
**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*

ISO 22854:2008

<https://standards.iteh.ai/catalog/standards/sist/032fcafc-4b3d-40d8-b843-6736ea92a2a9/iso-22854-2008>



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Published in Switzerland

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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 the European Committee for Standardization (CEN) Technical Committee CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*, in collaboration with Technical Committee ISO/TC 28, *Petroleum products and lubricants*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

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Introduction

This first edition of ISO 22854 is an update of the first edition of EN 14517:2004 [10]. Recent round-robin work has been incorporated to check whether the precision data for additional oxygenates fall within the ones given in Table 5. The scope has been updated. An instrument configuration has been added to the informative Annex A, describing an optimal set-up for the apparatus. In addition, Tables 1 and 2, with response factors, have been updated based on recent experimental data.

Originally the document was used for determination of saturated, olefinic and aromatic hydrocarbons in automotive motor gasoline according to European fuel specifications. The method is applicable for finished automotive motor gasoline with a total aromatic content up to 50 % (V/V) and a total olefin content from about 1,5 % (V/V) up to 30 % (V/V).

The inter-laboratory study within CEN had been performed on automotive motor gasoline samples with a maximum of 30 % (V/V) olefin content. Within some countries, the need for higher olefin percentages was expressed and an inter-laboratory study had been set up to determine precision data for automotive motor gasoline samples with higher olefin contents of up to 50 % (V/V). In the first round robin, no samples with a high-olefin content in this range were delivered and hence they could not be taken into account (see test after Note 3 in the Scope). Once further results are known, this International Standard will be updated.

Applicability of this test method has also been verified for the determination of *n*-propanol, acetone, and diisopropyl ether (DIPE). However, no precision data have been determined for these compounds. 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 D 6839 [2].

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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 total oxygenate content can be determined.

This International Standard is applicable to automotive motor gasoline with a total content of aromatics of up to 50 % (V/V); a total olefin content from about 1,5 % (V/V) up to 30 % (V/V); oxygenate compounds, from 0,8 % (V/V) up to 15 % (V/V); a total oxygen content from about 1,5 % (m/m) to about 3 % (m/m); and a benzene content of up to 2 % (V/V).

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

NOTE 2 While developing this method, the final boiling point was limited to 215 °C.

NOTE 3 For oxygenate compounds, precision data have been established on 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.

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.

NOTE 4 There can be an overlap between C9 and C10 aromatics. 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 referenced documents are indispensable for the application of this document. 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 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, such as *n*-butane and *iso*-butane

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4 Principle

4.1 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).

4.2 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.

4.3 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.

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5 Reagents and materials

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5.1 Gases

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

5.1.1 Hydrogen, 99,999 % pure.

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

5.1.2 Helium, 99,999 % 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.

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, for example, 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 can 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 platinum 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.

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 Preparation of a test sample

Cool the test sample to prevent loss by evaporation. Transfer a sufficient portion of the test sample to a vial (5.2) and immediately tightly close and seal it using the self-sealing PTFE cap.

It is advised to cool the test sample to a temperature between 0 °C and 5 °C.

8.3 Test sample injection volume

Size the injection volume of the test sample in such a way that the capacity of the columns is not exceeded and that the linearity of the detector is valid.

NOTE An injection volume of 0,1 μl has proven satisfactory.

8.4 Verification of the apparatus and test conditions

Run the reference solution (5.3) and check for correct instrument parameters, cutting times and grouping times. If they are not correct, adjust the apparatus to the manufacturer's recommendations and rerun the reference solution.

Attention should be paid to components, such as benzene, olefins and oxygenates, that are near the boundaries of separation on the group-selective columns. Care should be taken to accurately identify the oxygen-containing compounds. It is recommended to verify the identity of possible oxygenates using a reference material that contains the pure component of interest. Annex B shows several chromatograms specifically for oxygenate compounds, providing evidence of their elution times and possible interferences.

8.5 Validation

Reprocess the validation reference solution and compare the obtained results with the consensus values. The absolute deviation from the consensus values shall not be greater than the reproducibility for the parameters as given in Clause 11.

It is strongly recommended to run the validation reference solution weekly to check the proper functioning of the equipment.

The validation reference solution(s) should contain the components in amounts similar to those found in the test samples. Validation of the apparatus should be performed prior to the analysis of any new oxygenates.

8.6 Preparation of the test sample

Prepare the test sample as specified in 8.2 and 8.3.

8.7 Preparation of the apparatus and test conditions

Set up the apparatus in accordance with 8.1 and check it out in accordance with 8.4.

9 Calculation

9.1 Calculation as percent mass fraction

The integrated peak areas are employed for the calculations. The peaks are arranged according to their presence in the groups described in Clause 3. Tables 1 and 2 give the relative response factors of partial groups and for oxygenated compounds. After correcting with the response factors, the mass contributions for all partial groups are calculated and normalized to 100 % (*m/m*). The partial groups are then classified according to the hydrocarbon type and carbon number.

If single compounds, e.g. oxygenate compounds, are determined by a different but accepted method, e.g. EN 1601 [3], ASTM D4815 [4], EN 13132 [5] or ASTM D5599 [6], they shall be excluded from integration. The total area is then not normalized to 100 %, but to 100 % minus the excluded quantified component. The external quantification shall be noted in the report.