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Features of express control of volatile hydrocarbon media and their mixtures in visible light

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Abstract. The necessity of development of new methods of express control of hydrocarbon media and their mixtures, especially volatile ones is proved. The problems arising when controlling the condition of volatile hydrocarbon media using the phenomenon of refraction are noted. A new method for determining the components and the ratio between their concentrations in a mixture of volatile hydrocarbon media has been developed. The use of the new method makes it possible to determine the composition and percentage content of the components in hydrocarbon mixtures. The design of a small-size refractometer for the implementation of the new method has been developed. There are no analogs of the new method and refractometer design. The developed instrument can also measure n with an error of ±0.0004 in the range from 1.250 to 1.740. This is sufficient for express control of the state of all hydrocarbon media and their mixtures. The results of studies of gasoline and oil mixtures are presented.

Keywords: hydrocarbon medium, mixture, refraction, express control, refractive index, visible light, light-shadow boundary, concentration, measurement error

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Особенности экспресс-контроля летучих углеводородных сред и их смесей в видимом свете

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Аннотация. Обоснована необходимость разработки новых методов экспресс-контроля углеводородных сред и их смесей, особенно летучих. Отмечены проблемы, возникающие при контроле состояния летучих углеводородных сред с использованием явления рефракции. Разработан новый метод определения компонентов и соотношения между их концентрациями в смеси летучих углеводородных сред. Использование нового метода позволяет определять состав и процентное содержание компонентов в углеводородных смесях. Разработана конструкция малогабаритного рефрактометра для реализации нового метода. Аналогов новому методу и конструкции рефрактометра нет.

Разработанным прибором также можно проводить измерения n с погрешностью ±0.0004 в диапазоне от 1.250 до 1.740. Этого достаточно для экспресс-контроля состояния всех углеводородных сред и их смесей. Представлены результаты исследований смесей бензинов и масла.

Ключевые слова: углеводородная среда, смесь, преломление, экспресс-контроль, показатель преломления, видимый свет, светотеневая граница, концентрация, погрешность измерения

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Introduction

The reduction of energy resources in the world, as well as high prices of raw materials have led to the need for them careful use [1–6]. One of the priority directions in the field of their rational use is the development of fast and reliable methods of express - control of the state of condensed media [3, 7–10]. It should be noted that express - control is now in demand in many areas of human activity. In recent years, a number of rather stringent requirements have become imposed on the instruments and methods of express control. The main of them is connected with the fact that measurements of various parameters of the medium did not introduce irreversible changes in it [3, 5, 8, 10]. Almost for all liquid media - it is necessary to obtain a confirmation of the results of express control on devices of high resolution in a special laboratory. In addition, the methods used in express control should be applicable to the study of a large number of media. The error of measurement of parameters should be no more than 1.5%. These requirements are currently satisfied by only two methods: nuclear magnetic resonance (NMR) and refraction [3, 4, 9–12]. Refractometers have an undeniable advantage over small-sized NMR spectrometers and relaxometers in size, mass, and cost [5, 11–13].

There is a significant disadvantage in the currently used in the designs of industrial refractometers for express control when working with mixtures of different media. It is impossible to determine the composition of the mixture and the concentrations of its components (even if the mixture consists of media that have not reacted chemically with each other) from the measured n value. This problem is especially relevant for hydrocarbon media and their mixtures. Desktop NMR spectrometers allow to solve this problem. Therefore, the purpose of our work is to develop a new method and design of refractometer for its realization, so that by measured values of n it is possible to determine the composition of hydrocarbon mixtures and the concentration of components. And also to identify the medium if it is free of impurities.

Materials and Methods

For the light-shade boundary, by which we will measure the refractive index nm we will use daylight (for example, radiation from the Sun). In its spectrum there is a yellow line Na (λ = 589.3 nm), on which measurements of refractive indices of condensed media are made for comparison with standard ones made in laboratories. This requires that light enters only the face of one of the prisms. The second prism must not receive light. As a result, the light-shadow boundary is formed at the output of prism 1 (lower prism) and nb is measured. Then the light coming to prism 1 is blocked and the light goes to prism 2 (upper prism) and nt is measured. The temperature T of the medium under study is constantly monitored. During our measurements of nt and nb it is necessary to realize everything very quickly (in 6–8 seconds), so that significant movements between the media in the measured layers do not occur. In our proposed sealed volume evaporation of volatile hydrocarbon media will not occur in such a time. The temperature also does not change so quickly. To determine the concentrations of the media in the mixture, we use the refraction equation:

$$n_m = F_1 n_1 + F_2 n_2 + \ldots\ldots + F_n n_n, \quad (1)$$

where n_m is the refractive index of the medium measured at the initial moment ($n_m = n_t = n_b$), n_1, n_2, ..., n_n are the refractive indices of the media of which the mixture under study may consist, F_1, F_2, ..., F_n are the coefficients that characterize the relative content of various media in the mixture under study (in case it is necessary to determine the percentage content, these coefficients are multiplied by 100%). Them also characterize the concentrations of components in the mixture.

Experience with volatile hydrocarbon media and analysis of the results of various studies showed that in equation (1) two terms should be left initially:

$$n_m = F_1 n_1 + F_2 n_2. \quad (2)$$

Taking into account our developed measurement technique and the data obtained, equation (2) takes the following form:

$$n_m = F_l n_b + F_2 n_t. \quad (3)$$

The values of n_t, and n_b are determined for equation (3). Note that (according to Fig. 1) the value of n_t is the refractive index of the upper layer of the investigated mixture, the value of n_b is the refractive index of the lower layer in the investigated mixture. The indices *t* and *b* will be further used to define the ratio of the measured refractive index value nm to the upper or lower layer of the investigated mixture.

In hydrocarbon mixtures in a closed volume, stratification of the media into layers occurs. Light media rise to the top, heavy media sink to the bottom. By measuring the values of n_t and n_b after stratification, the temperature T of the components can be determined. Then (3) is solved and the concentrations of components in the mixture are determined.

For practical implementation of our developed method, we assembled a new optical design of the laboratory refractometer layout. In the design, the possibility of placing the liquid medium in a sealed volume, which is located between two prisms, was realized. Also, control of the visible light entering the two prisms was realized (possibility to measure the refractive index of the medium using the upper or lower prism). Fig. 1, *a*, *b* shows the refractometer block diagram and the course of optical beams for two cases of measurement, n_t (*a*) and n_b (*b*).

The light flux that falls on the prisms is controlled using the flaps 5. Fig. 1 shows two positions of flaps *5* during measurements.

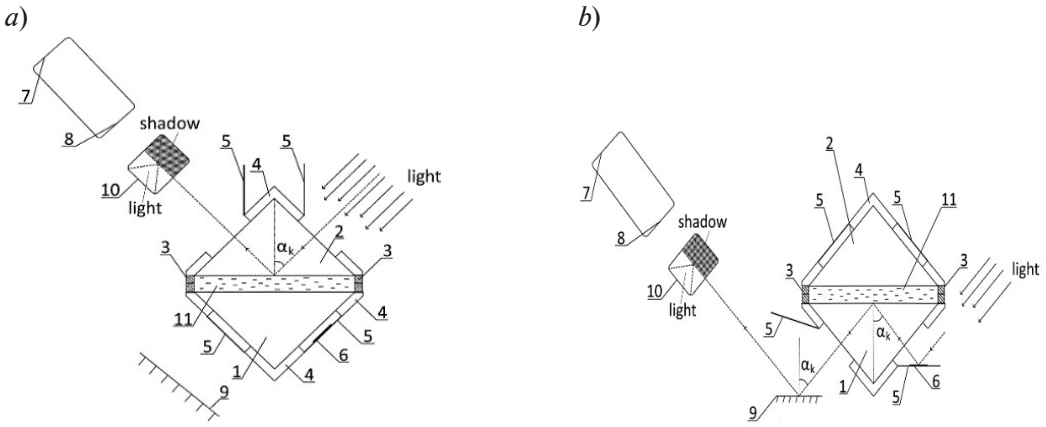

Fig. 1. Schematic diagram of the optical part of the refractometer and ray path for the upper (*a*) and lower (*b*) prisms: lower triangular prism *1* (material leucosapphire), upper triangular prism *2* (material leucosapphire), silicone spacers *3*, rotating prism mount *4*, closing flap *5*, mirror *6*, eyepiece *7*, lens *8* on movable mount, mirror *9*, plate *10* for registration of the light-shade border, medium *11* under study

Results and Discussion

Fig. 2, *a*, *b* and *c* shows, for example, the research results for mixtures, which consists of two gasoline Ai-92 and Ai-95 in the proportion 0.3 to 0.7 using two prisms. At the initial measurement time $n_t = n_b = 1.4252 \pm 0.0004$ at $T = 301.2$ K (Fig. 2,*a*). Next (after 140 seconds), two measurements were performed using upper and lower triangular prisms *2* and *1* (Fig. 1, *a*, *b*). The results of these measurements are presented in Fig. 2,*b* and Fig. 2,*c* at respectively. These measurements were carried out at a temperature $T_1 = 301.1$ K. The difference between T and T_1 is within the measurement error and does not have a significant impact on the final result.

According to Fig. 2,*b* and Fig. 2,*c* were determined two values of n_m^t and n_m^b. Value $n_m^t = 1.4112 \pm 0.0004$ corresponds to Ai-95 gasoline. Value $n_m^b = 1.4262 \pm 0.0004$ corresponds to Ai-92 gasoline. These three measurements are marked in Fig. 2 with a circle with a red arrow.

Further, using (3) for the measured values of refractive indices n_t, n_m^t and n_m^b, coefficients $F_1 = 0.7017$ and $F_2 = 0.2983$ were obtained. The values of coefficients F_1 and F_2 correspond with an insignificant error to the content of gasoline Ai-95 and Ai-92 in the mixture prepared. This mixture was prepared by using 70 ml of Ai-95 gasoline and 30 ml of gasoline Ai-92. This confirms the adequacy of our proposed methodology.

a) *b*) *c*)

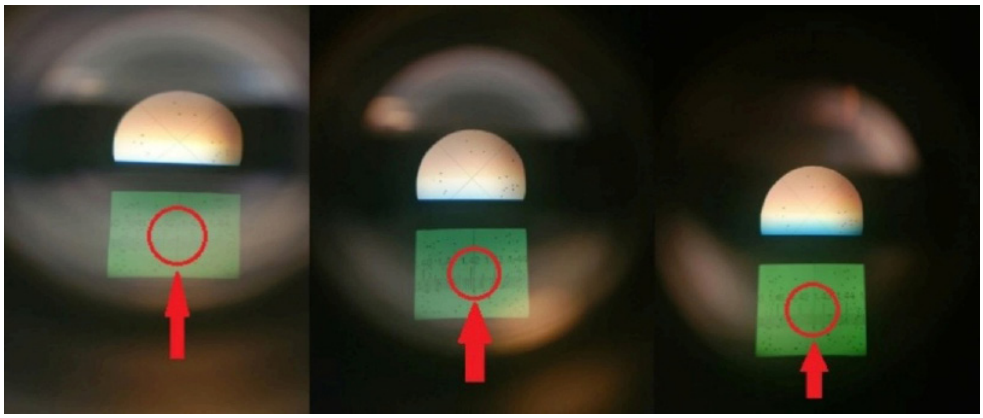

Fig. 2. Light-shade boundary and refractometer scale a during the measuring a mixture of two gasoline Ai-95 and Ai-92 in the proportion 0.7 to 0.3 (*a*, *b*, *c*)

Table 1

Dependence of change a refractive index n_m on temperature T

T, K	Laboratory model of developed refractometer	Industrial refractometer Abbe NAR - 2T
277.2 ± 0.1	1.5328 ± 0.0004	1.5326 ± 0.0002
282.1 ± 0.1	1.5322 ± 0.0004	1.5320 ± 0.0002
287.1 ± 0.1	1.5314 ±0.0004	1.5312 ± 0.0002
290.0 ± 0.1	1.5308 ± 0.0004	1.5306 ± 0.0002
293.1 ± 0.1	1.5300 ± 0.0004	1.5298 ± 0.0002
298.1 ± 0.1	1.5282 ± 0.0004	1.5280 ± 0.0002
303.1 ± 0.1	1.5262 ± 0.0004	1.5260 ± 0.0002
307.0 ± 0.1	1.5240 ± 0.0004	1.5238 ± 0.0002
312.0 ± 0.1	1.5213 ± 0.0004	1.5213 ± 0.0002

To check the reliability of the optical design developed by us, a comparison of the measured refractive indices n_m of synthetic oil at a small change of temperature T in the laboratory was implemented. These oils are highly viscous and are used in machine tools for metal working. Volatile solvents are often added to them. These solvents evaporate from the open oil into the air, just as with gasoline. This makes the research we are conducting close in terms of the aggregate state of the media. The change of nm from T was measured with an industrial Abbe NAR-2T refractometer (measuring error $\pm$ 0.0002). Table 1 shows the results of n_m studies using two refractometers.

The obtained results coincide within the measurement error. This confirms the reliability in conducting measurements of refractive indices using our developed refractometer design. The results of these studies show great functional possibilities of application of the developed refractometer design in comparison with the previously used ones.

Conclusion

The analysis of the obtained new results of the study of media with high viscosity (synthetic oils, which require special high degree purification), as well as complex mixtures of media by fuel (gasoline Ai-92 and Ai-95, a similar situation may occur with aviation kerosene) showed the reliability of our methodology and the design of the developed refractometer for its implementation. The quality of synthetic oil is determined unambiguously. The absence of impurities in it, which are removed by purification at the end of the technological cycle of production, is also unambiguously determined. For the most complex two-component fuel mixture, which is a mixture of gasoline Ai-92 and Ai-95 (the density of gasoline Ai-92 is greater than that of Ai-95, and the quality of gasoline Ai-92 is lower than that of gasoline Ai-95) the composition of the mixture and the concentrations of components in it are determined unambiguously. When comparing other brands of gasoline with each other, there is no such thing (the higher the quality of gasoline, the higher its density). Such a fact in density, which is related to the structure of the molecule in two gasolines, creates a number of problems in express control of such a mixture by various spectrometers at the place of sampling (before that the mixture was subjected to intensive treatment with additives). It is impossible to get an unambiguous answer on the composition of the mixture and concentration of components in it by chemical shift in spectra at (concentration of gasoline Ai-92 in the mixture 5 - 10 %) unlike the method developed by us.

It should be noted that the developed design of a small-size refractometer allows measuring nm values in visible light with an error of $\pm$0.0004. During the measurements we took the maximum value of the error (40 % of the scale discreteness).

The obtained results allowed us to determine the further direction of research. This direction will be connected with the study of three-component fuel mixtures. Nowadays there are frequent cases of making a mixture from gasoline Ai-92, Ai-95 and Ai-98, which is passed off as gasoline Ai-98. Intensive treatment with additives makes it possible to raise the octane number of this mixture to the required level with small additions of the other two gasolines to Ai-98 gasoline. When layers are formed in the refractometer, the Ai-92 gasoline will be placed between the Ai-95 and Ai-98 gasolines, creating difficulties. This layer will not be measured by the refractometer. In the future we will try to solve this problem using our method and instrument to get an unambiguous answer on the composition of such a mixture and concentrations.

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