



## ISO/TC 28 Petroleum products and lubricants Advisory Group

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**ISO/TC 28 AG N 240**

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**To: Members of the ISO/TC 28 AG**

Dear Member,

### **Discussion document on a proposal for new work for a replacement for the FIA method**

Please find attached a discussion document on the above submitted by Ortwin Costenoble, Netherlands.

This document will be discussed under agenda item 12 at the forthcoming ISO/TC 28/AG meeting, and under item 6.8 at the forthcoming [22<sup>nd</sup>] ISO/TC 28 meeting.

Yours sincerely

**Paula Watkins**

Paula Watkins  
Secretary to ISO/TC 28

## 22<sup>nd</sup> meeting of ISO/TC 28, November 2002 Milan Proposal for new work, parallel with CEN

### Replacement of FIA method

#### 1) Background

At the moment the text of the European test method prEN 14517 is being drafted for enquiry stage. This method is titled "Liquid petroleum products — Determination of hydrocarbon types and oxygenates in petrol — Multidimensional gas chromatography method". This method has been accepted for measuring olefin, aromatics and benzene content of European unleaded petrol (EN 228). It has been acknowledged as a multi-use method identifying both hydrocarbons and benzene, whereas a study on oxygenates determination has been intensified.

Several parties concerned around the globe, especially in Asia, show great interest adopting an international method on this subject, if available. Also in America there is interest in a FIA replacement method for multi-purpose use. ASTM has started drafting work for a ballot on a similar document replacing ASTM D 1319.

#### 2) Proposal

Following the Vienna Agreement, NEN would propose to start parallel work (CEN-lead) on this method. However, we also acknowledge that CEN will soon enter the enquiry stage on this document and that adopting it into the ISO/TC 28 work program will involve administration and renumbering of the document. This might unnecessarily slow down the process in CEN. Therefore we can, from a more practical point of view see adoption without change of the standard by ISO/TC 28 right after official CEN publication, or even better, having the adoption questionnaire being sent around within ISO/TC 28 at the formal vote stage in CEN.

All these options require consideration by the ISO/TC 28 secretariat in cooperation with the correct CEN partners.

#### 3) Scope of the work item

This International Standard specifies the gas chromatographic determination of saturated, olefinic and aromatic hydrocarbons in finished petrol. Additionally, the benzene content, oxygenate compounds and the total oxygenate content can be determined.

The method is applicable for finished petrol with total aromatic content up to 50 % (V/V), total olefin content from about 1,5 % (V/V) up to 30 % (V/V), oxygenate compounds up to 15 % (V/V) and benzene less than 2 % (V/V).

#### 4) Principle of the method

The sample to be analyzed is separated into hydrocarbon group types by means of gas chromatographic analysis using special column-coupling and column-switching procedures.

The sample is injected in the gas chromatographic system and after vaporization separated into the different groups. Detection shall always be done by FID (flame ionization detector).

The mass concentration of each detected compound or hydrocarbon group is determined by the application of response factors to the area of the detected peaks followed by normalization to 100 %. For 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 such as EN 1601 or EN 13132. The liquid volume concentration of each detected compound or hydrocarbon group is determined by application of density factors to the calculated mass concentration of the detected peaks followed by normalization to 100%.

A typical sequence is, for example: 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 (OV275). 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 (Silver salt) in two steps. This is necessary due to the limited capacity of such traps for high amounts of butene or high total olefin contents. Permitting trap capacity and 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 atom number using a 13X column. The ethers are then eluted from the 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 column. The alcohols and higher-boiling aromatics are eluted from the OV275 and Sulfate I column and separated and detected according to boiling point.

After this analysis the petrol is separated into hydrocarbon groups and carbon numbers. By the use of the corresponding response factors (see Table 1) the mass distributions of the groups can be calculated.

## 5) Apparatus

### Gas chromatograph

Computer controlled multi dimensional GC equipment, Injector, FID. Suitable columns, traps, and hydrogenations catalysts are described in annex A.

The test equipment shall be set up to work according to the above mentioned method and have all the necessary items installed (check specifications of the supplier).

### Switching valves

Suitable switching valves which are used for the transfer of compounds in the gas chromatograph from one column to the other. They shall have a chemically inactive surface and a small dead volume.

### Traps

Suitable short columns used for retaining certain selected chemical groups of the petrol using temperature control. The absorption of the trapped compounds shall be reversible.

## 6) Procedure

### 6.1 Preparing the apparatus

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

### 6.2 Preparation of a sample for analysis

A generic sample is cooled to prevent loss by evaporation. A vial fitted with a cap of rubber-membrane covered with self-closing PTFE is filled with the sample to test.

The sample is transferred to the sample vial and the vial is tightly closed immediately.

### 6.3 Injection volume

The injection volume shall be sized in such a way that the capacity of the columns is not exceeded and that the linearity of the detector is valid.

Proven is an injection volume of 0,1 µl.

### 6.4 Verification of proper function

NOTE As the separation performance of the columns may vary by stock and also can decrease in time, the columns should be verified with a reference sample in regular time intervals.

#### 6.4.1 Take a sample of known composition.

6.4.2 Run the sample and check for correct instrument parameters, cutting times and grouping times. If they are not correct adjust your instrument to the manufacturer's recommendations and rerun the sample.

NOTE 1 The composition of the sample should have been determined in a round robin or by other methods. The known composition should show the same properties as are to be determined.

NOTE 2 Attention should be paid to components that are on the boundary of separation on the group selective columns. Examples are benzene, olefins and oxygenates.

## 6.5 Validation

Reprocess the validation sample and compare the obtained contents with the consensus values. The absolute difference to the consensus values should not be greater than the reproducibility for the parameters in the Table under 9.

It is strongly recommended to run the consensus sample weekly to check the proper function of the equipment.

NOTE The validation sample or samples should contain components and amounts as found in the samples to be analyzed. Introduction of new oxygenates to be analyzed requires prior validation of the instrument.

## 7) Preparation

### 8) Calculation

#### 8.1 Calculation as % (m/m)

By means of integration the areas under the peaks are determined. The peaks are arranged according to their presence in the groups described in 4. After correcting with the response factors, the mass contribution for all partial groups is calculated and normalized to 100 % (m/m). The partial groups are now classified according to the hydrocarbon type and carbon number.

$$RRF_i = \frac{((C_{aw} \times C_n) + (H_{aw} \times H_n)) \times 0,7487}{C_{aw} \times C_n} \quad (1)$$

where

$RRF_i$  = relative response factor for a hydrocarbon type group of a particular carbon number.

$C_{aw}$  = atomic mass of carbon, 12,011;

$C_n$  = number of carbon atoms in the group;

$H_{aw}$  = atomic weight of hydrogen, 1,008;

$H_n$  = number of hydrogen atoms in the group;

0,7487 = the correction factor to set the response of methane to unity.

#### 8.2 Calculation as % (V/V)

The conversion into % (V/V) is done using the densities of the partial groups. For 15 °C the group density values are shown in Table 3 and Table 4. The conversion is done according to:

$$j_{pg} = m_{pg} * r_{PG} / \sum m_{PG} \times r_{PG} \quad (2)$$

in which:

$j_{PG}$  is the volume fraction of the partial groups PG

$m_{PG}$  is the mass fraction of the partial group PG

$r_{PG}$  is the value of the partial group PG

#### 8.3 Calculation of total oxygen content (in % (m/m))

For each identified oxygenate component  $i$ , calculate the oxygen content according to the following formula:

$$O = \sum \frac{n \times W_o}{W_i} \mu_i \quad (3)$$

where

$n$  the number of oxygen atoms in the molecule (generally 1);

$W_o$  the atomic mass of oxygen;

$W_i$  the molecular mass of oxygenate component;

$\mu_i$  the mass fraction of the component in the mixture, in % (m/m);

## 9) Precision

The precision shall be given as determined by statistical examination of inter-laboratory test results in accordance with ISO 4259.

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 values give in the Table only in one case in twenty.

The difference between two single and independent 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 values given in the Table only in one case in twenty.

**Repeatability and Reproducibility**

Component or group	Repeatability (V/V)	Reproducibility (V/V)
Aromatics	$r = 0,009\ 5\ X + 0,195\ 2$	$R = 0,045\ 0\ X + 0,138\ 4$
Olefins	$r = 0,018\ 5\ X + 0,141\ 5$	$R = 0,117\ 6\ X + 0,511\ 8$
Benzene	$r = 0,014\ 7\ X + 0,003\ 1$	$R = 0,077\ 7\ X - 0,025\ 0$
Oxygenate compounds	$r = 0,019\ 3\ X + 0,002\ 4$	$R = 0,025\ 1\ X + 0,351\ 5$