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Features of investigation of liquid media by optical differential method in express-control

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Abstract. The features of liquid media investigation during express control using the phenomenon of refraction are considered. The advantages of using the differential method for investigation of liquid media in comparison with the others are noted. The features of liquid media investigation with using the differential method are established. A new technique for liquid media investigation has been developed, which allows changing the discreteness of the scale for measuring the refractive index n in the range from 1.2300 to 2.230. The design of the Anderson differential cuvette has been developed for carrying out research with required accuracy, by changing the discreteness of the measurement scale n. The results of experimental investigations of liquid media (water and water with iron oxides) are presented.

Keywords: liquid, refraction, refractive index, Anderson differential cell, laser radiation, axis, medium state control

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Особенности исследования жидких сред оптическим дифференциальным методом при экспресс-контроле

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Аннотация. Рассмотрены особенности исследования жидких сред при экспресс-контроле с использованием явления рефракции. Отмечены преимущества использования дифференциального метода для исследований жидких сред по сравнению с остальными. Предложена новая методика исследования жидких сред в широком диапазоне изменения показателя преломления n. Разработана кювета Андерсона для проведения исследований с необходимой точностью, за счет изменения дискретности шкалы измерения n. Представлены результаты экспериментальных исследований различных сред.

Ключевые слова: жидкость, рефракция, показатель преломления, дифференциальная кювета Андерсона, лазерное излучение, ось, контроль состояния среды

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Introduction

A huge number of negative factors, which are not decreasing in the world, has led to the development of various express methods [1–6] for solving many problems. One of these methods is the express control of liquid media at the sampling site [1, 3, 5–7]. The requirements for express control methods include the fact that they do not change the physical structure and chemical composition of the medium under study during measurements [1, 3, 5, 8]. This has significantly reduced their number for use in devices that can be used to monitor the condition of a large number of liquid media. The most universal devices for solving express control tasks are devices whose operating principle is based on the phenomenon of nuclear magnetic resonance (NMR) and refraction [1–5, 8–10]. Refractometers are given the greatest preference during express control, because these devices are simpler to use and have less weight and dimensions.

To perform express control of a large number of liquid media using refraction, measurements of the refractive index n in the range from 1.230 to 2.230 (with a measurement error of at least 0.001) are required [8–11]. Such a complex problem can be solved only using the differential method of measuring the indicator [11]. The main problem that arises when solving this problem is related to taking into account the peculiarities of changing the trajectory of the laser radiation axis in the Anderson differential cuvette in the designs of differential refractometers. The mathematical models used to determine the refractive index n in the differential method do not take into account the features associated with the thickness of the partition, the walls of the cuvette and the properties of the material from which they are made. This leads to errors in the measurement of n. Therefore, solutions to eliminate these shortcomings are proposed in our work.

Features of study a liquid media by differential method

Earlier in [12, 13], we obtained a mathematical relation for determining the n_m value of the liquid under study based on the results of measuring L (displacement of the axis of the trajectory of laser radiation on the photodiode ruler). This relation is an implicit function $L(n_m)$.

To obtain an analytical expression for nm from various parameters of the Anderson cuvette, the distance l between the cuvette wall and the photodiode ruler, the refractive index n_s of the reference liquid, a 12th degree polynomial was obtained (by transformation (1)). The solution of this polynomial is a separate task.

The simulation of the change in L from changes in various parameters of the Anderson cuvette, the distance l between the cuvette wall and the photodiode ruler, the refractive index n_s of the reference liquid showed that there are a number of features. These features must be experimentally verified and taken into account when conducting studies of liquid media.

Several different designs were made to investigate the features of the formation of the axis of the trajectory of laser radiation in the Anderson differential cuvette. One of them is shown in Fig. 1.

$$
\begin{aligned}
L = \sin\alpha_1 & \left(d\left(1-\frac{n_s\cos\alpha_1}{\sqrt{n_q^2-n_s^2\sin^2\alpha_1}}\right)+\left(\sqrt{n_m^2-n_s^2\sin^2\alpha_1}-n_s\cos\alpha_1\right)\right)* \\
& *\left(\frac{l}{\sqrt{n_a^2-\sin^2\alpha_1\left(n_m^2-n_s^2\sin^2\alpha_1+n_s^2\cos^2\alpha_1-2n_s\cos\alpha_1\sqrt{n_m^2-n_s^2\sin^2\alpha_1}\right)}}+\right. \\
& +\frac{d_1}{\sqrt{n_q^2-\sin^2\alpha_1\left(n_m^2+n_s^2\cos^2\alpha_1-n_s^2\sin^2\alpha_1-2n_s\cos\alpha_1\sqrt{n_m^2-n_s^2\sin^2\alpha_1}\right)}}+ \\
& \left.+\frac{K_1}{\cos\alpha_1\sqrt{n_m^2-n_s^2\sin^2\alpha_1}+n_s\sin^2\alpha_1}\right)
\end{aligned}
\qquad (1)
$$

Formula (1) uses the following quantities: α_1 is the angle at which the partition in the Anderson cell is located to the axis of laser radiation propagation (Fig. 3), d is partition thickness, n_a is refractive index of medium in which the Anderson cell is located (in our work this is air), n_q is refractive index of which the cuvette is made (in this work it is quartz), n_s is refractive index of the reference liquid, d_1 is thickness of the cell wall through which laser radiation passes, l is the distance between the wall of the cell through which the laser beam exits and the photodiode array (Fig. 3), K_1 is coefficient in units of length, which takes into account the geometric dimensions of the cuvette and the location of radiation input into Anderson cuvette.

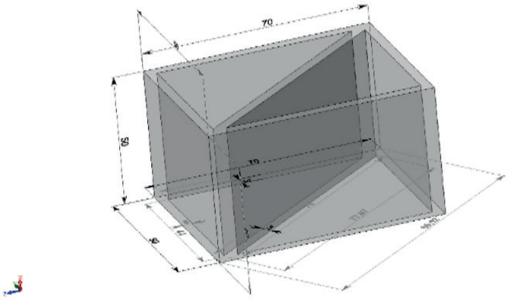

Fig. 1. The 3D model of differential cuvette of Anderson. All sizes are presented in mm

Fig. 2 shows the appearance of the Anderson cuvette (Fig. 1) with a sensor for measuring the temperature T in the test and reference liquid.

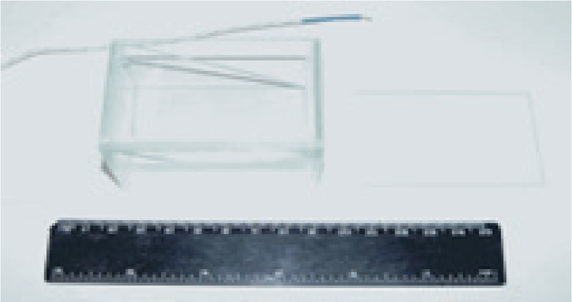

Fig. 2. The appearance of the Anderson cuvette with a thermocouple

The partition and the walls of the cuvette are made of the same material in this version. There may be cases when the walls of the cuvette and the partition are made of different materials. This creates a number of features associated with changing the axis of the trajectory of laser radiation. To study these features, an experimental installation of a differential refractometer was assembled. Fig. 3 shows its block schema.

During investigations of liquid media using a refractometer with a differential Anderson cuvette, three situations may arise ($n_m > n_q$, $n_m = n_q$ and $n_m < n_q$), where n_q is the refractive index of quartz (the material from which the cuvette is made). In addition to quartz, sapphire and various glasses can be used to make cuvettes, etc. The partition and the walls of the cuvette are made of the same material. In some cases, for certain Anderson cuvette designs, complete internal reflection of laser radiation can occur at the interface of two media. In this case, laser radiation will not be transmitted to the photodiode array 8 (Fig. 3). It will be impossible to measure n_m. Therefore, laser radiation with $\lambda = 632.8$ n_m (the red line of the spectrum) is used in research. Visually, it is possible to determine the exit point of the axis of the laser radiation trajectory from the Anderson cuvette. By changing the reference fluid or cuvette parameters, the axis of the laser radiation trajectory can be returned to array. This is one of the features of studies of liquid media by the differential method.

For the case $n_m > n_q$, the trajectory of the laser radiation axis change is shown in Fig. 3. Our experiments have shown that in the case of $n_m = n_q$, the equation obtained when considering the

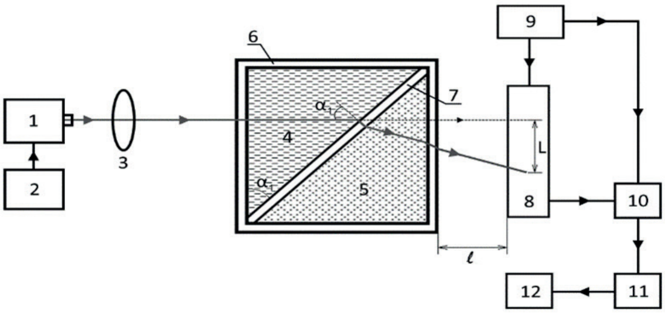

Fig. 3. Block diagram of a differential refractometer: 1 — semiconductor laser, 2 — laser power supply; 3 — lens; 4 — reference liquid; 5 — measured liquid; 6 — Anderson cuvette wall; 7 — partition between compartments in Anderson cuvette; 8 — photodiode array; 9 — analog-to-digital converter; 10 — multifunctional power supply unit; 11 — processing device; 12 — laptop

case of $n_m > n_q$ in [12, 13] can be used to describe the change in the trajectory of the laser radiation axis. The case associated with the ratio $n_m < n_q$ leads either to a complete internal reflection of the axis of the trajectory of the laser radiation (this has already been considered). Or the refracted laser beam (Fig. 3) goes above the straight line between 3 and 8. This may lead to the impossibility of n_m measurements (a photodiode ruler with 1024 sensors is used for measurements). In this line, 1000 sensors are used for measurements with a step for n_m equal to 0.001. The remaining 24 sensors (12 on each edge) to provide this measurement range. In this case, a cuvette with a partition made of another material is installed, so that the n_m value is greater than the refractive index of this material. This is another important feature when conducting studies of liquid media. Taking into account these features allows you to obtain a minimum error when measuring n_m in the range of 1.0 or 0.1.

Results of experimental studies and discussion

To confirm the adequacy of taking into account the established features of the study of liquid media using the developed laboratory model of a differential refractometer, tap water with various degrees of purification was studied. Fig. 4 shows the results of these studies as an example.

The analysis of the data in Fig. 4 showed that the results of measuring the value of n_m, as well as the nature of the change in the dependence of n_m on T coincides with the research results obtained by other scientists in the works [10, 11, 14–17]. These results coincided with the data of studies of these water samples on an industrial refractometer (NAR 2T).

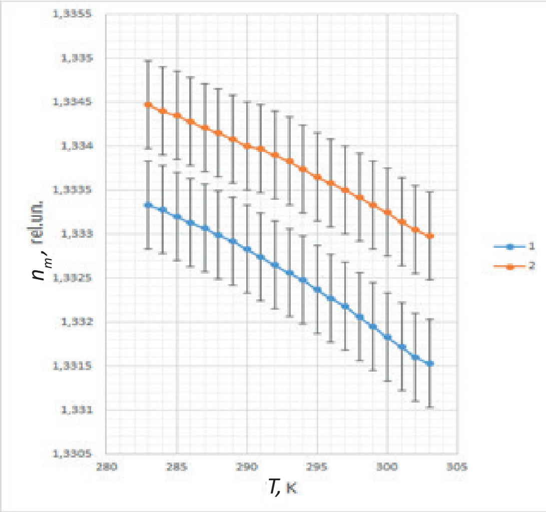

Fig. 4. The dependence of the change in the refractive index n_m on the temperature T for various aqueous media. Graph 1 corresponds to filtered tap water. Graph 2 corresponds to tap water containing iron oxides

The composition of this refractometer includes a thermoblock, the measurement error is 0.0002. The results of a comparison of the measured values n_m by two devices for filtered water are presented in Table.

Table

Dependence of a refractive index n_m of filtered tap water on temperature T

T, K	Laboratory model of the developed refractometer	Industrial refractometer Abbe NAR - 2T
283.1 ± 0.1	1.3333 ± 0.0003	1.3332 ± 0.0002
285.1 ± 0.1	1.3332 ± 0.0003	1.5330 ± 0.0002
287.1 ± 0.1	1.3331 ± 0.0003	1.3329 ± 0.0002
290.0 ± 0.1	1.3328 ± 0.0003	1.3327 ± 0.0002
293.1 ± 0.1	1.3326 ± 0.0003	1.3324 ± 0.0002
296.1 ± 0.1	1.3324 ± 0.0003	1.3322 ± 0.0002
298.1 ± 0.1	1.3321 ± 0.0003	1.3319 ± 0.0002
300.0 ± 0.1	1.3318 ± 0.0003	1.3316 ± 0.0002
303.0 ± 0.1	1.3315 ± 0.0003	1.3314 ± 0.0002

Conclusion

The obtained results of studies of liquid media confirm the validity of taking into account the features in the Anderson differential cuvette of the propagation of the laser radiation axis to obtain n_m values with an error not worse than 0.0001.

In addition, taking into account the features in the mathematical model [12, 13] to determine the n_m features of the formation of the trajectory of the laser radiation axis in the Anderson differential cuvette allows you to change the discreteness of the refractometer scale from 0.001 to 0.0001 (without changing the location of the main elements of the device). This allows us to study the state of media in which the n_m range varies from 1.200 to 2.200 or from 1.300 to 2.300, or 1.400 to 2.400 with an error of 0.001 (changing the design of the cuvette and the reference fluid in it). With the use of a single device, the entire range of n_m variation for liquid media is overlapped, which was previously unavailable. Further, after determining the n_m value, you can switch to a narrow range of 0.1 with a scale discreteness of 0.0001 and determine the n_m value up to the fourth digit with an error of 0.0001. Higher measurement accuracy is not required for express control.

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