMENT IS A DRAFT CIRCULATED FOR COMMENT AND APPROVAL. IT IS THEREFORE SUBJECT TO CHANGE AND MAY NOT BE REFERRED TO AS AN INTERNATIONAL STANDARD UNTIL PUBLISHED AS SUCH.

IN ADDITION TO THEIR EVALUATION AS BEING ACCEPTABLE FOR INDUSTRIAL, TECHNOLOGICAL, COMMERCIAL AND USER PURPOSES, DRAFT INTERNATIONAL STANDARDS MAY ON OCCASION HAVE TO BE CONSIDERED IN THE LIGHT OF THEIR POTENTIAL TO BECOME STANDARDS TO WHICH REFERENCE MAY BE MADE IN NATIONAL REGULATIONS.

RECIPIENTS OF THIS DRAFT ARE INVITED TO SUBMIT, WITH THEIR COMMENTS, NOTIFICATION OF ANY RELEVANT PATENT RIGHTS OF WHICH THEY ARE AWARE AND TO PROVIDE SUPPORTING DOCUMENTATION.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Full standard:
<https://standards.iteh.ai/catalog/standards/sist/fe7f9b82-25f5-4749-9ab8-d4414e01a5e1/iso-22854-2014>

Copyright notice

This ISO document is a Draft International Standard and is copyright-protected by ISO. Except as permitted under the applicable laws of the user's country, neither this ISO draft nor any extract from it may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, photocopying, recording or otherwise, without prior written permission being secured.

Requests for permission to reproduce should be addressed to either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Reproduction may be subject to royalty payments or a licensing agreement.

Violators may be prosecuted.

Contents

Page

| | |
|--|----|
| Foreword | iv |
| Introduction..... | v |
| 1 Scope | 1 |
| 2 Normative references | 1 |
| 3 Terms and definitions | 2 |
| 4 Principle..... | 2 |
| 5 Reagents and materials | 3 |
| 5.1 Gases | 3 |
| 6 Apparatus | 4 |
| 7 Sampling..... | 4 |
| 8 Procedure | 4 |
| 8.1 Conditioning | 4 |
| 8.2 Sample preparation | 4 |
| 8.2.1 Procedure B only – sample dilution | 4 |
| 8.2.2 Procedure A and B - sample cooling | 5 |
| 8.3 Test sample injection volume | 5 |
| 8.4 Verification of the apparatus and test conditions | 5 |
| 8.5 Validation..... | 5 |
| 8.6 Preparation of the test sample | 5 |
| 8.7 Preparation of the apparatus and test conditions | 5 |
| 9 Calculation | 5 |
| 9.1 General | 5 |
| 9.2 Calculation as percent mass fraction | 6 |
| 9.3 Calculation as percent volume fraction | 7 |
| 9.4 Calculation of total oxygen content in percent mass fraction..... | 9 |
| 9.5 Data report according to automotive motor gasoline specification | 9 |
| 10 Expression of results | 10 |
| 10.1 Procedure A | 10 |
| 10.2 Procedure B | 10 |
| 11 Precision..... | 10 |
| 11.1 General | 10 |
| 11.2 Repeatability | 10 |
| 11.3 Reproducibility | 10 |
| 12 Test report..... | 11 |
| Annex A (informative) Instrument specifications | 12 |
| Annex B (informative) Examples of typical chromatograms..... | 14 |
| Bibliography..... | 19 |

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

ISO 22854 was prepared by Technical Committee ISO/TC 28, Petroleum products and lubricants, and by Technical Committee CEN/TC 19, Gaseous and liquid fuels, lubricants and related products from petroleum, biologic and synthetic origin in collaboration.

This second edition cancels and replaces the first edition (EN ISO 22854:2008). The scope of the method has been updated to include petrol with higher oxygen percentages than mentioned in the first edition and the test is now applicable for automotive motor gasoline's up to and including 3,7 % (*m/m*) of oxygen and for ethanol (E85) automotive fuel which is used in so-called flex-fuel vehicles. See also the Introduction. In addition some procedural text has been updated and the examples of chromatograms in Annex B have been improved.

Introduction

This edition of ISO 22854 is an update of the first edition of 2008. Originally the document was used for determination of saturated, olefinic, aromatic and oxygenated hydrocarbons in automotive motor gasoline according to European fuel specifications. Recent Round Robin work has shown that the scope of the method can be updated without alteration to include petrol with higher oxygen percentages than mentioned in the first edition and will now be applicable for automotive motor gasoline up to and including E10.

An interlaboratory study organized by CEN has shown that the method can also be used for high-ethanol gasoline (also called ethanol automotive fuel, E85), provided that the sample is diluted with a component that will not interfere with any of the components or group of components that need to be analysed. Details of how to perform such analysis are given in Clause 13.

The derived precision data for methanol do not comply with the precision calculation as presented in this International Standard. No precision calculation for methanol has been established as the need for such data has not been expressed. If any of these oxygenated compounds are present in the automotive motor gasoline sample, it is appropriate that their contents best be verified by use of other appropriate test methods, for instance as given in EN 228 [1].

The test method as described in this International Standard is harmonized with ASTM D6839 [2].

ITeH STANDARD PREVIEW
(standards.iteh.ai)
Full standard:
<https://standards.iteh.ai/catalog/standards/sist/fe719b0c-25f5-4749-9ab8-d4414e01a5e1/iso-22854-2014>

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Full standard:
<https://standards.iteh.ai/catalog/standards/sist/fe7f9b82-25f5-4749-9ab8-d4414e01a5e1/iso-22854-2014>

Liquid petroleum products — Determination of hydrocarbon types and oxygenates in automotive-motor gasoline — Multidimensional gas chromatography method

1 Scope

This International Standard specifies the gas chromatographic (GC) method for the determination of saturated, olefinic and aromatic hydrocarbons in automotive motor gasoline. Additionally, the benzene content, oxygenate compounds and the total oxygen content can be determined.

This method defines two procedures, A and B.

Procedure A is applicable to automotive motor gasoline with a total volume fraction of aromatics of up to 50 %; a total volume fraction of olefins from about 1,5 % up to 30 %; a volume fraction of oxygenates, from 0,8 % up to 15 %; a total mass fraction of oxygen from about 1,5 % to about 3.7 %; and a volume fraction of benzene of up to 2 %.

Although this test method can be used to determine higher-olefin contents of up to 50% (V/V), the precision for olefins was tested only in the range from about 1,5 % (V/V) to about 30% (V/V).

Although specifically developed for the analysis of automotive motor gasoline that contains oxygenates, this test method can also be applied to other hydrocarbon streams having similar boiling ranges, such as naphthas and reformates.

Procedure B describes the procedure for the analysis of oxygenated groups in (automotive) ethanol fuels containing an ethanol volume fraction between 50 % and 85 %. The gasoline is diluted with an oxygenate-free component to lower the ethanol content to a value below 20 % before the analysis by GC.

NOTE 1 For the purposes of this document, the terms “% (m/m)” and “% (V/V)” are used to represent respectively the mass fraction, μ , and the volume fraction, φ .

NOTE 2 For Procedure A, precision data have been established for the oxygenate compounds in automotive motor gasoline samples containing ethyl-tert-butyl ether (ETBE), methyl-tert-butyl ether (MTBE), tert-amyl-methyl ether (TAME), iso-propanol, iso-butanol, tert-butanol, methanol and ethanol. The derived precision data for methanol do not comply with the precision calculation as presented in this International Standard. Applicability of this International Standard has also been verified for the determination of n-propanol, acetone, and di-isopropyl ether (DIPE). However, no precision data have been determined for these compounds. For Procedure B the precision can be used for an ethanol fraction from about 50% (V/V) up to 85% (V/V), total ether fraction from about 0,5% (V/V) up to 11% (V/V) and a total C3 to C5 alcohol fraction from about 1% (V/V) up to 6% (V/V). Methanol can also be determined using this procedure, but no precision data was established.

NOTE 3 While developing this test method, the final boiling point was limited to 215 °C.

NOTE 4 An overlap between C9 and C10 aromatics can occur. However, the total is accurate. Isopropyl benzene is resolved from the C8 aromatics and is included with the other C9 aromatics.

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.

ISO 3170:2004, *Petroleum liquids — Manual sampling*.

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling*.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

hydrocarbon group

family of hydrocarbons such as saturated hydrocarbons, olefinic hydrocarbons, etc.

3.1.1

saturated hydrocarbon

saturate

type of straight-chain or cyclic hydrocarbon that contains no double bonds with a carbon number of 3 to 12

EXAMPLE *n*-Paraffins, iso-paraffins, naphthenes and poly-naphthenes.

3.1.2

olefinic hydrocarbon

olefin

type of straight-chain hydrocarbon that contains double or triple bonds with a carbon number of 3 to 10

EXAMPLE *n*-Olefins, iso-olefins and cyclic olefins.

3.1.3

aromatic hydrocarbon

aromatic

type of cyclic hydrocarbon that contains double or triple bonds

EXAMPLE Benzene, toluene and higher homologous series with a carbon number of 6 to 10 and naphthalenes, with a carbon number of up to 12.

3.2

oxygenate

oxygenated compound

type of straight-chain or cyclic hydrocarbon that contains an oxygen group, the addition of which is allowed according to current petrol specifications

EXAMPLE Alcohols and ethers.

NOTE See Clause 1, Note 3.

3.3

partial group

PG

one carbon number in an individual group, being either a single compound like toluene or an isomeric mixture

EXAMPLE *n*-Butane and *iso*-butane.

4 Principle

4.1 Procedure A and Procedure B use the same separation technique and analysis procedure, the difference between the parts is that for Procedure B the sample is diluted. The diluting solvent is considered in the integration, this makes it possible to report the results of the undiluted sample after normalization to 100 %.

4.2 The automotive motor gasoline sample being analysed is separated into hydrocarbon groups by means of gas chromatographic analysis using special column-coupling and column-switching procedures.

The automotive motor gasoline sample is injected into the gas chromatographic system and, after vaporization, is separated into the different groups. Detection is always done by a flame ionization detector (FID).

4.3 The mass concentration of each detected compound or hydrocarbon group is determined by the application of relative response factors (see 9.1) to the area of the detected peaks, followed by normalization to 100 %. For automotive motor gasoline samples containing oxygenates that cannot be determined by this test method, the hydrocarbon results are normalized to 100 % minus the value of oxygenates as determined by another method. The liquid volume concentration of each detected compound or hydrocarbon group is determined by the application of density values (see 9.2) to the calculated mass concentration of the detected peaks followed by normalization to 100 %.

IMPORTANT — It is essential to the correct execution of the method that great care be taken to ensure that all compounds are correctly identified. This is especially true for the identification of oxygen-containing compounds because of their wide range of response factors. It is, therefore, highly recommended for correct identification to verify possibly unknown oxygenates using a reference mixture that contains these pure compounds.

4.4 After this analysis, the automotive motor gasoline is separated into hydrocarbon groups and then by carbon number. By the use of the corresponding relative response factors, the mass distributions of the groups in the automotive motor gasoline sample can be calculated.

5 Reagents and materials

5.1 Gases

NOTE Installation of suitable moisture filters is recommended for helium and hydrogen lines.

5.1.1 Hydrogen, 99,995 % pure.

DANGER — Hydrogen is explosive when mixed with air at concentration between 4 % volume fraction and 75 % volume fraction. See the equipment manufacturers' manuals concerning leaks in the system.

5.1.2 Helium, 99,995 % pure.

5.1.3 Compressed air.

5.2 Vials, airtight and inert, e.g. with rubber-membrane caps covered with self-sealing polytetrafluoroethylene (PTFE).

5.3 Reference solutions, finished automotive motor gasoline(s) used as reference and which contain components and concentration levels comparable to those of the test sample.

The composition of the reference solution should have been determined in a round robin or by other methods.

DANGER — Flammable. Harmful if inhaled.

NOTE Sulfur-containing compounds are irreversibly adsorbed in the olefins trap and can reduce its capacity to retain olefins. Sulfur can also be adsorbed in the alcohol and ether-alcohol-aromatic traps. Although the effect of low amounts of sulfur components on the various traps or columns is very small, it is important to exercise care with automotive motor gasoline samples with high levels of sulfur.

5.4 Diluting solvent, used in Procedure B, shall not interfere with any other component in gasoline being analyzed. Dodecane (C₁₂H₂₆) or tridecane (C₁₃H₂₈) are recommended solvents.

6 Apparatus

6.1 Gas chromatograph, computer-controlled, multidimensional GC equipment, injector, FID, suitable columns, traps and hydrogenation catalysts, of which an example is given in Annex A.

6.2 Switching valves, suitable switching valves that are used for the transfer of compounds from one column to the other in the gas chromatograph.

They shall have a chemically inactive surface and a small dead volume.

6.3 Traps, suitable short columns (see Annex A for an example) used for retaining certain selected chemical groups of the automotive motor gasoline using temperature control.

The absorption of the trapped compounds shall be reversible.

EXAMPLE A typical sequence is the following.

- First, the alcohols and higher-boiling aromatics are absorbed in a trap (sulfate column I). The remaining aromatics are separated from the other components by means of a polar column (for example, OV 275).
- The ethers are separated from the remaining fraction by means of another trap (sulfate column II).
- The olefins are separated from the saturates by the olefin trap (for example, silver salt) in two steps. This is necessary due to the limited capacity of such traps to retain high amounts of butene or total olefins. If the trap capacity is sufficient for the olefin concentration, the separation may be performed in one step.
- Next, the remaining saturated hydrocarbons are separated into paraffins and naphthenes according to their carbon number using a 13X molecular sieve column.
- The ethers are then eluted from the trap (sulfate column II) and separated and detected according to boiling point.
- The olefins are desorbed from the olefin trap and hydrogenated in the Pt-column. They are separated and detected as the corresponding saturated compounds using a 13X molecular sieve.
- The alcohols and higher-boiling aromatics are eluted from the polar column and the trap (sulfate column I), separated using a non-polar column (for example, OV 101 methyl silicone) and detected according to boiling point.

Examples of typical chromatograms with this order of elution of the hydrocarbon fractions are shown in Figures B.1 and B.2. Specifically for Procedure B, a typical chromatogram is shown in Figure B.6.

7 Sampling

Unless otherwise required by national standards or by the regulations for the sampling of automotive motor gasoline, samples shall be taken in accordance with ISO 3170 for manual sampling or in accordance with ISO 3171 for automatic pipeline sampling.

8 Procedure

8.1 Conditioning

Condition the apparatus according to the manufacturer's instructions after shutdowns.

8.2 Sample preparation

8.2.1 Procedure B only – sample dilution

The procedure as described in this section is used to analyse gasoline samples containing higher amounts of ethanol such as automotive ethanol fuel (E85) with ethanol content between 50 % (V/V) and 85 % (V/V).