Some Issues of Fluorescence Characteristics Aqueous Media via Diagnosis of Laser Spectroscopy Method

Nugzar Gomidze, Kakha Makharadze, Miranda Khajishvili, Izolda Jabnidze, Zurab Shashikadze

Abstract— Fluorescence spectroscopy represents the effective method of studying dynamic processes in solutions. This method will be greatly applied in biology, medicine, material studies and nanotechnology, and of course, in ecology. The parameters of fluorescence spectroscopy, like: radiation spectrum, life duration, quantum yield, fluorescence anisotropy – represent the sensitive functions of the processes, which depend of the life duration of excited condition. The molecules can participate in these processes which are in 10 nm distance from fluorofore at the moment of excitation. The diagnostics of water media applying laser fluorescence method is essentially different from the early standard methods (chromatographic or gravitational), resulting in sensibility, distances and express-diagnostics. A special device - fluorometer, is a complex of devices, which enables us to get the spectrums of any water media and discuss about the quality of its pollution.

Index Terms— Fluorescence excitation spectrums, internal Rapper method, Spectro fluorimeter

I. INTRODUCTION

As a result of man's intensive activities, the pollution of the world oceans and the pollutions of domestic waters reached such scales that the natural mechanisms of clearance are not capable of their utilisation. It causes the breakage of ecological balance, which is more and more difficult to control and causes natural excitation on the future of biosphere [1].

Anthropogenic pollution includes various components, among which nowadays, the first place belongs to oil and oil products, as well as a number of organic compounds. Fighting against this pollution is a modern problem [2]. By the statistic data, the annual anthropogenic flow of oil products in the sea is caused by the loss of oil on tankers.

Protecting environment from pollution is closely related to its discovery and then its control. This is a difficult problem since the pollution factors represent the complex of different complicated organic substances. After being in water many different processes take place (for instance: transfer in atmosphere, degradation, influence of biological factors etc.), which are less studied. A number of methods of watery media analyses have been applied and studied so far (for instance: infrared spectroscopy method, core magnetic resonance on Shpolski effect, gravitational or weight method, chromatography etc.). It is admitted that the limited accepted concentration in sea water is 50 mkg/L [3,4].

Nowadays, for discovering and studying the oil products and organic compounds in water spectral optical methods are used the principal advantage of which towards other methods is their express-diagnostics and distance. The express-diagnostics implies the quick discovery of pollution in water via optical methods in order to eliminate the pollution sources on time and liquidation of pollution sources as possible (we mean tankers, terminal etc). Though, there are some differences even among optical methods. One of them is laser fluorescence [5,6]. There are lots of organic substances, which have peculiar features after optical excitation, they start radiating – fluorescence.

Fluorescence – represents a physical process and is considered as one of the kinds of luminescence. During radiating a substance with light, it is possible the electron to move among the different levels of energetic levels. The difference of energy among the energetic levels and the frequency of absorbed light oscillation are connected to each other with **Bohr's** third postulate. While absorbing light, the part of the energy received by the system is used for relaxation and the other part is radiated in the image of photon of determined energy. Schematically, the photon radiation and the absorption is expressed with **Iablonski** diagram [11], according to which the fluorescence

is radiation during transferring from S_1 singlet oscillation level to S_0 level or it can be discussed as radiation not limited with spin during triplet $T_1 \rightarrow T_0$ transfer. The life duration of the fluorescence is $10^{-11} - 10^{-6}$ seconds. Singlet-triplet transfers are characterized to fluorescence. Due to quantum-mechanic limitations, the life duration of the excited condition during fluorescence equals to $10^{-3} - 10^{-2}$ seconds. In normal conditions, the significant part of the molecules is in S_0 condition. During absorbing light, the molecule moves in S_1 condition. During the excitation of the electron on the higher energetic levels, the excessive energy is rapidly used on relaxation processes and the electron appears on lowest oscillation sublevel of S_1 level. Though, there are some exceptions.

For instance, **Azulene's** fluorescence may take place on both, S_1 or S_2 levels.

The organic substances are conditionally divided in four classes, they are: photosynthesizing substances – phytoplanktons, amino acids, water humus-like substances, oil and oil products [7]. There always exist and always fluorescence solved organic substances in water media. Their fluorescence signal makes up a background on oil fluorescence signal and it significantly blocks its discovery. We receive the fluorescence spectrums simultaneously, which reflect the spectrums received from both: oil and other organic substances. There are different ways of separating these spectrums [8], but none of them is perfect. Due to this reason, it is required to investigate the spectrums of fluorescence of additional organic substances apart from oil and oil products. It is rather easy to discover the solid particle floating in the water and substances and to determine their concentration [9].

Making scientifically well-grounded connections between fluorescence characteristics of water media and the concentration of components in it is a difficult problem. For instance, take a natural dissolved organic substance, which is in all kinds of water and any part of it is not exactly known so far, it gives fluorescence. Due to this fact, the **research is reduced to establishing empiric connections and to establishing corresponding correlative attitudes.** Establishing these kinds of attitudes is the first stage of the research, which is to be followed by theoretically certified connections.

The fluorometer enables us to register the fluorescence spectrums of organic molecules and the combinative scattering (Raman's scattering) of water graphically, as curves. For the signal calibration the **internal Rapper method** is used. It is based on the comparison of the intensities of spectrums of organic molecules and combinative scattering [10]. Thus, we can determine the concentration of fluorescencing admixtures if their spectral-luminescent characteristics are known. The special peculiarity of this method is that the mentioned spectrums are displaced along the long waves. This phenomenon received the name of **Stokes Displacement** in scientific society [12]. The reason of this displacement is the **relaxation – absorption processes** (Relay and Me's scattering). The part of the photon energy absorbed by the system as light is lost and the photon radiated by the system has less energy, consequently, it has longer wavelength [13]. The relaxation processes cause the creation of the background of strong "electronic noise", which overlays to fluorescence signal, though, it is possible to suppress using spectral filter.

The excitation of fluorescence with laser radiation, which is characterized with high spectral brightness and with direction give additional possibilities for resolving the given problem.

Via using lasers, an important light field can be made on large distances from the device and distance sounding to be carried out [13]. In short impulses ($\approx 10^{-8}$-10^{-9} c) the light concentration enables us to do lab analyses without darkening (on the expenses of the receiver's gating). High spectral brightness of laser radiation provides the high sensibility of laser fluorometer and we can make an express-analysis of natural waters sample (some cm^3) without their concentration, we can also register the Raman-scattering signal of water molecules and use it as a comparative signal - internal Rapper [14, 15].

The oil and organic compounds are characterized with fluorescence during the excitation with ultraviolet or visible light. Not all the molecular system is characterized with the own fluorescence in more or less intensity. Polysaturated condensed and of course, aromatic and polyaromatic compounds are well fluorescencing. Hetero

atomic or electron-domain systems should be particularly mentioned. Special organic and non-organic substances are fluorescencing perfectly, which are used in making displays, monitors, photodiodes and lasers. Natural compounds are fluorescencing in comparatively less quality. From natural admixtures which are fluorescencing well, should be mentioned natural paints, some amino acids (Tryptophan and Tyrosine) and the protein containing them, cofactors (NADH), vitamins (riboflavin). ***The own fluorescence is the basis of discovering and identifying natural admixtures and oil products***. For solving this problem the following characteristics of fluorescence are significant:

- **Fluorescence excitation spectrums** [15-18];
- **Time of reducing fluorescence**, which is determined as time during of which the intensity of fluorescence is reduced e – times [19-23].

During laser excitation these characteristics can be added by the parameters of fluorescence non-linearity, for instance, the **factor of fluorescence saturation**, which represents one of the interesting problems.

In fundamental point of view, the processes of natural fluctuation are very interesting, which take place in water. Molecular scattering of light in water is connected to the thermal fluctuation processes, which represent the function of reflection indicator, density, pressure, temperature, entropy and molar concentration. According to **Onsager's** hypothesis, the fluctuation processes in water can be described with the macroscopic hydrodynamic rules. And fluctuation attenuation is described with time auto-correlative function, the Fourier-transform of which gives the analytical expression of the intensity of the optical spectrum, according to **Wiener-Khintchin** theorem. Of course, the chaos of fluctuation processes in water makes us consider the diffusion processes as well (Einstein-Stokes formulae), which are finally reflected in analytical expression of the spectrum intensity.

II. ABOUT OF FLUORESCENCE CHARACTERISTICS

In natural watery media, the fluorescence compounds are organic molecules. Their spectrum is caused as a result of widening by the shakes and rotation of singlet and triplet level system. The relationship of this kind of molecules with light can be described by means of cinematic equation system. Their salvation in quasi-stationary approximation (excitation impulse duration τ_i is much more than the time of relaxation of excited levels settlement), for the number of registered fluorescence photons, gives the following expression:

$$N_f = \Delta^{-1} n \sigma_f F_V \tau_i V T_{rec}(\lambda_f) T_D(\lambda_f), \tag{1}$$

where n - is the concentration of fluorescence particles (cm^{-3}); σ_f - is the fluorescence cross ($cm^2 \cdot stereos^{-1}$), in the simplest case, when one and the same molecule absorbs and florescences.

$$\sigma_f = \frac{1}{4\pi} \sigma_a \cdot \eta, \tag{2}$$

σ_a - is the absorption cross (cm^2) on the length of excitation wave; η - is fluorescence quantum efficiency corresponding; $F_V = F \cdot T_D(\lambda_f)$ - is the density of the photon flow of exciting radiation from research mediums; F – is the density of laser radiation photons flow; τ_i - is excitation impulse duration; V - is the excited capacity of the media; $T_{rec}(\lambda_f)$ - apparatus factor, which depends on the receiver's characteristics; $T_D(\lambda_{ex})$, $T_D(\lambda_f)$ - are factors which depends on conditions of laser radiation from fluorimeter to the investigated media and distribution of fluorescence from the investigated media to fluorimeter.

$$\Delta = 1 + \sigma_a \cdot \tau \cdot F_V, \tag{3}$$

Δ - is the fluorescence saturation factor, τ - is the life duration of excited state. We discuss the case when the effect of fluorescence saturation is connected to the poverty of basic level of the molecules by the action of rather large density flow of F_V photons.

According to the determination…

$$\Delta = \frac{N^0{}_f}{N_f},\tag{4}$$

where $N_f^0 = n\sigma_f F_V \tau_i V T_{rec}(\lambda_f) T_D(\lambda_f)$ is the registered number of the fluorescence quanta during nonexistence of the saturation.

To measure N_f - it is useful to use spontaneous Raman scattering of the light on the water molecule, in the range of comparison signal, the number of photons of which is calculated by the formula:

$$N_{RS} = n_{H_2O}\sigma_{RS} F_V \tau_i V T_{rec}(\lambda_{RS}) T_D(\lambda_{RS}),\tag{5}$$

where n_{H_2O} is the molecular concentration of water, σ_{RS} - Raman scattering cross ($cm^2 \cdot stereos^{-1}$).

The simultaneous registration of Raman scattering of fluorescence of organic molecules and water enables us to move onto rational volumes:

$$\Phi = \frac{N_f}{N_{RS}}; \quad \Phi = \frac{N^0{}_f}{N_{RS}}; \quad \Delta = \frac{\Phi_0}{\Phi}.\tag{6}$$

Their measurement is rather easy than measuring absolute volumes. The given formulas enable us to determine the concentration n of fluorescence compounds if we know its spectral characteristics

$$n = \Phi_0 \cdot \frac{n_{H_2O} \cdot \sigma_{RS}}{\sigma_f} \cdot \frac{T_{rec}(\lambda_{RS}) T_D(\lambda_{RS})}{T_{rec}(\lambda_f) T_D(\lambda_f)}.\tag{7}$$

The equation $T_{rec}(\lambda_{RS})/T_{rec}(\lambda_f)$ can be easily determined if to accept in a view that in laboratory measuring

$$T_D(\lambda_{RS})/T_D(\lambda_f) = 1.$$

We direct laser beam of definite wavelength through the water sample, then carry out the spectral analyses of the signal received as a result of light interaction with molecules. Two components are distinguished in this spectrum, first, the one which is caused by the interaction of laser radiation with the molecules of the selected mixtures in the water and, second - with the water molecules themselves. The number of photons in this component will be:

$$N_f = n_f \sigma_f N_0,\tag{8}$$

$$N_{H_2O} = n_{H_2O}\sigma_{H_2O} N_0,\tag{9}$$

where n_f and n_{H_2O} (cm^{-3}) are the concentrations of mixtures and water, respectively. σ_f and σ_{H_2O} - are the crossings of interaction processes of laser radiation with mixtures and water molecules. N_0 is the number of photons of exciting laser radiation. We receive concentration calculating formula from (8) and (9) pictures, since the concentration of water molecules is practically constant and $n_{H_2O} = 3,33.10^{22}$ cm^{-3}. In particular,

$$\frac{n_f}{n_{H_2O}} = \Phi_0 \frac{\sigma_{H_2O}}{\sigma_f},\tag{10}$$

where

$$\Phi_0 = \frac{N_f}{N_{H_2O}}.\tag{11}$$

In our case, N_{H_2O} is the number of photons of Stokes component of spontaneous Raman scattering of light in the water and the crossing of this scattering has already been known, and N_f is the number of fluorescence photons of the organic mixture dissolved (floated) in the water. N_f and N_0 are proportional to the areas surrounded by

correspondent spectrums and their ratio, or ϕ_0 parameter can be determined by means of rationing these areas. If we know σ_f then we can finally calculate n_f from (10) and (11) and resolve the problem.

It was found out that the fluorescence signals of two necessary components – phytoplankton and dissolved organic substances belong to Rapper's (signal of Raman scattering in the water) order. Apart from these natural mixtures, artificial organic mixtures (oil, oil products, solutions, pesticides, etc.) fluorescent in the water can also be defined via applying the same method. It is not difficult to evaluate that

$$\frac{n_f}{n_{H_2 0}} \approx 10^{-9} = 10^{-3} \, ppm = 1 ppb \,.$$

This is corresponded by the value $\rho \approx 0,1$ mkg/l.[*] Fluorescence parameter Φ_0 can be used as a numerical dimension for at least four fluorescence mixtures existing in the sea water: *1) phytoplankton; 2) natural dissolved organic substance; 3) oil products; 4) solutions and similar compounds*. It should be mentioned here that even the problem of laser diagnostic for the mentioned objects has not been resolved yet. Let's discuss the solutions illustrations, since this is the case where everything goes better.

The solutions (and other similar organic compounds) are used in oceanology in the image of fluoroindicators. They facilitate the process of studying water dynamics, measuring the velocities of turbulent diffusion in the direction of both, horizontally and vertically. For solutions everything is known which are necessary for determining them in the water – fluorescence spectrums and fluorescence crossing σ_f .

As an illustration, let's evaluate the concentration of paint Rodamin 6J, when fluorescence parameter $\Phi_0 = 1$ when $\lambda_0 = 532 \, nm$;

$$\sigma_a = 2.45 \cdot 10^{-16} \ cm^2; \quad \eta \approx 0.9;$$

$$\sigma_f = \frac{1}{4\pi} \sigma_a \cdot \eta = 1.7 \cdot 10^{-17} \, cm^2 \cdot stereos^{-1}; \ \ \sigma_{H_2 0} = 0,53 \cdot 10^{-29} \ cm^2 \cdot stereos^{-1} \,.$$

Then from (10) we receive:

$$\frac{n_f}{n_{H_2 0}}\Big|_{\Phi_0=1} = 3.10^{-13}, \quad \text{from this} \ \ n_f\Big|_{\Phi_0=1} = 10^{10} \ cm^{-3} \,.$$

Comparatively high efficiency of transferring the exciting radiation into fluorescence enables us to use a fluorescence method while investigating oil. At the same time, it is known that there are a lot of varieties of oil and oil products, the fluorescence spectrums of which are different from each other. Spectral interval, in which the maximum of fluorescence exists, starts 360 nm (petrol) and ends up on 494 nm (heavy fractions of oil). The maximums of the rest of oil and oil products fluorescence hold an internal place. The spectrums of raw oil fluorescence are located in the part of long waves, the spectrums of petrol, Diesel fuel, kerosene – in the part of short waves and the oil spectrums hold the internal place.

We for measuring applied a method of an interior reference point when the signal of fluorescence mineral oil in water is compared to a signal Stokes component a water or Hexane Raman effect (for Hexane extracts and solutions) [18].

By test preparation emulsive oil was poured on a surface of the distilled water then for correlation the jarring by means of the ultrasonic correlator was spent. Light dispersion on frequency excitation from the sample of an emulsion in 2-6 times exceeded the Rayleigh scattering on water molecules [19]. The shape of a spectrum of fluorescence dissolved of mineral oil depends on type mineral oil on initial stage a little and does not depend on time of finding the mineral oil in water. It is stable also intensity of fluorescence in the course of ageing and feebly depends on type mineral oil on initial stage.

The method consists in examination of the processes natural fluctuation which are taking place in fluids. The diffusion of these fluctuations is characterized by usual macroscopical kinetic coefficients. An effective method of studying of processes of a diffusion fluctuation in the transparent fluids is the molecular dispersion of light. The physical reasons of the molecular light dispersion is thermal fluctuations of an exponent light refractive. These fluctuations are in turn caused by fluctuations of the thermodynamic quantities which function is the refraction index. Generally unitary dipole dispersion of light in an intermixture of two fluids for intensity of a diffused light validly expression:

$$I = \left(\frac{\partial n}{\partial \rho}\right)_{T,x}^2 \left(\frac{\partial \rho}{\partial p}\right)_{S,x}^2 \left(\bar{\Delta}p\right)_{T,x}^2 + \left(\frac{\partial n}{\partial \rho}\right)_{T,x}^2 \left(\frac{\partial \rho}{\partial s}\right)_{P,x} \left(\bar{\Delta}s\right)^2 + \left(\frac{\partial n}{\partial x}\right)_{P,T} \left(\bar{\Delta}x\right)^2 ,$$

where n - a refraction index, ρ - density, P -pressure, T -temperature, s -entropy, x - molar concentration of a solution.

The diffused light spectrum is diagrammatically figured on fig.1. Bias rather ω_0 - frequencies of exciting light on $\omega_0 \pm \Omega$ line, are termed as builders of Mandelstam - Brillion (MB). Detrusion component is caused by a Doppler effect at light dispersion on running spontaneous sound waves and, accordingly, is proportional to velocity of a sound in medium. The line broadening occurs at the expense of absorption of sound waves.
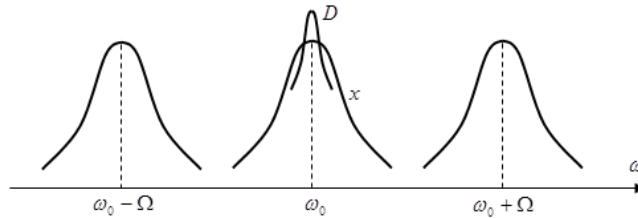

Fig. 1. Spectrum of a diffused light an intermixture of two fluids

Central a builder located on frequency of exciting light, consists of two lines: the narrow line is caused by signal attenuation of fluctuation of concentration - diffusion processes, wide - signal attenuation of fluctuation of heat - thermal conduction processes. According to a hypothesis of Onsager's, process in a fluid can be featured a fluctuation diffusion by means of macroscopically magneto hydrodynamic equations. So, for process of a diffusion of fluctuations of concentration δx(r,t) expression is valid:

$$\frac{\partial \delta x(r,t)}{\partial t} = D\nabla^2 \delta x(r,t), \tag{12}$$

From this:

$$\delta x(k,t) = \delta x(k,0) \cdot e^{-\Gamma t}, \quad \Gamma = Dk^2 . \tag{13}$$

Γ - The characteristic frequency signal attenuation of fluctuation of concentration, D - a coefficient of diffusion, k - change of a wave vector of light at dispersion.

Fluctuation signal attenuation is convenient for studying using a temporary autocorrelation function:

$$G(\tau) = \frac{1}{T}\int_0^T f(t) \cdot f(t+\tau)dt = < f(t)f(t+\tau) > . \tag{14}$$

Then for the fluctuations featured by expression (13), autocorrelation function looks like:

$$G_x(\tau) = <|\delta x(k,t)|^2 > e^{-\Gamma \tau} . \tag{15}$$

According to (15), the autocorrelation function of light diffused on decadenting fluctuations of concentration will register in a view (for an electric field of a light wave with frequency ω_0):

$$G_E(\tau) = E_p \cdot e^{-\Gamma \tau} \cdot e^{-i\omega_0 \tau} , \tag{16}$$

the optical spectrum can be found under Wiener-Khintchin theorem:

$$S_E(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega\tau} \cdot G_E(\tau)d\tau . \tag{17}$$

From the solution (17) follows that the optical signal with exponential autocorrelation functions (16), has a spectrum in a view:

$$S_E(\omega) = E_p \frac{\Gamma}{\pi\left[\Gamma^2 + (\omega - \omega_0)^2\right]} \ . \tag{18}$$

Here Γ - a half-breadth of a spectroscopic line at semi height.
Gained above expression allow to calculate, using the corresponding measured value of breadth central builders of diffused light Γ, diffusion constant D.

For Brownian particles the diffusion constant and radius of particles r_0 is related by following expression (Einstein-Stokes formula):

The characteristic frequency of process of diffusion $\Gamma \approx 10^5\,\text{sec}^{-1}$ and usual spectrometer methods do not allow to measure such narrow spectroscopic lines. Overcoming of the arisen difficulties probably at use of a method of spectroscopy of optical mixture. The essence of a method consists that bending around a spectrum from optical frequency ω_0 is transferred to fields of low frequencies where the further analysis is carried out by spectrum analyzers or correlators of signals. Spectrum transport to frequency domain - the non-linear transformation grounded on method quadratic detection of light.

The radius of an emulsion for different tests was spotted. Their values lay in limits 0,270÷0,338 micron. Any monotonous changes of radius of an emulsion in the course of "ageing" emulsify oil product were not observed. Attempts to estimate breadth of allocation of particles on radiuses have shown a system monodispersity. It was not observed also changes of spectral characteristics of an old emulsion after additional crushing on ultrasonic monochromator. Last fact speaks also in favour of equilibrium inconvertible character of emulsions.

III. EXPERIMENTAL MEASUREMENTS

The applied part of the work is constructing experimental laser spectrofluorimeter. During modernizing experimental laser spectrofluorimeter, in 2009-2012, within the limits of the grant project GNSF/ST08/5-451, we put forward the nonstandard problem, which can be basically divided in three parts: 1. NL-100 control of nitrogen laser frequency from external device [24]; 2. Measuring the signal received on the photoelectric multiplier in synchronization of strobe signal; 3. Keeping and processing the obtained results using computer techniques.

But the experimental measures were complicated with the background of "noise", which was caused by echo signal of Raman-scattering from water molecules. It is clear that, the intensity of Raman's signal is significantly higher than the fluorescence signal intensity which we are interested in a great deal. That is the reason why we used special optical filters for weakening the intensity of Raman-scattering. Although, the optical filters, naturally, could not provide the important decrease of the background of "electronic noise". Due to the rotating-oscillating movement of the molecules in water solutions, the "noise" caused by the relaxation processes was added by the external "noise" caused by the age of the monochromator "МДП-72" and photomultiplier „ФЭУ-100" (fig.2).

In case the project is funded, we will have possibilities to eliminate the "noise" background at all, which is quite possible if we purchase the monochromator compatible with impulsive nitrogen laser (frequency 0-25 Hz) and sensitive photomultiplier (external "noise"), and in reducing the background of "electronic noise" caused by relaxation processes, multi channel analyzer will be helpful, which represents the system of electronic devises compatible with computer, such as: ADC (analogical-digital converter), DAC (digital-analogical converter) and electronic systems of management [20-24].
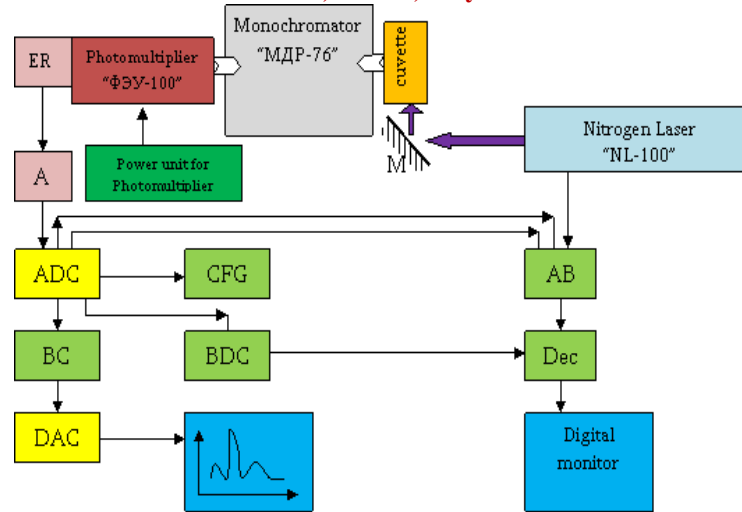
Fig. 2. Bloc-scheme of laser fluorimetry
M – flat mirror; ADC – analog–digital converter. DAC - digital–analog
converter; ER - emitter repeater; A – amplifier; BC - binary counter;
BDC - binary-decade counter; Dec – decoder; AB – automatic block;
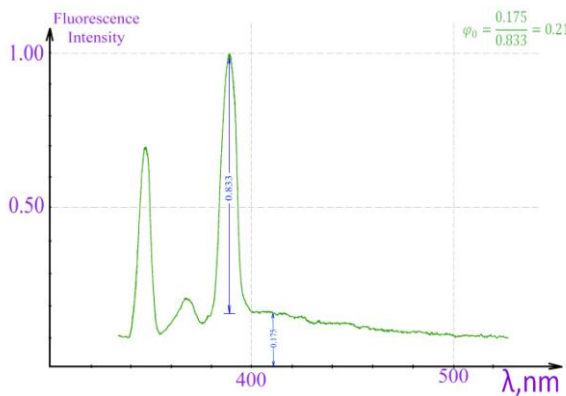**CFG – calibrated frequency generator**

Fig. 3. Spectrum of echo-signals of Hexane an
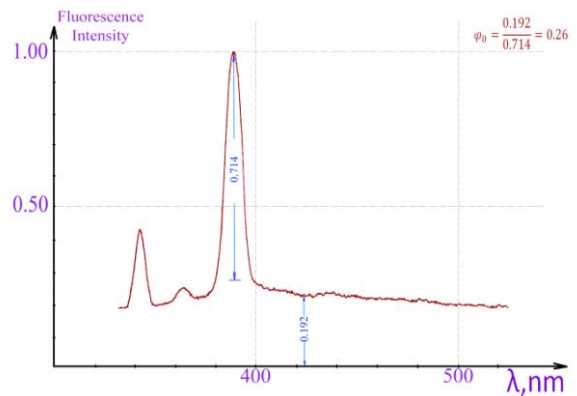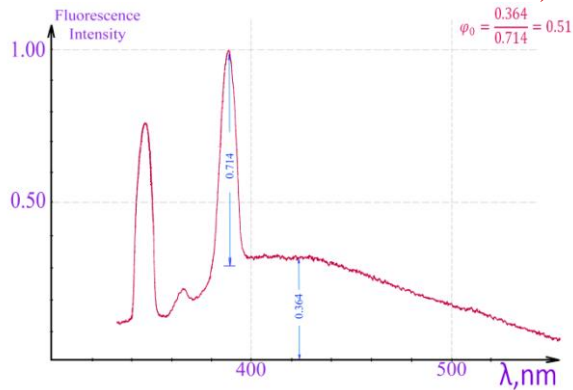**excitation by the nitrogen laser ($\lambda_0 = 337$ nm)**

Fig. 4. Spectrum of echo-signals of Distillate an
excitation by the nitrogen laser ($\lambda_0 = 337$ nm)

Fig. 5. Spectrum of echo-signals of Fresh Water an excitation by the nitrogen laser ($\lambda_0 = 337$ nm)

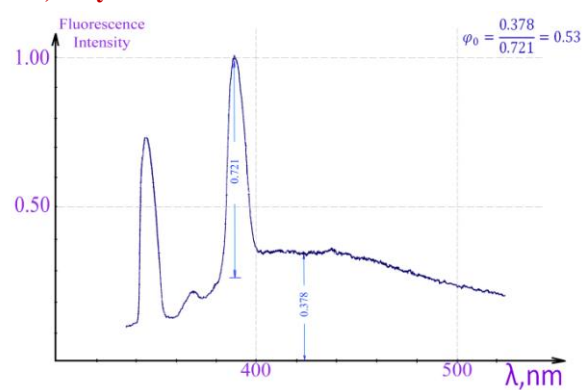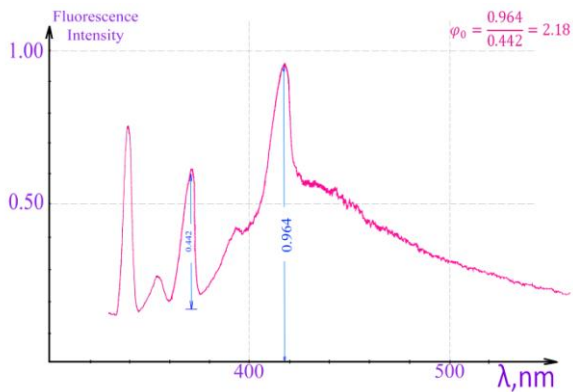**Fig. 6. Spectrum of echo-signals of Sea Water an excitation by the nitrogen laser ($\lambda_0 = 337$ nm)**

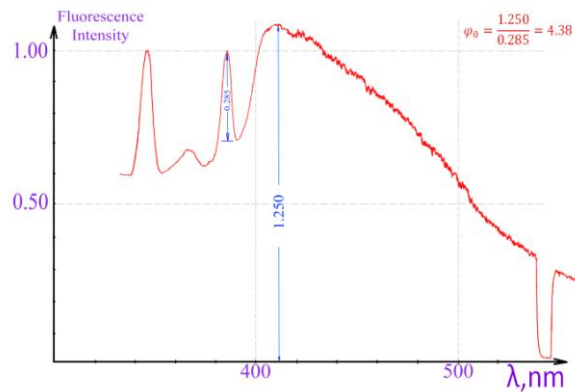**Fig. 7. Spectrum of echo-signals of oil extracts an excitation by the nitrogen laser ($\lambda_0 = 337$ nm)**

Fig. 8. Spectrum of echo-signals of oil an excitation by the nitrogen laser ($\lambda_0 = 337$ nm)

In order to receive the extractions we can use organic solvents, in our case Hexane (C_6H_{14}, fig.3). We have recorded the spectrums of spontaneous Raman scattering and fluorescence for Hexane together with pure water and water with oil (fig.4-8). The spectrums were taken in the similar conditions. By means of analytical treatment of the spectrums we can calculate the values which are interesting for us and judge about quality and numerical characteristics of fluorescence source (oil products in this case). As we see from the spectrums given above, the length of nitrogen laser ($\lambda = 337.1$ nm) is close to optimal in order to define the concentration of salved organic substances via the method of comparing water Raman scattering to its fluorescence, or internal rapper.

IV. CONCLUSION

In the conclusion it is possible to tell the following: by using $\Phi_0 = 1$ parameter it is impossible to diagnose thoroughly natural organic substances dissolved in water, since the fluorescence crossing is not known for them σ_f . The dissolved organic substance, which is in any natural water in different amounts, is ten thousands of organic compounds, which are not completely chemically identified. In sea water their fluorescence is well excited on radiating nitrogen laser, the wavelength of which ($\lambda = 337,1$ nm) is close to the maximum of excitation line of these substances. The mentioned prevents from processing diagnostic methods of oil and oil products in sea water which are interesting for us. The superposition of oil products and naturally dissolved fluorescence spectrum of organic substances take place. The reason is that the spectrums of both naturally dissolved organic substances and the fluorescence of different oil and oil products are wide spectrums and are not strongly different from each other.

At least, the spectrum should be separated and the oil or oil products existing in water should be identified in order to resolve the basic problem –diagnostics of water media.

The diagnostics of water media applying laser fluorescence method is essentially different from the early standard methods (chromatographic or gravitational), resulting in sensibility, distances and express-diagnostics. A special device - fluorimeter, is a complex of devices, which enables us to get the spectrums of any watery media and discuss about the quality of its pollution. The primary hydro optical characteristics of water media (absorption indicator, propagation indicator and indicatrix) can be used for receiving information on the situation of the media – about mineral and organic admixtures, solved organic substances, phytoplanktons and so on.

We have ascertained that the fluorescence form of oil products is less dependent to the primary sample type and is stable in time. The spectrums of different types of fluorescence of oil products strictly differ from each other, which is conditioned by their chemical consistency. We have ascertained that light fractions of oil is comparatively soluble, which cause the fluorescence of the oil products in water.

Thus, the diagnostics of water media is very complicated and difficult problem. The numerical analyses of oil products and organic compounds in sea water are especially difficult since their fluorescence qualities are changed according to time which is caused by different factors. For instance, first the oil is extend on the water surface, this process is characterized with: vaporization of light fractions, rusting, and salvation of more solvable fractions in water, influence of heavy sea, creation of non-stable emulsion, sedimentation and biological degradation. Only after this we can get a stable emulsion, though this time, the salvation process, biological degradation and sedimentation still continue, but the vaporization slows down. Theoretical formulation of the velocity of these processes, even for the given type of oil, is not accessible up to this moment. It means that, **the researches have to be continued in order to find out how the oil fluorescence is changed numerically in accordance to its existence in water.** This change, first of all, will be reflected on fluorescence spectrums.

V. ACKNOWLEDGMENT

REFERENCES

[1] Nelson-Smith A. Oil and ecology of the sea. 1998.

[2] Holcomb R.W. Seince, v.66, p.3902, 1966.

[3] Albani J.R. Fluorescence Spectroscopy. Blackwell Publishing. 2007.

[4] Oradovski S.G. Management on methods of the chemical analysis of sea waters. Leningrad, Hydrometeoizdat, 1977 (in Russian).

[5] Abraskin A.G., Holde S.E., Shashikadze Z.Kh., Fadeev V.V. Conferences "Optics of the sea and an atmosphere". Rostov-on-Don, Leningrad, 1988 (in Russian).

[6] Abraskin A.G., Holde S.E., Fadeev V.V., Chubarov V.V. Doklady AN USSR, #2, 1988 (in Russian).

[7] Fadeev V.V. Nonlinear fluorescence of complex organic substances. G. Soros educational magazine. #12, pp. 104-110, 2000 (in Russian).

[8] Omenetto N. Analytical laser spectroscopy. 1982.

[9] Abraskin A.G., Holde S.E., Galenko A.A., Shashikadze Z.Kh. Proceedings of III conference of Moscow State University. "Investigation of world ocean", Moscow, 1986 (in Russian).

[10] Davitadze Z.D. Definition of concentration of organic compounds and suspensions in natural waters using methods of laser spectroscopy with internal reference point. Ph.D. thesis, Tbilisi State University, 1994 (in Russian).

[11] Lakovich J. "Principles of Fluorescence Spectroscopy". Springer Science, 2006. p. 960 .

[12] Stokes G. G., Über die Veränderung der Brechbarkeit des Lichts, Annalen der Physik, B. 163 (11), 1852, S. 480-490 .

[13] Lidar Methods of discovering oil pollution sources. (hhtp://ecoline.kiev.ua/articles/pider/lidmru.htmi) .

[14] Beridze J. Davitadze Z. Fadeev V. Shahsikadze Z. Chubarov V."Laser fluorimweter for oil pollution control in sea water areas". Scientific conference. Batumi.1988. p. 177.

[15] Shashikadze Z., Gomidze N., Davitadze Z., Nakashidze O. "Fluoroscence spectrums of water soluble and emulsive oil". RSU works. Series: Natural Sciences and Medicine, Volume 13, pp: 238-241. Batumi.

[16] Gomidze N.Kh., Shashikadze Z.Kh. "Fluoroscence of emulsive oils and oil products in water". 3rd International Radio Electronic Forum "Applied Radio Electronics, Situation and Prospects of Development". "МРФ" – 2008. Ukraine, Kharkov, October 22-24, 2008.

[17] Shashikadze Z.Kh., Makharadze K.A., Gomidze N.Kh. Fluorescence Emullsive Oil and Oil Product in Water Media. 6th International youth scientific and technical conference "Modern problems of a radio engineering and telecommunications PT-2010". Sevastopol, Ukraine, 19 - 24 April, 2010.

[18] Gomidze N.Kh, Makharadze K.A, Shashikadze Z.Kh. Effective and expressive Method of water media diagnostics. Works of 17th Scientific Conference of TDASU Professor-Teachers and Students. Tbilisi, pp. 193-196, 2010.

[19] Shashikadze Z.Kh, Davitadze Z., Nakashidze O., Gomidze N.Kh. The problems of sea water diagnostics applying the laser spectroscopy method (fluoroscence). RSU works, series: Natural Sciences and Medicine. Volume 15, Batumi, 2009.

[20] Gomidze N.Kh., Shashikadze Z.Kh. About Laser Spectroscopy Method. International Conference & Exhibition Batumi – Spring – 2010. May 7 – 9, Batumi, Georgia.

[21] Gomidze N.Kh., Makharadze K.A., Shashikadze Z.Kh., Jabnidze I.N. Numerical Analyses of Sea Water with Laser Fluorescence Method. International Scientific Conference "Modern Issues of Applied Physics". Tbilisi, GTU, 30 March, 2011. pp. 95-97.

[22] Gomidze N.Kh., Makharadze K.A. Khajishvili M.R. Shashikadze Z.Kh. About Numerical Analyses of Sea Water with Laser Spectroscopy Method. 2011 XXXth URSI General Assembly and Scientific Symposium, pp,1620-1624, ISBN 978-1-4244-5117-3, Istanbul, Turkey, August 13-20, 2011.

[23] Gomidze N., Jabnidze I., Makharadze K., Khajishvili M., Shashikadze Z., Surmanidze Z., Surmanidze I. Numerical Analyses of Fluorescence Characteristics of Watery Media via Laser Spectroscopy Method. Journal of Advanced Materials Research Vol. 590 (2012), pp. 206-211.

[24] Davitadze Z., Gomidze N., Makharadze K. Control Laser Spectrofluorimeter with Microcontrollers. Journal of Advanced Materials Research Vol. 590 (2012), pp. 201-205.