The effect of optical density of the flowing liquid on the measurement error of its refractive index

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Abstract. The main factors responsible for measurement errors in the determining of the refractive index of the flowing fluid are considered. It was found, that the most significant effect on the measurement error have changes in optical density and temperature of the investigated flowing fluid, scattering of radiation in cuvette transducer and wedge shape of the cuvette glass. A new design of differential refractometer has been developed to study the influence of the optical density values of the flowing fluid on the measurement errors. The results of experimental studies are presented.

1. Introduction

Conducting different studies, introduction of automatic processes in production of various products and other reasons require constantly improving methods of monitoring state of condensed medium [1-7]. One of the most difficult tasks is to control liquid media flowing state in pipelines of different diameters [6, 8-13]. It is especially important, if measurements taken to determine the state should not make irreversible changes in the physical structure and chemical composition of the media. Therefore, the great preference is given to contactless methods [5-8, 12-16]. Among them, methods based on the use the phenomenon of refraction [17–23] and nuclear magnetic resonance [2–5, 14–16] have the greatest advantages. The refraction method, in contrast to NMR, besides ensuring the sterility of measuring process, allows to monitor fluid state in stationary or in flowing condition using one device. The main parameter by which medium state is monitored is the refractive index \( n \). Using refraction ratios and measured values of \( n \), it is possible to determine the concentration of substances dissolved in liquid.

For successful application of refractometers in scientific research, as well as in automatic control systems, for example, in pharmaceutical industry, it is necessary to improve their accuracy characteristics and expand the range of measurement of \( n \). Experiments have shown that for scientific research, determination of impurities in medium or monitoring media state, measurements of \( n \) values with an error of \( 10^{-4} \) or less are necessary [21–24].

One the most difficult problem that needs to be solved in order to provide these reduced measurement error values is the reduction the influence of the optical density of the flowing fluid on determining result \( n \). In refractometers, where liquid is in stationary state when measuring \( n \), various compensation schemes are used to solve this problem. This allows to make insignificant the effect of changes in optical density of liquid on measurement errors. In the study of liquid flow, the use of compensating devices is possible only if the device is built according to differential scheme. The influence of other errors on result of \( n \) the measurement increases when the flow-type design refractometer of differential type is used on compared with studies of stationary media. It does not make sense to investigate the effect of optical density on measurement error together with other errors whose effect on the value of \( n \) is not
compensated. It is impossible to separate contribution from optical density to the value of \( n \) from the contributions from other phenomena and factors.

On the other hand, it is impossible to get measurement error of \( n \) less that \( 10^{-4} \) impossible without compensation of error connected with optical density. That is why at this time the refractometer flowing type design of different type are not manufactured. The measurement of \( n \) of flowing medium are carried out on refractometer using the effect of the tall internal reflection at the boundary of to media \([17, 18]\). At some designs of these devices single-mode optical fiber used for the transmission of laser radiation to the lower face of the prism. This type of refractometers has a disadvantages number the main of which is the influence of flowing medium temperature at measurement process (the refractive indices of the prism and the liquid change simultaneously). This complicates the automatic adjustment of the optical system and limits the measurement range of \( n \). Besides, that of big velocities of flowing liquid the phenomenon of Gus-Hansen shift leads to the increase of the \( n \) measurement error. The technical solution on stream rate reduction by expanding the pipeline or introduction of additional valves not always possible to practically implement. This significantly limits the application of refractometers based on the effect on to full internal reflection.

Therefore, it is necessary to develop a new method to study the influence of optical density of the flowing fluid on measurement error in determining \( n \). Based on our earlier obtained results, we propose methods and design solutions for compensation of such kind of errors in designs of differential refractometers. One of the possible solutions is presented in this paper.

2. Experimental installation and methods of compensation of negative factors influence on the measurement error

In developed designs of automatic differential-type flow-through refractometers, the Anderson difference prism method with a differential cell is used to control liquid media \([17, 19, 21, 22, 25, 26]\). The basic design of differential cell consists of two containers. In one container (flow cell) the investigated liquid moves. Its refractive index \( n_f \) is necessary to be controlled. In the second container (closed cell) liquid medium with a known refractive index \( n_c \) is placed. A closed cuvette is placed inside a flow cell \([21, 25, 26]\) to equalize temperatures in two media. This arrangement creates a number of problems. The main of them due to is associated with formation of stagnant zones, especially with fast flows liquid medium near a closed cell. In these zones, impurities accumulate, which then when released into medium (especially in biological solutions) can cause irreversible processes. This was in addition of low accuracy was of the reasons for the refusal to use previously developed flow refractometers of different type.

That is why we have developed the new design laboratory refractometer of different type. The structural diagram of this refractometer is presented in figure 1.
Figure 1. Structural diagram of the refractometer: 1 – semiconductor laser; 2 – multifunctional power supply; 3 – optical system; 4 – prism Dove; 5 – closed cell; 6 – flow cell; 7 – делительная призма; 8 – photodiode array; 9 – analog-to-digital converter; 10 – processing device and control; 11 – laptop computer; 12 – temperature sensor; 13 – information processing unit from a temperature sensor.

Radiation from semiconductor laser 1 with $\lambda = 632.8$ nm enters the optical system 3 (prism collimator), at the output of which parallel beam of a given shape is formed. The new design of the refractometer uses measuring cells of cylindrical shape namely the flow cuvette 6 and the closed cuvette 5. The liquid flow moves along the flow cell 6 in the direction perpendicular to the laser radiation entering its wall.

The cuvettes 5 and 6 are located in a vertical position. This new way of cuvettes placement allows to exclude presence of voids in the flow cuvette at low flow rates, unlike the previously used cuvette designs in differential refractometers. Such placement of the cuvette makes it possible to completely eliminate the formation of stagnant zones and to ensure a more efficient heat exchange between the liquid flow and the reference one as compared to the previously used refractometer designs. In addition, influence contribution of the error due to change in temperature $T_f$ of flowing fluid (especially when the $T_f$ changes sharply) on the measurement error $n_f$ is significantly reduced.

Another principal difference its refractometers from the flow refractometers on the effect of full internal reflection is as follows. In refractometer developed by us there is no direct contact of optical elements with the flowing medium. It allows to eliminate the influence of some negative factor on the error of measurement of refractive index $\delta n_f$ of flowing liquid.

Our studies have shown that in standard designs of flow refractometers of differential type on the measurement accuracy of $n_f$ are affecting the following errors:

1. The error $\delta_1(\Delta n)$ associated with voltage unbalance on photoelectric converter. To compensate it, optical wedge is used, which introduces an additional error due to increase in the number of reflections between optical elements of laser radiation. This error can contribute to the total measurement error more than 0.0003;

2. Dynamic error associated with the change in temperature of flowing fluid. The error significantly affects the measurement result when abruptly changes temperature or flow rate $q$ of flowing fluid. This error can contribute to the total measurement error more than 0.0004;

3. The error $\delta_3(\Delta n)$ associated with presence of a transport link for the selection of liquid flow in the refractometers of differential type based on the Anderson cell. The presence of the link leads to appearance of delay time $t_d$ during the measurements. This error can contribute to the total measurement error more than 0.0002:
4. The error $\delta(\Delta n)$ associated with the change in optical density of flowing fluid over cross section of pipeline. This error can contribute to the total measurement error more than 0.0005:

It is impossible not to take into account the influence of these factors on the $n_f$ measurement errors. The analysis obtained by us [18, 23, 27–29] and other scientists [17, 19–22, 24–26] of research results of different media using design refractometer of differential type allowed us to receive a formula for determining the measurement error $\delta n_f$. This formula takes into account all the main factors affecting $\delta n_f$:

$$\delta n_f = \delta(\Delta n) + \delta_1(\Delta n) + \delta_2(\Delta n) + b(T_f - T_c) + \left(\frac{b\tau_c\tau_{t1} + k_1\tau_{t1} + L_p}{(p_1 - p_2)(p_1 - p_3)} - \frac{b\tau_c\tau_{t2} + k_2\tau_{t2} + L_p}{(p_1 - p_2)(p_2 - p_3)} + \frac{b\tau_c\tau_{t3} + k_2\tau_{t2} + L_p}{(p_1 - p_3)(p_2 - p_3)}\right),$$

where $p_1 = -1/\tau_c; p_2, 3 = (-\tau_c - \tau_{tp}) \pm \sqrt{(\tau_c - \tau_{tp})^2 - 4k_1\tau_c\tau_{tp}}/(2\tau_c\tau_{tp}),$ $\tau_c$ – time constant of the closed cuvette, $\tau_{tp}$ – time constant of the flow cuvette, $L_p$ – distance from the differential cuvette to the photodetector, $b$ – temperature gradient of the refractive index of the flowing fluid, $k_1, k_2$ – coefficients characterizing the dimensions of the flow and closed cell, mass and heat capacity of liquids that are in them and other parameters; $T_f$ – flow liquid temperature; $T_c$ – reference fluid temperature.

The analysis of the resulting equation 1 shows, that it is impossible to carry out the research of the optical density influence on the measurement error $\delta n_f$ using this formula. It is explained by the fact that contribution of different negative factors in the total measurement error differ little from each other. Compensating the influence of one increases the influence of the other.

In the design of the developed by us the laboratory layout of flow differential type, the new location of cuvettes 5 and 6 allows to eliminate from equation 1 of terms, caused by the errors from the delay time and imbalance voltage. The absence contact of measuring elements with flowing liquid and flow of laser radiation on the pipeline wall at a right angle allows to eliminate from the equation 1 the term $\delta_2(\Delta n)$. In this case the equation 1 for the error determine takes the next form:

$$\delta(\Delta n) = 0.993 \frac{a^2\Delta d}{L\Delta n}$$

where $\Delta d = d_f - d_0$ – change in the optical density of the measured liquid $d_f$ relative to the initial (unrated) value $d_0$, $a$ – light beam half width, $L$ - distance from the differential cell to the photodiode array.

For realization of the proposed new method of measuring of the refractive index $n_f$ in developed design of the refractometer of the laboratory layout the prism 4 of Dove is used. At the Dove prism exit, half of the laser radiation from the beam that passes through it changes direction to the opposite of the original one. Direction, when the laser radiation enters the closed cell 5 passes through the flow cell 6 with the test liquid and through the cell 5 enters the separating prism 7. At the separating prism 7, the light fluxes are separated. As a result, one part of the light flux reduces the amplitude of the signal of the first photodiode array and increases the illumination of the second array. Another part of the luminous flux increases the amplitude of the signal of the first photodiode array and decreases the amplitude of the signal of the second photodiode array. It is established that the magnitude of the difference in amplitudes of the normalized output signals from photodiode arrays is proportional to the value of $\beta$ and $L$ (the distance from the wall of the cuvette 6 to the photodiode array). In this case, the classical formula [19-22] to determine the formative parameter $\beta$ is converted to the following form:

$$\beta = \Delta A = A_{1ar}^1 - A_{2ar}^2 = LK_{ar} \Delta n = LK_{ar} (n_f - n_c)$$
where $K_{ar}$ – coefficient of proportionality $A_{ar1}^1, A_{ar2}^2$ – normalized output signals from photodiode arrays.

Normalization of the output signal $A$ from the photodiode array is carried out according to following principle:

$$A = \frac{\sum_{i=1}^{512} A_i}{A_{\text{max}}}$$

where $A_{\text{max}}$ – the maximum value of the light signal from the photodiode array element, $A_i$ – signal amplitude from photodiode cell unit, $i$ – number of units.

The coefficient of proportionality $K_{ar}$ is determined by the preliminary calibration of the refractometer. For this purpose, two liquids with known refractive indices are used: distilled water and ethanol (ethyl alcohol). As a result of the experiments it was established that for transparent media the $K_{ar}$ value does not change. The temperature of the flowing fluid in the flow cell and the reference fluid in a closed cell is monitored by temperature sensors 12. Information from them through special devices 13 is fed to the information processing device 10.

To register the radiation in the newly developed refractometer design, we use two TSL1406RS photodiode arrays, consisting of 512 photosensitive sensors (AMS-TAOS USA), with a photosensitive layer length of 40.16 mm. In the design of the photodiode array TSL1406RS, there are no focusing optical elements in front of the photosensitive layer, as in other models of arrays. Therefore, the influence of the effects associated with repeated reflection of laser radiation between the photosensitive layer and the edges of the prism 7 on the signal-to-noise ratio on photosensitive sensors is insignificant.

From the photodiode arrays 8, signals through analog-digital converters enter the information-processing device developed on the basis of the STM32 microcontroller (ARM Cortex M3 core - STM32F100RBT6B). From the microcontroller, information is fed to a laptop, which is used to determine the value of $n_f$ and visualize different information. The use of a microcontroller is necessary, as the refractometer is used in automatic control systems. Without such electronic components in processing devices, this design of a refractometer will not be demanded by consumers.

3. The results of experimental studies and discussion

The reliability and accuracy of measurements of the refractive index $n_f$ of the flowing liquid using the design of the refractometer developed by us was tested on several liquid media for different temperatures $T_f$. Figure 2, as an example, shows the dependence of the change in the refractive index of liquid flows on temperature.

![Figure 2. The dependence of the refractive index $n_f$ on temperature $T_f$. Graphics 1, 2, 3 corresponds of next media: distilled water, tap water, ethyl alcohol.](image-url)
The obtained results coincided within the measurement error with the values of the refractive indices, previously obtained by scientists on other refractometer designs [17, 19-22].

Figure 3 shows the dependence of the refractive index $n_f$ of the liquid distilled water on its salinity at various temperatures. Dissolved salts in a liquid medium when measured in stagnant zones and on the walls of a flow cell form a precipitate, which negatively affects the operation of the refractometer. The measurement error increases. In the design of laboratory refractometer layout developed by us these zones are absent.

![Figure 3](image.png)

**Figure 3.** The dependence of the refractive index $n_f$ of water salinity $N_s$ for different temperatures $T_f$. Graphics 1, 2, 3 corresponds $T_f$ in K: 283.1, 293.1, 303.2.

The obtained results coincided within the limits of measurement error with the results of other studies [19-22, 24, 25] for media which are in a stationary state. In case of the investigation of media in a stationary state the measurement accuracy was higher compared to the measurements in the flowing media. The experiments confirmed the efficiency of the proposed method for measuring the $n_f$ liquid medium.

In refractive index measurements using flow-through refractometers, the most uninformative parameter is the temperature of the flowing fluid $T_f$. The temperature of controlled fluid and the temperature of comparative fluid are connected. As temperature $T_f$ changes, the value of $n_f$ changes. A change in $T_f$ also leads to a change in $T_c$ and the refractive index $n_c$ of the liquid in the closed cell. There is a dynamic error $\varepsilon^\theta$, the value and nature of the change of which depends on the mode and parameters of the instrument. At a fixed time $\varepsilon^\theta$ can be determined by the following function:

$$\varepsilon^\theta \approx b(T_f - T_c)$$

(5)

Temperature compensation in refractometers is carried out in the mode of passive temperature heat exchange between liquids in two cuvettes and depends on the design of the cuvette converter of the refractometer. In figure 4 as an example, the dependences of the study of the dynamic error of measuring $n_f$ for different modes of changing the flow rate of a fluid $q$ are presented.
Figure 4. The dependence of the dynamic error of the flow refractometer on the nature of the change in flow $q$. Graphs 1 and 3 correspond to a change in $q$ abruptly in the previously used and developed refractometer design. Graphs 2 and 4 correspond to the $q = \text{const}$ mode in the previously used and developed refractometer design.

The result obtained shows that in the design of the refractometer developed by us, the influence of the dynamic error on the measurement result of $n_f$ is much less than in the previously used refractometer. This allows one to study the effect of optical density on the measurement error of $n_f$ in both the laminar and turbulent flow regimes. For different modes of fluid flow at a stabilized temperature of two liquid media, the value $\Delta n$ was measured. The measurement of the value of $n$ is carried out 10 times. After that, the value was calculated the value $\delta(\Delta n)$. Then in accordance with equation 2, the value of $\Delta d$ is calculated. In figure 5 as an example, the dependences of the change in $\Delta d$ on the fluid flow rate in a flow cell for various media are presented.

Figure 5. The dependence of the change in optical density $\Delta d$ on the flow rate $q$ of various media at $T_f = 293.2$ K. Graphs 1, 2, 3 correspond to: water; an aqueous solution of sodium hydroxide; water solution of apple juice with dissolved sugar and pulp.
Our studies have shown that, if the liquid flow is homogeneous (the water without impurities or additives), then regardless of the mode of its flow in the pipeline and the temperature range from 283 to 343 K, the effect of a change in optical density on the measurement error $\delta n_f$ is insignificant. In table 1 presents the results of comparing the changes in the measurement error $\delta n_f$ from changes in optical density with a change in flow rate $q$ of the flowing liquid. For comparison, we used the results of error measurements of $n_f$ of the liquid in the stationary state. To determine the error ratio is also used, obtained in [26].

| q, ml/s | Laboratory layout of flow refractometer | Stationary refractometer |
|---|---|---|
| 0 | 0.00002 | 0.00002 |
| 10 | 0.00002 | 0.00002 |
| 20 | 0.000022 | 0.00002 |
| 30 | 0.000023 | 0.00002 |
| 40 | 0.000024 | 0.00002 |
| 50 | 0.000026 | 0.00002 |
| 60 | 0.000027 | 0.00002 |
| 70 | 0.000028 | 0.00002 |
| 80 | 0.000029 | 0.00002 |

If the medium consists of several components (dissolved in each other), for example, an aqueous solution of sodium hydroxide, then due to the unequal absorption of light across the width of the light flux in the layers of the flowing liquid, especially when they are mixed, the $\Delta d$ value slightly increases. The compensation scheme developed by us eliminates mismatches in the optical line segment of laser beams. This allows you to measure the refractive index with an error of $10^{-3}$ and less. In the case of a more complex medium, for example, an aqueous solution of juice with sugar and pulp (transparent) to a certain value of flow $q$ and temperature of the liquid medium, the compensation scheme operates successfully. In the future, the influence of changing of $\Delta d$ on the measurement error $\delta(\Delta n)$ increases. To measure $n_f$ in this case with an error of $10^{-3}$ and less becomes difficult.

4. Conclusion

The experimental results obtained by us confirmed the possibility of studying the influence of the optical density of a flowing liquid on the error in measuring the refractive index $\delta(\Delta n)$ by the new method developed by us. Besides that the design of the differential type laboratory refractometer developed for realization of this method allows to carry out measurement of $\Delta n_f$ for flowing homogeneous liquids at any values of the flow rate of liquids $q$.

The relation proposed by us (2) makes it possible, knowing the values of the change in optical density $\Delta d$, to estimate the measurement errors $\delta(\Delta n)$ associated with the change in optical density for various liquid media. This allows us to choose the design of a refractometer for more reliable control of the state of flowing medium. For example, to solve this problem to use the design of a laboratory refractometer model of differential type developed by us or to use the refractometer, wherein for determining the value $n_f$ is registered the position of the light-shade boundary [27-31].

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