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APPLYING THE GAS CHROMATOGRAPHIC METHOD FOR THE DETECTION OF ADULTERATED WINDSHIELD WASHER FLUIDS

SUMMARY. The purpose of the paper is to develop a method for the detection of alcohol in the car care products to identify their adulterations. Using the method of gas chromatography, the authors investigate commercial samples of windshield washer fluids for winter period. The authors propose the variant of the gas chromatography analysis of windshield washer fluids using capillary columns of non-polar phase. The perfect separation of components is achieved, which allows determining the compliance of goods with their specifications. The graduation of the chromatograph for individual components is carried out. The concentrations and the type of alcohol in the windshield washer fluids are determined without additional sample preparation. The temperature of fluid crystallization is determined by Bauman-Froma's method. It is stated that in the market, there are adulterated brands of windshield washer fluids where methyl alcohol is used as a basis. The proposed chromatographic method can be recommended for the detection of alcohol in windshield washer fluids.

KEY WORDS. Gas chromatography, windshield washer fluids, identification.

Nowadays, in the market of car care products, the problem of adulteration of windshield washer fluids is very critical. Previously, ethanol had been used as the organic component of the "washer"; later, it was replaced by methanol. Now only isopropylic alcohol (IPA) is permitted to be used in windshield washers on the territory of the Russian Federation [1-2]. Since in the market the percentage of counterfeit alcohol is significant, some manufacturers of windscreen washer fluids find it possible to use confiscated surrogate vodka, thus the problem of determining the compliance of washers with their specifications is quite critical. Therefore the purpose of this research is to develop the rapid method of qualitative and quantitative detection of spirits (ethanol, methanol, IPA) in windshield washer fluids.

There are two types of washers (Table 1): the first one is used in summer period and the second one is used in winter. Since the fluid must not freeze under low temperatures, it contains a large amount of alcohol, glycols and a small amount of SAA as a moisturizing agent [3-4].

According to the production specifications, the compliance assessment of the compound composition is based only on determining the freezing temperature of the solution, without identifying the spirits included. However, there are techniques of determining the spirit concentrations and their identification, based on the gas chromatography method.

Table 1

The compound composition of windshield washer fluids

Component	Mass fraction, %	
	Compound 1 (Summer)*	Compound 2 (Winter)*
IPA	10.0	45.0-70.0
SAA	0.5-0.7	0.5-2.0
Flavoring	0.05-0.1	0.3-0.5
Colorant	0.001-0.0001	0.001-0.0001
Water	Up to 100	Up to 100

*The compound data are based on the production specifications [3-4].

The experiment. The chromatographic analysis was carried out with 3 calibration solutions on the *Kristall 2000M* gas chromatograph (Khromatek ltd., Russia), with the flame ionization detector (FID). The components were separated on the DB-1 fused silica capillary column, with the length of 60 m, the inner diameter of 0.32 mm, the stationary phase film thickness of 24 µm. The evaporator temperature was 290 °C; the detector temperature was 300 °C. The programmed mode of the thermostat was: 70 (1 minute delay) — 265 °C. The linear rate of the temperature increase was 5 degree / min. The linear rate of the carrier gas (helium) was 25 cm / sec. The option of the probe insertion with flow division was used. The division ratio was 1:15.

The chromatographic analysis of calibration solutions, prepared by the volumetric method and consistent dilution, resulted in the deduction of linear equations giving the opportunity to calculate the spirit concentrations in fluids.

All the values of the fluid density were measured with an areometer. The spirit concentrations were determined on the calibrating curve, plotted basing on the reference dependence of the values of density on the volumetric spirit concentrations, according to the density values.

Results and discussion. The water solutions under investigation are recommended to be used under negative temperatures; therefore it was important to find out their crystallization points. For all the samples of fluids, the crystallization temperature was determined at the Bauman-From's apparatus [5]. The freezing temperatures declared by the manufacturer and the determined ones are presented in Table 2. Many samples failed the tests: the ice was found inside the apparatus at the temperature higher than that declared by the manufacturer.

As many samples failed the crystallization temperature test, it was necessary to determine the volumetric concentrations of spirits contained in the antifreeze solutions.

On the assumption that the washing fluids are prepared from water and alcohol only, according to the dependence of the density on the spirit concentrations, the spirit concentrations were determined in the solutions under investigation. The results of these measurements are presented in Table 2. As the analyzed compounds contain other additives, the density cannot be considered as an objective value when determining the alcohol concentration.

Table 2

Physicochemical properties of the fluids

Sample No.	Density, g/cm^3, at 20 °C	Declared t_{cryst}, °C	Determined t_{cryst}, °C
1	0.920	- 30	- 23
2	0.962	- 20	- 15
3	0.963	- 20	- 18
4	0.972	- 25	- 20
5	0.940	- 20	- 24
6	0.905	- 30	- 23.5
7	0.960	- 31	- 20.5
8	0.968	- 30	- 25

Washer fluids may contain such spirits as methanol, ethanol, and IPA. To separate the polar compounds including spirits, packed columns with polymer sorbing agents are often used. In alcoholic beverage industry, to control the trace elements including spirits, capillary columns with a polar phase, e.g. FFAP, Carbowax, are used [7-9]. However, these types of phases are unable to dissociate the critical pair of components, IPA and ethanol, effectively. To solve this problem, we should use the phase which would separate methanol, ethanol, and IPA basing on their boiling temperatures. Such phases are non-polar liquid phases, e.g. methylsilicone and its analogues. To separate the volatile organic compounds, polar and non-polar phases are used.

The chromatographic analysis of calibration solutions resulted in determining the linear dependencies of the component areas and their concentrations, as well as in identifying the type of spirit in the washer fluids. For example, in Fig.1, there is a chromatogram of the artificial spirit mixture with the concentrations: methanol — 25% of vol., ethanol — 50% of vol., IPA — 25% of vol. As the chromatogram demonstrates, the separation number for spirits (Trennzahl — TZ) is not less than 3, which is sufficient for the correct integration of the component peaks and their quantitative determination.

Fig. 2 presents a fragment of the chromatogram of sample No. 1, it is seen that the main component is IPA (the retention time is 4.28 min). The chromatograms of samples No. 2-6 are similar to it. It is necessary to emphasize that in addition to spirits, other components are eluted in the chromatograms. For example, in Fig. 1, a component with the retention time of 7.03 min appeared. It can be assumed that this compound is added as a flavoring. From all the analyzed samples, only samples No. 7 and 8 contain methanol as the alcohol base (Fig. 3-4).

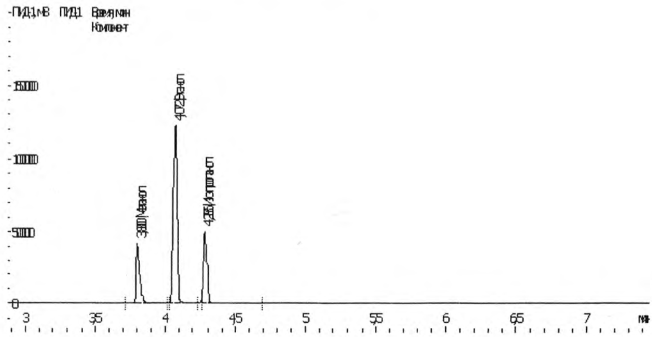

Fig. 1. The fragment of the chromatogram of the reference spirits (methanol, ethanol, and IPA)

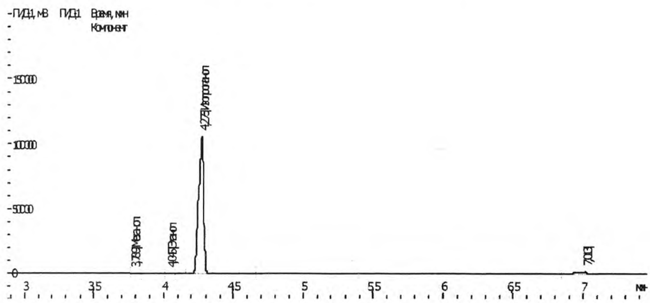

Fig.2. The fragment of the chromatogram of washer sample No. 1.

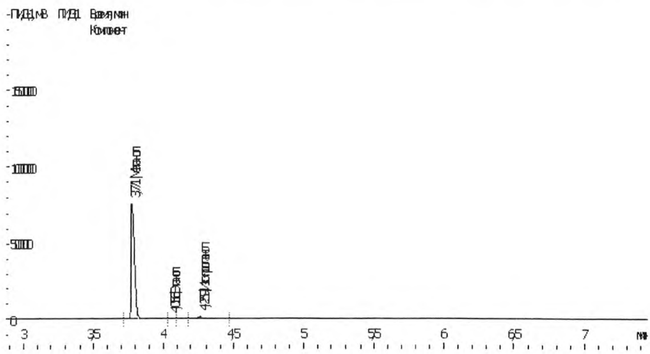

Fig.3. The fragment of the chromatogram of washer sample No. 7.

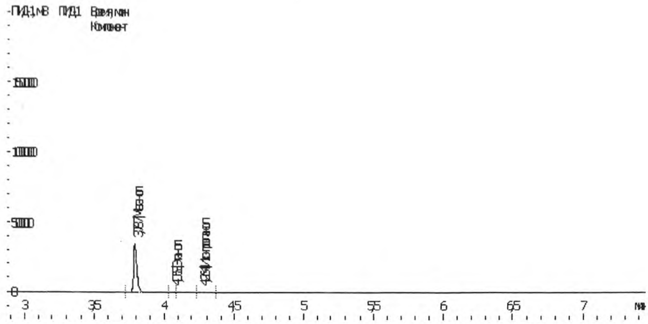

Fig.4. The chromatogram of washer sample No. 8.

Table 3 demonstrates the experimental data on spirit concentrations determined by two methods (by density and by the results of gas-liquid chromatography).

Table 3

Physicochemical parameters of the fluids

Sample number	Density g/cm^3, at 20 °C	Volumetric spirit concentration (by density)	Volumetric spirit concentration (by results of GLPC)
1	0.920	43.5	30.0
2	0.962	23.8	22.7
3	0.963	23.2	34.0
4	0.972	18.0	25.6
5	0.940	36.8	52.9
6	0.905	57.4	51.6
7	0.960	22.3 (MeOH)	32.2 (MeOH)
8	0.968	16.6 (MeOH)	28.3 (MeOH)

According to the labels of the washers under investigation, the main organic component in all the fluids is IPA. This is an important fact which must be emphasized: it is forbidden to use methanol and ethanol in washer fluids.

Thus, among eight washer fluid samples under investigation, two samples do not match the declared specifications on the alcohol composition (IPA is declared on the label). The majority of the samples fail the freezing test.

REFERENCES

1. Resolution of Chief Public Health Official of the Russian Federation No. 4 dd. 25.05.2000 «*O zapreshhenii ispol'zovanija stekloomyvajushhih zhidkostej, soderzhashhih metilovyj spirt (metanol)* [On Prohibition of Windshield Washer Fluids Containing Methyl Alcohol (Methanol)]» (in Russian).

2. Resolution of Chief Public Health Official of the Russian Federation No. 47 dd. 11.07.2007 «*O prekrashhenii ispol'zovanija metilovogo spirta v sredstvah po uhodu za*

avtotransportom [On Cessation of Use of Methyl Alcohol in Car Care Products]» (in Russian).

3. Technical Specification 2384-004-73146355-2006 — *«Zhidkosti stekloomyvajushhie «Navigator»* [*Navigator* Windshield Washer Fluid]» (in Russian).

4. Technical Specification 2384-006-73146355-2007 — *«Zhidkosti stekloomyvajushhie universal'nye* [Universal Windshield Washer Fluids]» (in Russian).

5. National Standard 18995.5-73 (CMEA Standard 2336-80, CMEA Standard 2343-80) *Produkty himicheskie organicheskie. Metody opredelenija temperatury kristallizacii* [Organic Chemicals. Methods of Determining the Crystallization Temperature] (in Russian).

6. Sakodynskiy, K.I., Panina, L.I. *Polimernye sorbenty dlja molekuljarnoj hromatografii* [Polymeric Sorbing Agents for Molecular Chromatography]. Moscow: Nauka, 1977. 168 p. (in Russian).

7. Russian National Standards 51786-2001. *Vodka i spirt jetilovyj iz pishhevogo syr'ja. Gazohromatograficheskij metod opredelenija podlinnosti* [Vodka and Ethyl Alcohol from Food Raw Material. Gas Chromatographic Method of Determining Authenticity] (in Russian).

8. National Standard 30536-97. *Vodka i spirt jetilovyj. Gazohromatograficheskij metod opredelenija soderzhanija toksichnyh mikroprimesej* [Vodka and Ethyl Alcohol from Food Raw Material. Gas Chromatographic Method of Determining Trace Element Contents] (in Russian).

9. Sharma, K., Sharma, S.P., Lahiri, S.C. Novel Method for Identification and Quantification of Methanol and Ethanol in Alcoholic Beverages by Gas Chromatography-Fourier Transform Infrared Spectroscopy and Horizontal Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy. *Journal of AOAC international*. 2009. 92. V. 2. R. 518-526.

10. Volkov, S.M., Chernovets, A.N. Determining the Vapor Concentration of Volatile Organic Compounds at Their Co-Occurence in Gas Emissions of Industrial Enterprises by Capillary Gas-Liquid Chromatography. *Sorbcionnye i hromatograficheskie processy — Sorption and Chromatographic Methods*. 2009. Vol. 9. Issue 6. P. 862-867 (in Russian).