Monitoring toxicants by stimulated Mandelshtam-Brillouin scattering (SMBS) in a turbulent water flow

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Abstract - In this article we considered a method of monitoring of toxicants in a turbulent water flow. The technique was based on SBS (stimulated Brillouin scattering). We have developed a mathematical model of light distribution in the medium with optical inhomogeneities. In our case quantity and form of inhomogeneities depended on time. Also experiments for check of adequacy of mathematical model were made. The results were used to refine the scheme of optical device for rapid analysis toxicants in drinking water.

1. INTRODUCTION

Currently there is an acute problem of controlling toxicants (pathogens, toxins, and other highly dangerous substances) in drinking water. However there are no devices that could determine the presence of toxins directly in a water flow with required accuracy. Dangerous doses of these components vary generally from fractions of a percent to nano-concentrations. The presence of these substances can be detected by modern methods of monitoring, developed recently in chemistry, chromatography and infrared spectroscopy only for stationary solutions. In a non-stationary case the stability of zero signal and a scale factor are beginning to depend not only on a detecting method but also on the design features of a sampling device and the degree of turbulence, leading to false positives and reduced system reliability. Moreover, a number of accurate methods of determining concentrations of some pathogens can be conducted only in specialized laboratories, while the measuring time ranges from several hours to several days. Thus, drinking water needs to be monitored continuously for the presence of pathogenic organisms.

For several years now the company "SERVET" has been conducting an experimental work on controlling the compositions of pathogenic microorganisms and nano-particles in aqueous solutions by the method of Mandelstam-Brillouin scattering (SMBS). Studies were carried out to determine the intensities of Stokes and anti-Stokes components as functions of the composition of a solution. It was shown that for most substances it remains a linear dependence on the optical density for both Stokes and anti-Stokes components up to 10% concentration in a solution. The method accuracy made it possible to determine silver concentrations up to $10^{-4}$ mg/l, and virus concentrations up to $10^{-8}$ of infectious particles per 1 ml (-8 lg tds50) at high signal/noise.

Furthermore, being less dependent on flow parameters than other techniques, the method of stimulated Mandelstam-Brillouin scattering (SMBS) allows you to put an optical device directly into a pipeline and thus avoid the error correction for a sampling device. This advantage is used to control certain parameters in pipelines. Nevertheless, it was necessary to assess the impact of flow dynamics on the error signal occurrence, since errors might lead to false positives and reduced system reliability. A mathematical model of a turbulent flow in the pipe of a simple geometry was built to solve this problem, while calculations were carried out using software ANSYS. The model allows us to optimize various optical circuits in terms of minimizing the error of zero. Undoubtedly, assessing informative spectral

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characteristics and the parameters that affect the method sensitivity threshold is of great interest from a practical point of view.

2. THEORY

The non-stationary effect of SMBS in liquids has a certain peculiarity: it can be accompanied simultaneously by such effects as the stimulated Raman scattering, the stimulated Rayleigh scattering and the stimulated thermal scattering of light. The thresholds for these effects are usually higher than the threshold for SMBS. If there is a self-focusing, the threshold for Raman scattering and the SMBS threshold become close [1].

We observed a self-focusing of a laser beam in our experiments; therefore it was necessary to estimate theoretically the SMBS threshold to distinguish this effect from the others. The frequency of the sound generated by SMBS in the transient regime is defined by (1).

\[ \Omega_{\text{SMBS}} = \omega_0 \frac{\nu}{c} [(n_1 - n_2)^2 + n_1 n_2 (2 \sin \frac{\vartheta}{2})^2]^{1/2}; \]  

(1)

where \( \vartheta \) - a scattering angle; \( n_1, n_2 \) - the refraction indexes of the exciting and the scattered light waves.

If a generated sound enters a nonlinear mode, the effective sound absorption coefficient starts rising. It is defined by (2).

\[ \alpha_{\text{eff.}} = \alpha R; \]  

(2)

where \( \alpha \) - a normal linear sound absorption coefficient; \( R \) - an analogue of the Reynolds number defined by equation (3).

\[ R = \frac{mp}{\eta_{\text{eff}} \Omega_{\text{BS}}}; \]  

(3)

where \( p \) - a pressure amplitude of a sound wave; \( \eta_{\text{eff}} \) - the effective viscosity of a medium at a frequency \( \Omega_{\text{BS}} \).

If an acoustic non-linearity is observed, a hyper-sound of a basic frequency transforms into the harmonics of higher frequencies. The appearance of the second harmonic of a hyper-sound \( f_{\text{BS}} \sim 10^{10}\text{Hz} \) was observed in water at a basic frequency of \( f_{\text{BS}} \sim 5 \cdot 10^{9}\text{Hz} \).

To verify the fact that we are dealing with the SMBS effect, rather than with a wing of Rayleigh scattering, we can estimate the ratios of the amplitudes of Stokes and anti-Stokes components to the amplitude of laser radiation. These values differ considerably from the data presented in [2]. Moreover, the intensities of these components, as was shown earlier, are logarithmic functions of concentrations of dissolved substances [1].

Paper [2] presents the evaluation of the SMBS threshold. This value is much more than the source radiation density of the laser used. It is known that the threshold depends on a self-focusing. As shown in [2], the dynamics of mediums is defined considerably by the process of hydrodynamic interaction of a liquid and the bubbles of gas, contained in it. Therefore to assess the parameters of changing the form and concentration of bubbles we developed a dynamic model. The model was based on Euler's equations, and the calculation results were used earlier while studying variations in concentration of air bubbles with the speed of movement [3].

For the analysis of this phenomenon it was necessary to estimate the amplitudes of falling, scattered and reflected waves. Also we needed to analyze a distribution diagram of the scattering intensity. A scattering medium is a colloidal solution consisting of individual molecules, dissolved objects and air bubbles. They build clusters in the form of an elongated polymer structure with electrically active ions. We assume that the bubbles are much larger in size than toxins, and their concentration exceeds the concentration of electrically charged impurities. The concentration of electrically neutral impurities is small compared to the concentration of air bubbles and objects under research. So, the model of scattering was built for a structure of solution shown in Fig. 1.
Fig.1. The structure of the solution.

The determination of the scattered field from a given distribution of inhomogeneities in a medium is as follows:

After decomposing the spherical wave source into plane waves and taking into account the refraction at the interface, we can write the following expression for the field penetrating into a medium:

\[ \mathcal{U}(r_1) = \int_{-\infty}^{+\infty} \frac{i P(k_0) \exp(ik_0|c_1 - c_0| + ik_0z - Z_0| + ik_1z - Z_1|)}{2(2\pi)^2 k_0 z} d^2 k_0; \quad (4) \]

Where \( P(k_0) \) - a refraction index for the transition from the upper wave (water) in the bottom half (cluster), the half-space, which is calculated using Fresnel formula (5).

\[ k_{1z} = \frac{k_0^2 n^2 - k_0^2}{k_0^2 n^2 - k_0^2}; \quad (5) \]

where \( k_{1z} = k_{0n}; \)
\( k_0 \) - a wave vector in the upper half;
\( k_1 \) - a wave vector in the lower half;
\( c \) - a spatial vector in the horizontal plane;
\( h \) - a vertical coordinate of the surface relative to the chosen reference frame;
\( r_0 = (c_0, z_0) \) - a coordinate of a point source on the surface of a medium;
\( r_1 = (c_1, z_1) \) - a point in a medium.
Each plane wave is scattered by irregularities after penetration into the environment. Scattering by inhomogeneity can be calculated using a model of single scattering. In addition, each scattering heterogeneity becomes a source of spherical waves.

The scattered field at the receiver can be determined by the following equation:

\[ E(r_0, k_0) = k_0^2 \int \int_{r_1} \Delta e(r_1) U(r_1) \times \int_{-\infty}^{+\infty} \frac{P(k_0) \exp(ik_1(z_1+iz_2)+ik_2z_2)}{2(2\pi)^2k_1k_2} d^2k_0; \tag{6} \]

where \( P(k_0) \) - a transmission coefficient of the interface for the transition from the lower half to the upper half.

Formula (7) is a solution of the direct problem.

\[ f(c_p, k_0) = \int_{c_p} E(c, k_0)M(c_p - c, k_0)dc \tag{7} \]

where \( f(c_p, k_0) \) - the field focused at a point of near-surface heterogeneity;

M(k_0) - a transmission coefficient of the interface for the transition from the lower wavelength (cluster) to the top half (water).

We consider the problem of the effect of SMBS in a standard setting. The condition for the effect of SMBS is as follows:

\[ |E_2|^2 \geq \frac{8\rho_2^2r^2E_1\sigma_s\sigma}{4\pi} \tag{8} \]

where \( E, r \) - the elastic constant and the density of a medium [3].

This evaluation shows that there is not enough power for the formation of waves on air bubbles. We observe the effect of SMBS only on dissolved components. Assume that the acoustic field is defined by equation (9).

\[ U(r, t) = 0.5 \cdot U_s(r) \exp[i(\omega_s t - k_s r)] + m. k. \tag{9} \]

where \( r_1, r_2, r_s \) - distances along directions \( k_1, k_2, k_s \), so \( r_i = \frac{(k_i \cdot r_0)}{k_i} \),

where \( \alpha_s = \frac{-h}{\rho v} \) - an acoustic damping constant.

With the emergence of an acoustic non-linearity, the hyper-sound of a basic frequency should transform into the harmonics of higher frequencies, resulting in the strengthening of the second harmonica.

We can write the radiative transfer equation (10) to determine the field of dispersion in a medium with a finite value of concentration of scatterers. The scatterer is presented here as an ideal spherical particle.

\[ l_{rel} = l_0 = \int S_i(r, \varphi)dr = -k \cdot S_i(r) + \frac{\alpha}{4\pi} \int_{-\pi}^{\pi} \Phi(f_{ij}(r, r_0), S_j(r_0))dr_0; \tag{10} \]

where \( S_i \) - a relative component of the vector of Stokes parameters of the light field \( f(c_p, k_0) \) in a medium for each element [3].

\( r \) - the direction of a light beam;

\( k \) = \( (\pi + \sigma_i) \) - a relative attenuation coefficient;

\( \sigma_i = \sigma_p + \sigma_\eta + \sigma_{coll} \) - a relative scattering coefficient;

\( \alpha \) - a relative absorption coefficient;

\( f_\varphi(\varphi) \) - a relative scattering matrix;

\( \varphi \) - a scattering angle, i.e. an angle between the incident \( (r_o) \) and scattered \( (r) \) light beams;

\( \Phi \) - a relative density of luminous flux;

\( S_i(r_0) \) - a relative scattering on each element.

For the case of a semi-infinite layer the expression for reflection coefficients of multiple scattering in the first approximation becomes as follows:

\[ \ln \frac{R(\beta)}{R(\beta=0)} \approx -S(r, r_0)\eta \cdot \beta; \tag{11} \]

where \( q \) - an expansion coefficient of 1st degree, as shown in our earlier studies[3].

If a scattering medium with \( \alpha = \alpha_0 \) and \( \sigma = \sigma_0 \) has an impurity scattering or absorbing particles with \( \alpha_1 = \sigma_2, \sigma_1 = \sigma_2 \), then the rates of absorption of a dispersive medium is dependent linearly on concentration \( C \), therefore:

\[ \beta = \frac{\sigma_0 + \sigma_1}{\sigma_0 + \sigma_1} \tag{12} \]
If an effective radius $r$ of a scattering medium particle is large compared to wavelength $\lambda$, and if $\frac{4\pi\chi}{\lambda} \ll I$, where $\chi$ is an absorption coefficient for the substance of the particle, then:

$$\sigma = 2\pi r^2 N$$  \hspace{1cm} (13)

where $N$ - a number of particles per unit volume.

Substituting respectively $\alpha = \pi r^2 k \frac{4\pi\chi}{\lambda} N$ where $k$ is a factor for the particle shape, $\beta = k\rho\chi$, $\rho = \frac{2\pi r}{\lambda}$, we obtain equation (14)

$$\ln \frac{R(\beta)}{R(\beta=0)} \approx -5\eta \frac{k\rho x}{\xi}$$  \hspace{1cm} (14)

The relations obtained affect reflectivity only depending on $h_\beta(r,r_0)$, while $S_\beta(r,r_0)$ have to be determined experimentally. They can be obtained also by solving the transport equation. For our case, we got these relations in the approximation of spherical scatterers. This approximation was verified experimentally by us in [3].

As is known, the scattering function for a marker is determined by the formula calculated in the Rayleigh-Gans approximation:

$$I_1 = \frac{(2\pi)^4}{\lambda^4} \frac{\lambda^2}{V} \left( \frac{n_2}{n_1} - 1 \right)^2 \cdot I_0(1 + \cos^2 \theta) G^2(2\sin \frac{\theta}{2})$$  \hspace{1cm} (15)

where $G(U) = \frac{9\pi}{2\xi^5} I_2(U)$, $x = \frac{2\pi dp}{\lambda} n_2$;

$I_0, I_1$ - intensities of the incident and scattered light;
$\lambda$ - a wavelength of the incident light in a vacuum;
$n$ - a refraction index for scattering particles;
$V$ - a volume of a particle;
$\theta$ - a scattering angle;
$r$ - a radius-vector from an observation point to a point of scattering;
$I_2(U)$ - Bessel function.

$$A(p,r) = \frac{\pi}{\xi^3} (1 - e^{-i\pi \xi}) I_0(2\cos r) \sin r \, dr$$  \hspace{1cm} (17)

The experimental verification of these relations is provided in work [3]. A general expression for the reflection index relation can be written as:

$$\ln \frac{R(\beta)}{R(\beta=0)} \approx I_1 I_2 \eta \frac{\beta}{\xi}$$  \hspace{1cm} (18)

We obtained a transcendental equation for $R(\beta)$, which is related to the relative intensities in the previous experiments. The constant is determined only by the parameters of a device.

Studying scattering patterns for biological solutions is a difficult task. However, the following function can be accepted semi-empirically in many cases.

$$\ln \frac{R(\beta)}{R(\beta=0)} = I_1 I_2 I_3 \beta_1 \beta_2 \beta_3$$  \hspace{1cm} (19)

where $I_i$ - relative intensities for the pollutants dispersed in a distilled water, in a turbulent flow and in a stationary aqueous solution, containing a toxin;

$\beta_3$ - a coefficient characterizing a scattering matrix, $\beta_3 = 1$ for a strictly parallel beam.

In the first approximation it holds:

$$\sigma = \alpha (1 - k_{pr})$$  \hspace{1cm} (20)

On using a set of experimental data and averaging, a scattering coefficient can be determined in aqueous solution. Let us assume that we are dealing with a parallel beam, having the difference between the angle of incidence and the
receiving angle of 180°. Then we can assume that a = 1. If we have a scatter plot, then a scattering coefficient can be determined by equation (21).

\[ \alpha(\varphi) = \frac{1 - k(\varphi)}{1 - k_2} \]  

(21)

where \( k_2 \) - a scattering coefficient at an angle of 180°;

\( k(\varphi) \) - a scattering coefficient at an angle \( \varphi \), which enters the expression for determining the intensity in the presence of lead salts in a medium.

This technique was tested in a typical medium for simulation - in milk. Milk is a colloidal solution of spherical particles of fat and protein. As a medium for simulation, it is used for the development of devices to study water in the seas and oceans. Thus, milk is known to be a good analogy of biological objects containing proteins and nucleic acids.

Formula (16) shows, that dispersion angles also can effect the determination of viruses, and therefore, the sensitivity range of the method. Thus, we paid particular attention to the calculations and experimental measurements of dispersion diagrams for the objects involved.

To establish any angular dependence we need to determine relative intensities. The following relation holds in the first approximation:

\[ \ln \frac{R(\varphi)}{R(0)} = D \left( \frac{l_1}{l_0} \right) = \ln \left( \frac{l_1}{l_0} \right) = I_1 I_2 \frac{\beta_1 \beta_2}{\beta_1(\varphi) \cdot \beta_2(\varphi)}; \]  

(22)

then:

\[ \frac{\beta_1(\varphi) \cdot \beta_2(\varphi)}{\beta_1(\varphi) \cdot \beta_2(\varphi)} = \frac{\Delta \ln \frac{I_1}{I_2}}{\frac{\Delta \ln \frac{I_1}{I_2}}{I_1 I_2}}; \]  

(23)

From this relation we can deduce the following formula:

\[ \frac{\beta_1(\varphi) \cdot \beta_2(\varphi)}{\beta_1(\varphi) \cdot \beta_2(\varphi)} = \sigma_1 \sigma_2; \]  

(24)

\( I_1, I_2 \) and \( \frac{\Delta \ln \frac{I_1}{I_2}}{\Delta \varphi} \) can be defined by formulas (16) and (17 .. 19).

Using only a single measurement for a differential scattering pattern results in a too big error. Therefore, ten scattering diagrams were calculated and used for deriving average values \( \sigma_1 \) and \( \sigma_2 \) in acetum.

For further developments we are interested in studying not only the total response of a scattering medium on toxins, but also in defining how exactly every dissolved component influences the scattering pattern. So, we have:

\[ \sigma_0 = \frac{\sigma_1 \sigma_2}{\sigma_1}; \]  

(25)

where \( \sigma_1^* \) - an average value of a maximum diameter for pollutant dispersion.

After substituting semi-empirical relations, the equation was solved in Rytov approximation. The calculations were made using data of the diffraction phenomena at the output of the fiber from [3-5]. Fig.3 shows the dependence of the divergence angle of a radiation cone on a distance.
Given a self-focusing associated with scattering from air bubbles, it should be noted that the threshold intensity for the solution is almost an order higher than the threshold set in [4]. Fig.4. shows the dependence of distribution of the relative intensity at the maximum on the concentration of air bubbles.

Fig.4. Dependence of beam radiuses relation on the concentration of air bubbles.
3. EXPERIMENTAL SETUP

1 - a laser with a wavelength of $\lambda = 830$ nm (or 1010 nm), 2 and 4 - optical waveguides, 3 - a rotating cuvette, 5 - Agilent spectrum analyzer with a resolution of 0.05 nm, 6 - PC.

We employed semiconductor lasers with a wavelength of $\lambda = 830$ nm or 1010 nm and a maximum output power of 150 mW. The power of lasers could be changed gradually. Stokes and anti-stokes components were defined accurately at a working power of 40 mW. The whole setup was placed in a light-tight enclosure. A standard fiber with the following parameters was used: a numerical aperture of NA 0.15 micron and a core diameter of 105. The beam diameter was much smaller than the diameter of a cuvette.

4. DESCRIPTION OF EXPERIMENTS

Primers were selected to simulate dissolved particles. We used oligonucleotides FAM, HEX etc., because they have a spherical shape [3] and do not cause peaks at infrared luminescence, as shown in Table 1. The primers were diluted with water, added to a cuvette and pre-centrifuged to obtain an evenly distribution of a solution. The concentrations of primers ranged from 1 to $10^7$ oml / (7 lgtds50).

The laser radiation (1) with a wavelength of $\lambda = 830$ nm (or 1010 nm) was applied along a waveguide (2) to a rotating cuvette with water (3). Then the reflected scattered light was fed through a waveguide (4) into a high-precision spectrum analyzer Agilent (5) with a resolution of 0.05 nm. The obtained spectra were stored and processed by a PC (6). To get stable results we chose the averaging of a high degree. Each result was recorded twice with an interval of at least five minutes. A laser wavelength was chosen based on the table of optical properties of the primers used (Table 1).

Table1. The optical properties of primers.

| Oligonucleotides | The maximum absorption | The maximum emission | absorption coefficient |
|------------------|------------------------|---------------------|-----------------------|
| FAM              | 494                    | 519                 | 65000                 |
| TET              | 521                    | 536                 | 99000                 |
| HEX              | 530                    | 556                 | 98000                 |
Fig. 6-10 presents the following spectral distributions:

Fig. 6 shows the spectral distribution of the laser power irradiated to a stationary cell with distilled water. The flow rate is zero in this case. There is only one peak here with the maximum at a wavelength of $\lambda = 811.73$ nm and an intensity equal to -5.476 dBm. The peak corresponds to the laser field.

Based on our calculations, we chose an angular velocity of a cuvette. It was done carefully to exclude an additional Stokes component due to scattering from air bubbles as well as to avoid multiple scattering by the diffraction of inverse components. An angular velocity of a cuvette was determined using an analogue of Reynolds number.

Fig. 7 shows the scattering spectrum, observed at an angular velocity of a cuvette equal to 6 rot/min.

Both Stokes and anti-Stokes components are weak. There is only one peak here with the maximum at a wavelength of $\lambda = 810.69$ nm and an intensity equal to -1.087 dBm. The peak corresponds to the laser field.

Fig. 8 shows the scattering spectrum, observed at an angular velocity of a cuvette equal to 30 rot/min.
Fig. 8. Spectral scattering at medium flow rates.

This case corresponds to the transient beam. We can see here that anti-Stokes component also increases with the velocity of the fluid. There are two peaks here: 1 - the maximum at a wavelength of $\lambda=815.18$ nm with an intensity equal to -14,274 dBm; 2 - the maximum at a wavelength of $\lambda=811.88$ nm with an intensity equal to -26,724 dBm. Peak 1 corresponds to the laser field, while peak 2 is associated with cavitation processes in the liquid.

Fig. 9 shows the scattering spectrum, observed at an angular velocity of a cuvette equal to 120 rot/min.

Fig. 9. Spectral scattering at high flow rates.

Again we can see that Anti-Stokes component increases with the velocity of the fluid. The second harmonic also increases significantly, as is shown in Fig. 11. There are two peaks here: 1 - the maximum at a wavelength of $\lambda=815.17$ nm with an intensity equal to -15,427 dBm; 2 - the maximum at a wavelength of $\lambda=812.22$ nm with an intensity equal to -18,803 dBm. Peak 1 corresponds to the laser beam, peak 2 represents Anti-Stokes component. The intensity logarithm is proportional to the concentration of the marker.
There are two peaks at a cuvette rotation speed equal to 120 rot/min.: 1 - the maximum at a wavelength of \(\lambda=1624.48\) nm with an intensity equal to -25.966 dBm; 2 - the maximum at a wavelength of \(\lambda=1630.49\) nm with an intensity equal to -23.881 dBm. The concentration of a marker is proportional to logarithm of the intensity for both of the peaks.

During the experiments we found that the intensities of both Stokes and anti-Stokes peaks increase with increasing an angular cuvette velocity. The complete analysis of the experimental data shows also that the second harmonic of the intensity increases significantly. However the intensity of the second harmonic is still much smaller than that of the first. Yet the second harmonic has a better signal/noise ratio, which makes possible to use it as an informative signal.

The experiments show that it was possible to observe only one of Stokes and anti-Stokes components up to a rotation speed about 60 rot/min. The results of both theoretical and experimental calculations were used to refine a scheme of an optical device for the rapid analysis of superecotoxicants in drinking water.

5. CONCLUSIONS

A mathematical model of the motion of a turbulent flow was developed to help us investigate the dynamics of air bubbles in water.

In a series of experiments for a flow of water with dissolved impurities, we found that the peaks that correspond to the second harmonic depend only on concentrations of dissolved substances. Analysing the spectral distributions of these peaks is more likely to determine the type of solute than analysing the Stokes and anti-Stokes peaks corresponding to the first harmonic.

We observed a self-focusing of a laser beam and found it to depend on the concentration of air bubbles.

Several peaks in the Stokes and anti-Stokes regions were observed with increasing flow rate. The intensity of the peaks was found to increase with the rising concentration of air bubbles.

The results were used to refine a scheme of an optical device for the rapid analysis of superecotoxicants in drinking water.

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