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# METHODS OF ANALYSIS

## DETERMINATION OF INSPECTION PARAMETERS OF DIESEL FUELS

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*A method is developed for determining the inspection parameters of diesel fuels using gas chromatography. After one measurement which lasts on the order of 140 min, it is possible to determine the n-paraffin content, distillation curve, cetane number, density, and flash point of a sample. The proposed method can be used by any manufacturers, suppliers, refiners, and purchasers of crude oil cuts or petroleum products and control laboratories and research organizations.*

The development of gas chromatographic methods using high-performance capillary columns made it possible to determine the detailed hydrocarbon composition (DHC) of naphtha cuts and commercial gasolines. Based on DHC data, methods have been proposed for calculating the effective parameters of petroleum products, including the inspection parameters of automotive gasolines [1-8].

Data on a metrologically certified method of determining the fundamental inspection parameters of automotive gasolines using gas chromatography were reported for the first time in [9-11]. In 2001, a State Standard, STB 1276–2001 [12], which regulates the method of determining the parameters of automotive gasolines, was developed, approved, and enacted in The Republic of Belarus' in 2001.

In the same year, the Laboratory of Analytical Studies at the Institute of Nuclear Problems in the State University was accredited for testing automotive gasolines under the indicated standard. Two successive years of intensive laboratory work demonstrated the relatively high demand for studies of diesel fuels as well.

The advances in gas chromatography are small with respect to diesel fuel inspection parameters. The distribution by boiling points is the only index regulated by standards [8]. The Laboratory was given the "minimum" task of determining the distillation curve, cetane number, density, and flash point of diesel fuel based on DHC data.

The following equipment was used for gas chromatographic measurement of these characteristics:

* CrystalLux-4000 gas chromatograph with a flame ionization detector – FID – (detection limits no greater than $2 \cdot 10^{12}$ °C/sec) and programming of column thermostat temperature from 50 to 320°C at the rate of 2°C/min;

* UniChrom* system [13, 14] for recording, processing, and storing the chromatographic data;

*The UniChrom system with the CrystalLux-4000 chromatograph is used for monitoring and controlling the chromatograph regimes. Its software allows processing and calculating the parameters of automotive gasolines and diesel fuels with the method of execution of measurements (MEM).

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*Rtx®-1 PONA quartz capillary chromatographic column (length: 100 m, diameter: 0.25 mm, film thickness: 0.5 μm) with nonpolar polydimethylsiloxane stationary liquid phase.

The chromatography conditions were:

* initial column thermostat temperature of 50°C, duration of initial isothermal section of 5 min, thermostat heating rate of 2°C/min, final column thermostat temperature of 320°C, duration of final isothermal section of 0 min;

* injector temperature of 300°C, separation factor at 35°C 1:100, sample volume of 0.2-0.6 ml;

* detector temperature of 300°C, hydrogen flow rate (fuel gas) of 30 ml/min, air flow rate (oxidizing gas) of 300 ml/min, helium (blowing) flow rate of under 30 ml/min;

* carrier gas: helium, pressure at column inlet 400 kPa, flow rate through column at 50°C 3.3 ml/min.

After entering the chromatograph, the fuel sample was converted to the vapor phase in the injector and was transferred to the column by the helium carrier gas, where the hydrocarbon components were separated in the order of their boiling points. The components were captured by the FID as they left the column.

The detector signal was processed by the recording system, which found the peaks, determined the areas under them, and identified them by comparing the retention parameters with the tabular parameters.

The content of the individual hydrocarbons was determined by normalizing the area. The cetane number and distillation curve were calculated with the content of the individual substances in the analyzed sample and the density and flash point were calculated with the cetane number and distillation curve.

The control samples of diesel fuel were prepared at Mozyr' Refinery and sent to accredited laboratories for analysis of the petroleum products by standard methods [15-19]. Each control sample was thus investigated

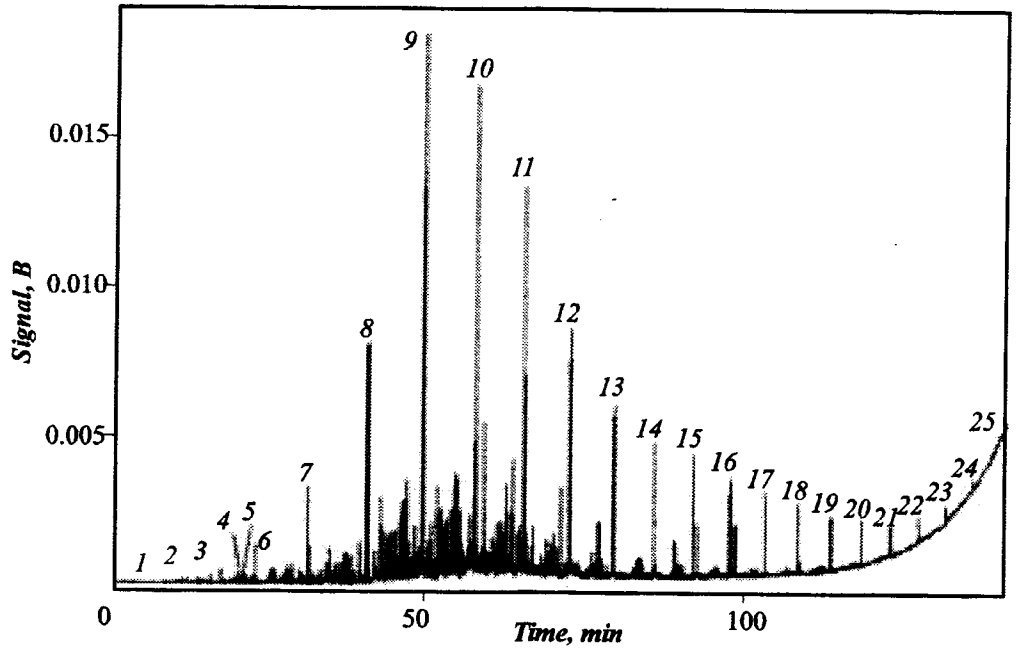


Fig. 1. Overall shape of the chromatogram of diesel fuel: 1) *n*-pentane; 2) *n*-hexane; 3) *n*-heptane; 4) 2-methylheptane; 5) 4-methylheptane; 6) *n*-octane; 7) *n*-nonane; 8) *n*-decane; 9) *n*-undecane; 10) *n*-dodecane; 11) *n*-tridecane; 12) *n*-tetradecane; 13) *n*-pentadecane; 14) *n*-hexadecane; 15) *n*-heptadecane; 16) *n*-octadecane; 17) *n*-nonadecane; 18) *n*-eicosane; 19) *n*-heneicosane; 20) *n*-docosane; 21) *n*-tricosane; 22) *n*-tetracosane; 23) *n*-pentacosane; 24) *n*-hexacosane; 25) *n*-heptacosane.

at the central plant laboratories at Mozyr' and Novopolotsk Refineries and in 202 laboratories of the Chemmotological Center of the Republic of Belarus' Ministry of Defense.

The metrological characteristics of the samples were determined with the data obtained – the certified values of the distillation curve, cetane number, density, flash point, and the boundaries of the absolute error of the certified characteristic for a confidence level of 0.95.

## IDENTIFICATION AND CONTENT OF INDIVIDUAL HYDROCARBONS

Diesel fuel contains compounds of different classes – paraffins, aromatics, naphthenes, unsaturated hydrocarbons, etc. However, it is based on *n*-paraffins and aromatics. The localized peaks of *n*-paraffins and distributed peaks of aromatic compounds determine the special overall shape of the chromatogram of diesel fuel (Fig. 1).

TABLE 1

| Number of diesel fuel chromatographic group | Chromatographic group | *A* (±0.1) | Number of diesel fuel chromatographic group | Chromatographic group | *A* (±0.1) |
|---|---|---|---|---|---|
| 1 | Under *n*-pentane | 36.1 | 25 | Between *n*-hexadecane and *n*-heptadecane | 44.9 |
| 2 | *n*-Pentane | 82.1 | 26 | *n*-Heptadecane | 57.2 |
| 3 | Between *n*-pentane and *n*-hexane | 53.0 | 27 | Between *n*-heptadecane and *n*-octadecane | 54.0 |
| 5 | *n*-Hexane | 34.4 | 28 | *n*-Octadecane | 56.3 |
| 6 | Between *n*-hexane and *n*-heptane | 78.7 | 29 | Between *n*-octadecane and *n*-nonadecane | 54.8 |
| 7 | *n*-Heptane | 47.3 | 30 | *n*-Nonadecane | 54.3 |
| 8 | Between *n*-heptane and *n*- octane | 13.6 | 31 | Between *n*-nonadecane and *n*-eicosane | 54.5 |
| 9 | *n*-Octane | 36.5 | 32 | *n*-Eicosane | 63.1 |
| 10 | Between *n*-octane and *n*-nonane | 52.6 | 33 | Between *n*-eicosane and *n*-heneicosane | 49.1 |
| 11 | *n*-Nonane | 52.6 | 34 | *n*-Heneicosane | 57.2 |
| 12 | Between *n*-nonane and *n*-decane | 39.9 | 35 | Between *n*-heneicosane and *n*-docosane | 57.8 |
| 13 | *n*-Decane | 42.9 | 36 | *n*-Docosane | 52.3 |
| 14 | Between *n*-decane and *n*-undecane | 52.4 | 37 | Between *n*-docosane and *n*-tricosane | 53.3 |
| 15 | *n*-Undecane | 52.7 | 38 | *n*-Tricosane | 57.5 |
| 16 | Between *n*-undecane and *n*-dodecane | 43.7 | 39 | Between *n*-tricosane and *n*-tetracosane | 55.8 |
| 17 | *n*-Dodecane | 42.7 | 40 | *n*-Tetracosane | 60.0 |
| 18 | Between *n*-dodecane and *n*-tridecane | 39.9 | 41 | Between *n*-tetracosane and *n*-pentacosane | 48.2 |
| 19 | *n*-Tridecane | 32.7 | 42 | *n*-Pentacosane | 53.1 |
| 20 | Between *n*-tridecane and *n*-tetradecane | 29.5 | 43 | Between *n*-pentacosane and *n*-hexacosane | 35.6 |
| 2 | *n*-Tetradecane | 98.7 | 44 | *n*-Hexacosane | 66.3 |
| 21 | Between *n*-tetradecane and *n*-pentadecane | 75.6 | 45 | Between *n*-hexacosane and *n*-heptacosane | 38.0 |
| 22 | *n*-Pentadecane | 72.9 | 46 | *n*-Heptacosane | 43.2 |
| 23 | Between *n*-pentadecane and *n*-hexadecane | 56.0 | 47 | After *n*-heptacosane | 55.2 |
| 24 | *n*-Hexadecane | 81.7 | | | |

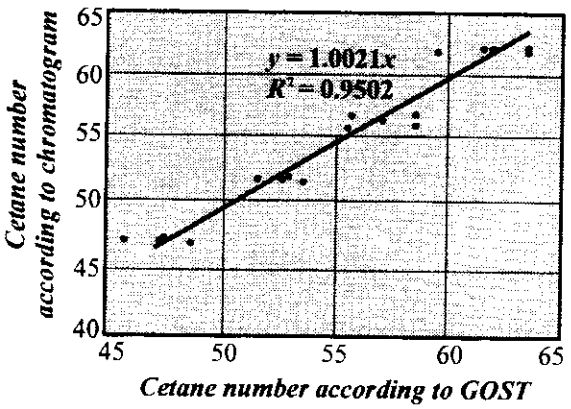


Fig. 2. Difference between values of cetane number determined with GOST 3122 (difference from average result of ±2 units) and chromatogram (±0.5 unit).

The number of peaks in the chromatogram varied from 700 to 900 as a function of the fuel sample and method of integration used. $C_5$-$C_{28}$ *n*-paraffins form a clearly visible ridge of peaks which is easy to verify by chromatographing a mixture of *n*-paraffins in the conditions indicated above.

More detailed identification of the individual hydrocarbons in the diesel fuel is not required to solve the "minimum" problem.

The content $X_i$ of individual compounds is determined by the method of internal normalization with the equation:

$$X_i = A_i / \sum_{j=1}^{L} A_j$$

where $A_i$, $A_j$ are the area under the peak of the $i^{th}$ and $j^{th}$ components; $L$ is the number of peaks in the chromatogram.

The relative sensitivity coefficients of the FID were close for all compounds and were not taken into consideration in calculating the concentrations.

## CETANE NUMBER

The gas chromatographic method of determining the cetane number is based on the assumption that a certain effective cetane number corresponds to each individual component of the fuel. The effective cetane number $A$ of fuel as a mixture is found by summation of the products of the proportion of individual components by their effective cetane numbers.

For simplifying the calculation procedure, the chromatogram was divided into 47 groups (Table 1):

$$A = \sum_{i=1}^{47} X_i A_i \qquad (1)$$

where $X_i$ is the total proportion of hydrocarbons of the $i^{th}$ fraction; $A_i$ is the effective cetane number for the $i^{th}$ fraction according to Table 1.

The values of the effective cetane number $A$ calculated by the method of linear regression with an error no greater than ±0.1 unit are reported in Table 1.

Based on the results of determining the cetane number (Fig. 2), the difference of the value calculated with the chromatogram from the value obtained on a standard one-cylinder engine [15] did not exceed 0.5 unit.

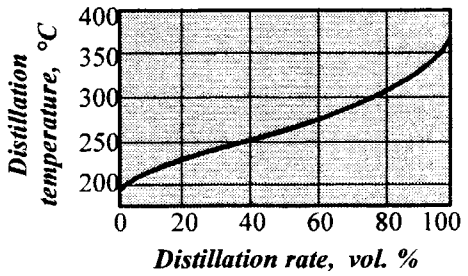


Fig. 3. Example of the distillation curve of diesel fuel obtained with the chromatogram.

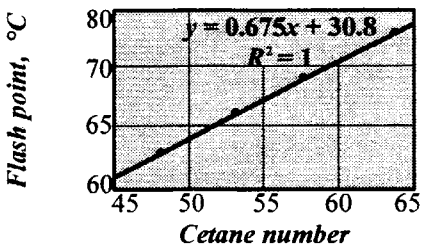


Fig. 4. Flash point vs. cetane number of diesel fuel.

**DISTILLATION CURVE**

This index is determined in two stages. The distribution of the cuts by boiling points is first found with the method in [8] and then converted from boiling points to distillation temperatures with the method in [17]. In contrast to the method in [8], the calculation is performed with the chromatogram, which is a discrete spectrum of peaks, with the method in [17]. The position of *n*-paraffins is clear here and eliminates the necessity of preliminary calibration of the system with a mixture of *n*-paraffins.

The curve of the boiling points according to [8] and the distillation temperatures according to [17] is a polynomial of the form:

$$t_\chi = 9.12 \cdot 10^{-16}\left(t_\chi^*\right)^2 - 1.446 t_\chi^* + 268 \qquad (2)$$

where $t_\chi$ is the distillation temperature corresponding to fraction $\chi$ (%) of distillation of the petroleum product according to [17], °C; $t_\chi^*$ is the boiling point of fraction $\chi$ (%) of the mixture according to [8], °C.

The difference between the distillation temperature measured with the chromatogram and the temperature determined with the method in [17] does not exceed 15°C.

An example of the distillation curve obtained with the chromatographic data is shown in Fig. 3.

**DENSITY**

The density $\rho$ (g/cm$^3$) of diesel fuel at 15°C is calculated with the equation:

$$\rho = 1.0593 - \sqrt{0.5352 + 0.000715 t_{50} - 0.1263(\lg t_{50})^2 + 0.00129 A}$$

where $t_{50}$ is the distillation temperature of 50% of the diesel fuel calculated with Eq. (2), °C; $A$ is the cetane number calculated with Eq. (1).

TABLE 2

| Indexes | Convergence index* | Limits of absolute error* |
|---|---|---|
| Cetane number | 0.3 | ±3 |
| Distillation curve, °C | | |
| 50% | 1.5 | ±15 |
| 96% | 1.5 | ±15 |
| Density at 20°C, kg/m$^3$ | 1.4 | ±8 |
| Flash point (closed cup), °C | 0.2 | ±6 |

Note. * For 0.95 confidence level.

**FLASH POINT (closed-cup)**

It was experimentally found that the flash point $t_f$ (°C) of diesel fuel is a linear function of the cetane number (Fig. 4). It is calculated with the equation:

$$t_f = 0.675A + 30.8$$

where $A$ is the cetane number calculated with Eq. (1).

**METROLOGICAL CHARACTERISTICS OF THE METHOD**

The method can be used to determine the physicochemical properties of diesel fuels with an error no greater than the values reported in Table 2. The values of the absolute error are due to the errors of the control samples of diesel fuels. The error of the method can be reduced by increasing the number of certified laboratories participating in certification of the samples.

It is thus possible to determine a set of important properties of diesel fuel with the results of only one gas-chromatographic analysis lasing approximately 140 min: *n*-paraffin content; distillation curve corresponding to GOST 2177; cetane number corresponding to GOST 3122; density corresponding to GOST 3900; flash point corresponding to GOST 6356.

The method can be used as an alternative to GOST, ISO, ASTM, and EN methods and in organizations that do not have special equipment for reproducing the standard methods. The stability of the reproducibility of the results allows clearly distinguishing petroleum products that do not correspond to their certificates in case of adulteration (mixing and diluting).

The possibility of calculating a relatively large number of effective parameters of both intermediate and commercial petroleum products using the data from hydrocarbon analysis allows using the MEM in refineries for constructing systems for predicting and optimizing compounding processes in manufacture of gasolines and jet and diesel fuels.

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