METHODS OF ANALYSIS

GAS CHROMATOGRAPHIC ANALYSIS OF AUTOMOBILE GASOLINES

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Control of technological parameters of oil refining processes requires detailed qualitative and quantitative analysis of the hydrocarbon composition of both crude oil and its fractions. Many analytical equipment manufacturers offer systems for such analysis [1 - 6].

Based on detailed hydrocarbon analysis (DHA) of gasolines, their fractional composition [7 - 9], saturated vapor pressure, density, and antiknock rating (knock resistance) expressed as octane number found by investigative and motor methods (RM and MM) can be calculated by a computer. Knowing the qualitative and quantitative composition of the gasolines, one can determine the content of n-paraffin, isoparaffin, aromatic, naphthene, and olefin (PIANO) groups of hydrocarbons as well as of oxyorganic compounds (alcohols and ethers) used to raise the octane number [6],

The opportunity for solving similar problems arises from application of high-resolution capillary columns
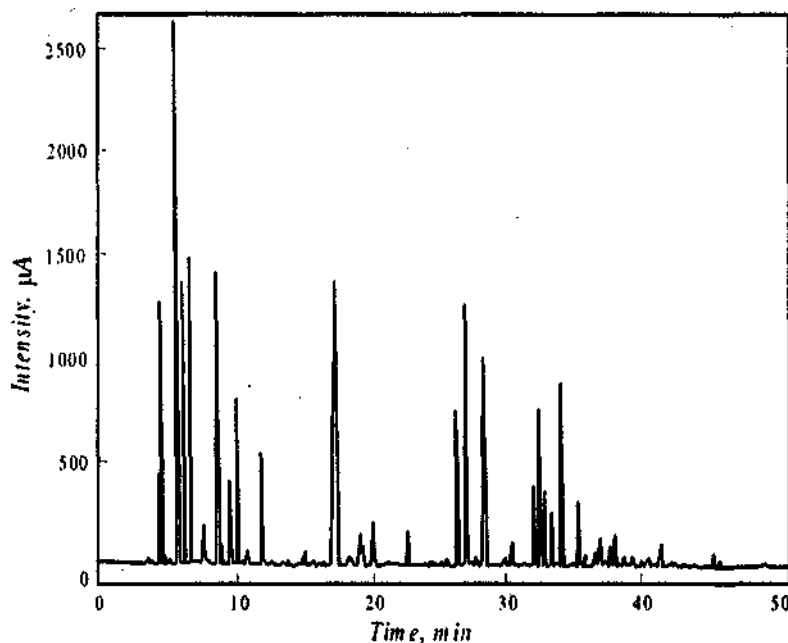

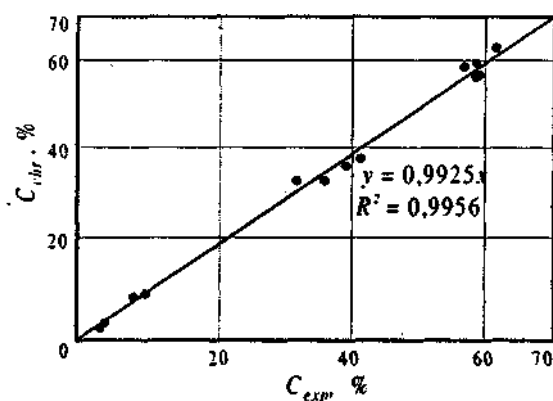Fig. 1. Typical chromatogram of automobile gasolines.

Fig. 2. Divergence between concentrations C_{chr} and C_{exp} of hydrocarbon groups determined respectively by the proposed method and the method used by the Mozyr Refinery *(R* is the correlation factor).
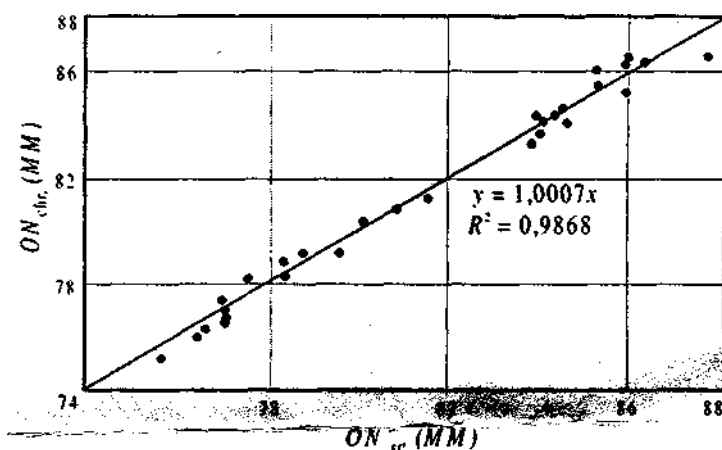

Fig. 3. Divergence between octane numbers ON_{chr} and ON_{st} obtained by MM and determined from the chromatogram and in keeping with GOST 511—82.

that allow complete separation of all hydrocarbon components (as many as 1000) of the analysis mixes. Use of analytical systems with such columns makes stringent demands on standards of data processing systems, especially on the algorithm for automatic identification of the found components. For instance, the well-known Hewlett-Packard and Varian software packages for detailed hydrocarbon analysis (DHA) are designed for operation with chromatographic data recording and processing systems (Chemstation and Star Workstation, respectively) of these companies only.

Control laboratories analyzing gasolines are generally equipped with a variety of gas chromatographs. And it is natural for analytical chemists to aspire to work with a DHA system that can be realized at the existing analytical equipment park.

Such demands are met by the system Unichrom-97 developed for recording, storing, and processing of chromatographic information [10]. It is equipped with a broad-range stand-alone analog-to-digital converter with a built-in low-current precision amplifier that allows one to record signals directly from the chromatograph detector, and, thanks to this, to connect the system to any type of chromatograph.

We have collected and systematized tabular data on the main hydrocarbons contained in gasolines. A procedure has been worked out for detailed analysis of the hydrocarbon composition and calculation of the key characteristics of unethylated automobile gasolines. The methods of calculation of the complex characteristics of these gasolines have been programmed and the developed software package has been integrated into the system Unichrom-97.

TABLE 1

Sr. No. of chromatographic gasoline group	Chromatographic group	Molecular mass	Saturated vapor pressure, kPa	Octane number	
				MM	RM
1	Up to n-butane	47	496.1	102.57	125.44
2	n-Butane	48	348.5	88.9	113.12
3	Between n-butane and 2-methylbutane	47	286.9	80.34	215.66
4	2-Methylbutane	72	141.5	89:78	96.25
5	Between 2-methylbutane and n-pentane	70	123.3	115.08	180.32
6	n-Pentane	72	107.8	59.71	30.85
7	Between n-pentane and 2-methylpentane	76	67.8	110.37	122.76
8	2- and 3-Methylpentanes and intermediate components	86	44.6	74.6	108.9
9	Between 3-methylpentane and n-hexane	82	36.3	77.28	104.4
10	n-Hexane	86	34.3	38.23	19.46
11	Between n-hexane and benzene	92	30.6	58.26	124.14
12	Benzene	78	22.3	87.33	111.94
13	Between benzene and 2-methylhexane	95	19.3	41.48	43.47
14	2- and 3-Methylhexanes and intermediate components	100	16.6	89.5	55.74
15	Between 3-methylhexane and n-heptane	96	14.6	91.53	90.36
16	n-Heptane	100	11.2	34.38	15.04
17	Between n-heptane and toluene	94	10.6	49.56	34.38
18	Toluene	92	7.2	93.85	126.28
19	Between toluene and 2-methylheptane	114	5.3	70.07	188.36
20	2- and 3-Methylpentanes and intermediate components	114	4.8	36.83	16.15
21	Between 3-methylpentane and n-octane	113	4	48.48	25.18
22	n-Octane	114	3.6	45.59	32.85
23	Between n-octane and ethylbenzene	126	2.7	49.22	39.55
24	Ethylbenzene	106	2.5	84.27	248.76
25	Between ethylbenzene and m-xylene	127	2.4	36.57	14.8
26	*m*- and p-Xylenes and intermediate components	106	2.3	109.87	62.54
27	Between *p*- and o-xylenes	127	2	33.39	19.95
28	o-Xylene	106	1.8	120.04	58.62
29	After o-xylene and up to n-nonane	130	1.3	34.49	16.1
30	Between n-nonane and n-decane	134	0.9	82.23	138.58
31	n-Decane and components after n-decane.	141	0.4	98.65	48.49

The procedure has been approved in three organizations: at the Scientific Research Institute of Nuclear Problems of the Belarus State University on a Tsvet-500 chromatograph, at the State Specialized Criminology Center of the Ministry of Internal Affairs of Belarus on an HP5890 chromatograph, and at the open joint-stock company Mozyr' Refinery on an HP589011 chromatograph. Identical columns HP-1 No. 19091 Z-115 were installed on all three chromatographs. Data recording and processing
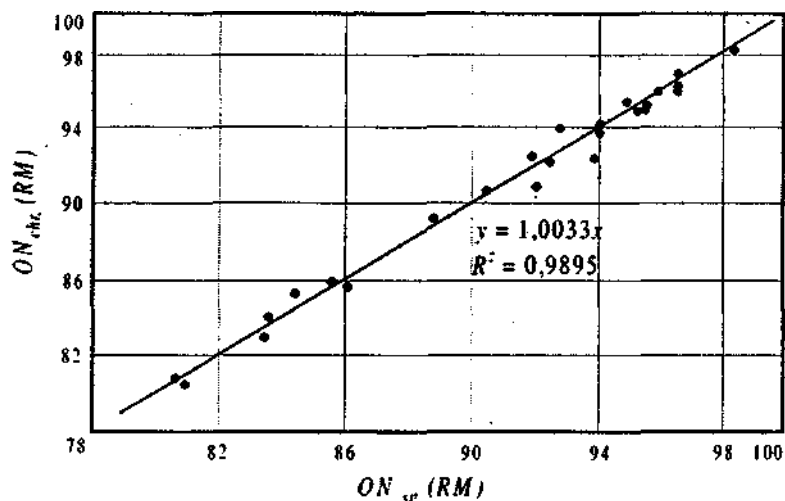
Fig. 4. Divergence between octane numbers ON_{chr} and ON_{st} obtained by RM and determined from the chromatogram and in keeping with GOST 8226—82.
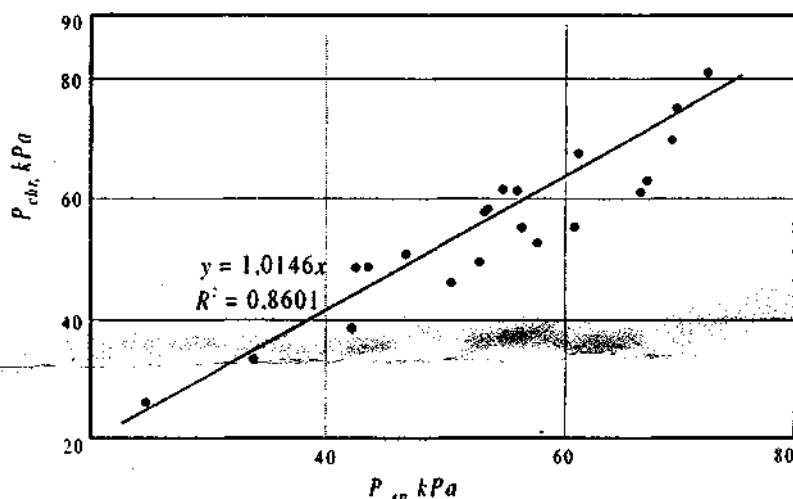

Fig. 5. Divergence between saturated vapor pressures P_{chr} and P_{st} determined from the chromatogram and in keeping with GOST 1756—52.

were done by the Unichrom system. On the Tsvet-500 chromatograph, to achieve stability and reproducibility of the obtainable data, all the temperature parameters were controlled directly by the Unichrom system without use of the standard control unit BU-125.

To perform interlaboratory comparative measurements, 20 samples of gasoline mixes were prepared at the fuel laboratories of the Novopolotsk and Mozyr' refineries as well as at the "Khimmotology" Center of Fuels of the MO RB (Ministry of Defense, Belarus). Their octane numbers based on RM and MM were determined on UIT-80 apparatuses in conformity respectively with GOST 8226—82 and GOST 511—82, fractional composition with GOST 2177—82 through 2% distillation, saturated vapor pressure with GOST 1756—52, and density with GOST 3900—82. In addition, investigated were samples of AI-98-grade high-octane gasolines produced in Finland.

Identification and Content of Individual Hydrocarbons

At the first stage of the gasoline analysis, the recorded chromatograms were interpreted (Fig. 1). The components with a concentration higher than 0.1 wt. % were identified. Initially, a library was built up to store data on reduced times as well as on linear and logarithmic retention indices of the most common gasoline
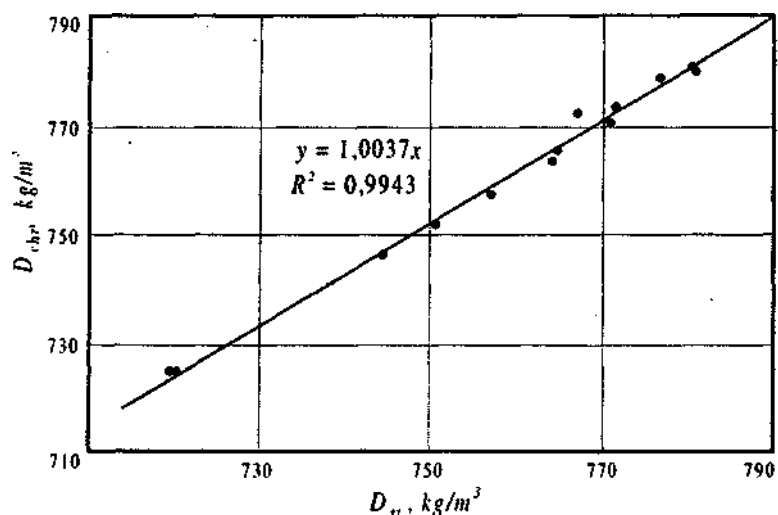
Fig. 6. Divergence between the densities D_{chr} and D_{st} determined from the chromatogram and in keeping with GOST 3900—82.

components.

For this purpose, on an HP-1 No. 19091 Z-115 capillary column (length 50 m, inner diameter 0.32 mm, film thickness 0.52 mm, dimethylpolysiloxane as the nonpolar liquid phase) were recorded chromatograms of standardized mixes produced by Supelco: PIANO-mix No. 4-7489, Petroleum Refinery Reformate No. 4-4593, Qualitative Reference Alkylate Standard No. 4-8267, Qualitative Reference Reformate Standard No. 4-8266, and Qualitative Reference Naphtha Standard No. 4-8265.

The peaks not indicated in the certificates for these mixes were identified on a HP 5890/5972 chromatomass spectrometer. In all, 330 peaks ranging from methane to n-hexadecane were identified. The mole fraction of the unidentified peaks of the test gasolines is generally not higher than 0.5%. The individual components were identified from the relative retention indices. The weight content of each component was calculated by the internal standardization method taking account of the detector response factor.

The concentrations of various classes of hydrocarbon groups were determined by summation of the measured concentrations of individual components. In order to determine the reproducibility of the quantitative hydrocarbon group analysis data by the method developed at the Mozyr' Refinery, the concentration data for these groups in five samples of gasoline mixes were given. Comparative analyses showed that the relative hydrocarbon group measurement error does not exceed 3% (Fig. 2).

Antiknock Rating

Gas-chromatographic method of determination of this characteristic expressed by octane number is based on the hypothesis that to each individual gasoline component corresponds a particular effective octane factor. The effective octane number of a gasoline as a mixture is determined by summing up the derivatives of the mass proportion of individual components into their effective octane factors.

To simplify the calculation procedure, the chromatogram is divided into 31 groups [1, 2]:

$$\theta = \sum_{i=1}^{31} W_i \theta_i$$

where q is the octane number of the gasoline, W is the mass proportion of the *i*-th octane group of the gasoline, and q is the effective octane number of the components of the *i*-th group.

The effective octane factors found by us by the linear regression method from the chromatographic data for the samples of the certified gasolines are listed in Table 1.
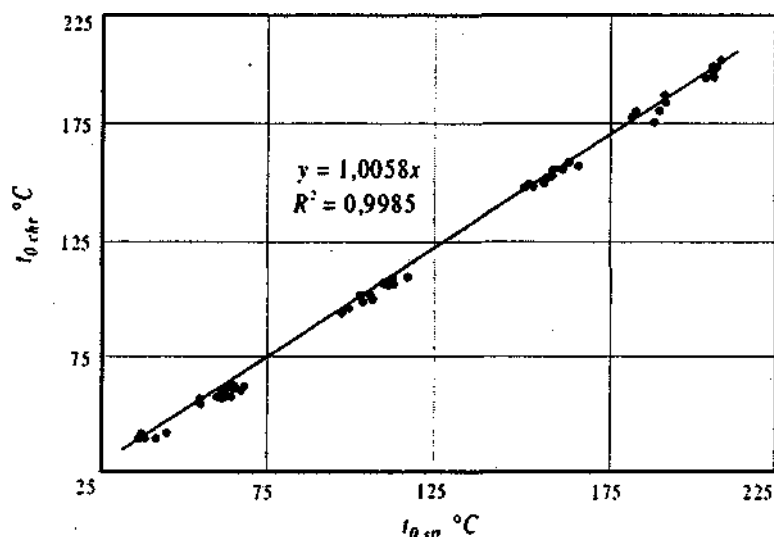
Fig. 7. Divergence between distillation temperature t_{0chr} and t_{0st} of fractions determined from the chromatogram and by the GOST 2177—82 method.
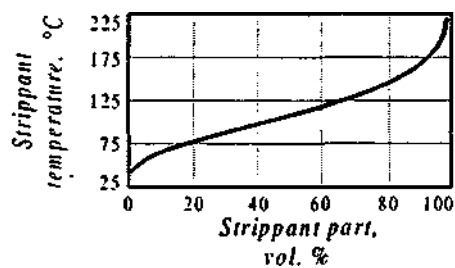

Fig. 8. Example of gasoline distillation curve obtained from the chromatogram.

An analysis of the octane numbers obtained by motor (Fig. 3) and research (Fig. 4) methods revealed that the octane number calculated from the chromatogram does not differ from the octane number determined on a standard single-cylinder engine in keeping with GOST 511—82 and GOST 8226—82 by more than 0.5 unit.

Saturated Vapor Pressure

The saturated vapor pressure, which is a gasoline characteristic of practical importance, is a function of molecular composition of the gasoline and can be calculated from the chromatographic data derived by DHA using the equation:

$$P = \sum_{i=1}^{31} C_{gi} p_i^0$$

where P is the saturated vapor pressure, C_{gi} is the mole fraction of the i-th octane group of the gasoline, p_i^0 is the effective partial pressure of the components of the i-th group determined from Table 1.

The saturated vapor pressure calculated from the chromatogram does not deviate from that measured in keeping with GOST 1756—52 by more than 5 pa (Fig. 5).

Density

Density is calculated by the equation:

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TABLE 2

Indexes	Convergence, %	Interlaboratory reproducibility, %	Determination error, %	Basic absolute error range at 0.95% fiducial probability
Distillation				
IBP	-	-	4.6	±9.2
10, 50, and 90 *%*	0.4	0.7	2.0	±4.1
EP	-	-	3.2	±6.5
Saturated vapor pressure P	1.0	0.03P-0.5	0.057P+2.8	±(0.116P+5.5)
Octane number				
MM	0.1	0.2	1.2	±2.4
RM	0.1	0.2	1.0	±2.0
Density	1.2	2.0	1.0	±4.5

$$D = \sum_{i=1}^{n} X_i \rho_i$$

where D is the density of the gasoline, X_i is the volume proportion of the i-th component, ρ_i is the density of the i-th component, and n is the number of peaks on the chromatogram.

The density calculated from the chromatogram does not deviate from the density derived in keeping with GOST 3900—82 by more than 3 kg/m^3 (Fig. 6).

Fractional Composition of Gasolines

The fractional composition of gasolines is determined from the chromatogram that represents a discrete spectrum of identified peaks. It allows one to certify in a single measurement cycle the fractional composition and all the above-listed characteristics of the gasoline. In addition, it makes precalibration of the system with a mixture of n-paraffins unnecessary [8].

The dependence of the distillation temperature t determined in keeping with GOST 2177—82 on the boiling point t_b determined by the method in [8] is a polynomial of the type:

$$t_0 = \sum_{i=0}^{n} a_i t_b^i$$

where a_i is the coefficient of the polynomial and n is the exponent of the polynomial.

The exponent of the polynomial is chosen on the basis of the required measurement precision. For instance, at $n = 3$. the distillation temperature measured from the chromatogram does not deviate from that determined by the GOST 2177—82 method by more than 2°C (Fig. 7).

An example of the distillation curve constructed from the chromatographic data is given in Fig. 8.

Metrological Characteristics of the Method

This method has passed through the Belarus State Standard certification process and has been registered as MVI.MN 998—99 [11]. It is assigned for determination of the following characteristics of unethylated automobile gasolines:

• volumetric, mass, and molar content of individual hydrocarbons and PIANO groups as well as of oxyorganic compounds in the 0.01 - 90 wt. % range;

• fractional composition (initial boiling point, 10%, 50%, 90%, end point) in the 25 - 260°C range;
• saturated vapor pressure at 37.8°C in the 20 - 100 kPa range;
• octane number based on MM and RM in the 70-90 and 80 - 100 unit range;
• density at 20°C in the 700-800 kg/m^3 range.

The relative error in the measurement of the volumetric, mass, and molar content of individual hydrocarbons and groups thereof is not higher than ± 3.6% and the relative convergence index is 0.7%. The errors in the determination of other characteristics are not higher than the values cited in Table 2,

Thus, from the results of just one gas-chromatographic analysis of a gasoline sample, that takes about 70 min, one can determine in a complex all the important characteristics of the gasoline. The reproducibility of results is better than the reproducibility attained by the respective standard methods.

The proposed method can be used by organizations that do not have specific equipment for reproducing standard methods. Stable reproducibility of results makes it possible to clearly show the nonconformity of the gasolines to their certificates in cases of adulteration (mixing and dilution).

Users of DHA systems may be any producers, suppliers, or consumers of oil products or oil fractions as well as control laboratories and organizations engaged in oil and oil products research. The possibility of high-precision calculation based on DHA of quite a large number of effective parameters of both intermediate and commercial oil products allows use of the proposed method for constructing, at oil refining enterprises, systems for predicting and optimizing compounding (blending) processes in production of gasolines, jet fuels, and diesel oils [12],

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