



Analysis of the Methods of Water Systems State Estimation

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The state of water ecosystem is constantly affected by natural processes. Moving substances and energy in this system form a new dynamic balance which changes the parameters of the system itself. In the system, substances rotate from one link to another, while energy moves to one or the other direction, therefore thermodynamic parameters: mass, energy, entropy, enthalpy and their transfers of a metabolism process are to be estimated.

Oxygen concentration in the system influences the processes of organic substances production and destruction i.e. their intensity, thermodynamic stability, spontaneous purification and ecosystem state. By oxidizing nutrients a cell gathers energy for biosynthesis reactions, movement, and substances transfer. The energy released during oxidation-reduction reactions is consumed to maintain the building of a cell. On the basis of the variation of oxygen concentration, organic chemical impurities in water ecosystem are qualitatively and quantitatively analyzed. Concentration of nutrients in the system is indirectly evaluated by BOD and COD parameters which are susceptible to time and may be unreliable.

For this reason, to monitor the parameters, to prevent the discharge of badly treated wastewater, to control the technological process of wastewater treatment equipment, the efficient, fast and low-cost methods are to be developed.

The existing methods of determining the qualitative parameters of water ecosystems have been studied, compared among each other with the experimental results obtained by the comparative analysis method. When comparative parameters are determined by technological, legal, consumer and scientific approach and their evaluation scale is set up, the methods are evaluated as to the rate of the system state estimation. After the analysis of the methods of water system condition evaluation, all methods based on estimation of chemical, physical and biological parameters have been found to be unsuitable for fast determination of the water system state. To estimate the water system state reliably, authors of this paper recommend adapting the method based on the parameters of thermodynamic nature.

Key words: water system (ecosystem), metabolism, catabolism, energetic potential, chemical oxygen demand COD, biochemical oxygen demand BOD, activity of dehydrogenase, activity of catalase, bioluminescence and total organic carbon TOC.

1. Introduction

After an evolutionary stage, biological (ecological) system with its living organisms (plants, animals and other living organisms - biocenose) and their particular habitat (biotope) make up a dynamic and complex aggregate possessing its own steady particular balancing parameters.

The medium of biological system is biotope, all its living organisms - biocenose.

Basic biotope parameters of water ecosystem may be physical (colour, odour, temperature,

transparency, salinity, amount of dissolved oxygen, etc.) and chemical (pH, quantity of organic and mineral impurities, etc.), whereas those of biocenose are biological (quantity of microorganisms, species, etc.) and thermodynamic (inner energy, entropy, enthalpy, etc.).

Various water systems are known as patterns of hierarchic systems. Hierarchy of nature, however, is often simply called a hierarchy of levels in a bio-system (bio-organization, biocenose). The structure of

all ecosystems is similar, they have the same functional groups which can be easily distinguished and predicted. The essence of organism ecological similarities lies in their energetic correlation, each creature possessing its own typical metabolism. Therefore, estimation of an ecosystem is best to begin with the energy access to it. Energy is one of the most versatile properties of ecosystem. In the study of ecosystems, and to be more precise in their description and their stability, energy streams are to be analyzed.

Biological systems as open complex heterogenic systems exchanging substances and energy with the environment are researched by thermodynamics of hierarchic systems. Conversions are analyzed by separate research studies, whereas it is advisable to estimate their general condition and state by common parameters which can be easily compared.

Applying thermodynamic potentials, the equations of any system condition can be set up according to their changes at any stage when passing from one condition to the other. Differences are estimated according to the initial and final state of the system independently of the transition path. Due to the interchange of separate subsystems with the medium, the system generally accumulates the most stable structures i.e. the structures with the increased aggregation Gibbs function. Virtually, these structures accumulate chemical compounds in the environment with increased energetic receptivity (Gibbs function). In this way, during the process the water system is enriched with lipids, proteins, polysaccharides and similar substances, and depleted by discharging water and carbon dioxide into the environment. If a change in demanded substances is either known or may be measured or calculated, the changes in composition can be recorded. During catabolism and anabolism processes, the variations of a chemical composition of living organisms in ontogenesis and phylogenesis are of thermodynamic nature. The ratios defining transfer of mass, condition, enthalpy and similar streams can be recorded by balancing equations for any biological system.

Any tested system may be analyzed as an open complicated heterogenic thermodynamic system whose biotic community organisms are interdependent on nutritional relations.

In the study of metabolism of ecosystems (which virtually are substrate solutions), an energy approach is widely recognized in estimating general nutrients balance in the systems (e.g. in reservoirs). A

thermodynamic approach makes it possible to estimate the general colorific (nutritional) balance of natural open ecosystem, and in this way to evaluate stability, balance and development tendencies of the system. Such approach should suit to all ecosystems - closed and open. The wide-ranging possibilities of this thermodynamic approach enable researchers in energy aspect to evaluate inputs and outputs of substances (substrate), an increment in mass (product), etc.

Physical, chemical and thermodynamic parameters of water biologic system (biotope) can be either measured by means of various measuring methods of different precision, estimation effectiveness, etc., or calculated by applying derived parameters. The possibility of all these methods of evaluation of the general system thermodynamic potential and its energy change affecting general system stability is not yet dealt with in scientific works. It bears a great importance to discharging treated wastewater to natural systems (open water), because only after the estimation of an energy potential, it can be evaluated whether it will do no harm to the water system.

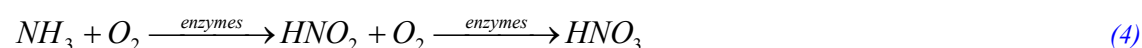
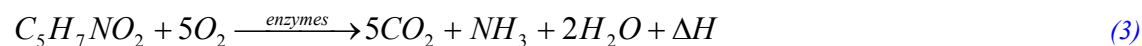
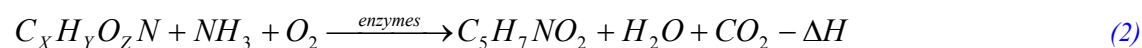
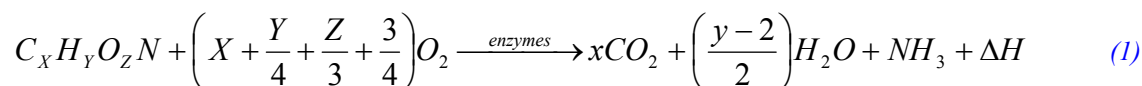
All these above mentioned aspects force to examine the existing methods of estimating water ecosystems parameters, to determine reliability of measured parameters, effectiveness of estimation and their inter-conformity, to evaluate thermodynamic parameters of any water system and compare them.

The aim of this research is by means of the reference analysis to compare the conventional research methods of the water system state with those of the legal, consumer and other specific direct water state estimation, with their correlative approaches, by formulating the comparative evaluation parameters typical of them.

The objectives of this research are 1) to compare the parameters of an analyzed water system experimentally estimated by different measuring methods; 2) to calculate the energy changes caused by an increase in pollutant concentration in the system.

2. Methods estimating the water systems quality parameters

A number of authors (*Matuzevičius A., 1998; Гончарук Е.И., 1984; Яковлев С.И. et al., 1985*) suggest describing the processes in water systems by generalized (1), (2), (3), (4) equations:



here:

$C_xH_yO_zN$ - generalized expression of organic substance (substrate) in substrate solution;

$C_5H_7NO_2$ - statistic average of basic elements assimilated by microorganism cells.

Substrate (organic compounds) usually consists of carbon, hydrogen and oxygen atoms, in some cases - together with nitrogen atoms. For example, a typical composition of organic pollutants in wastewater is: protein (40-60%), hydrocarbon (20-50%) and fat (8-12%) (*Dauknys R. et al., 1999*).

Equation (1) indicates that living organisms, while releasing enzymes, split organic substances into mineral compounds, thus cells acquire energy. Equation (2) describes the anabolism process when biomass synthesizes organics up to $C_5H_7NO_2$. The formulas involve a complex of simultaneous biochemical reactions which may be divided into 3 fundamental actions: oxidation, synthesis and auto-oxidation. Oxidation is energy release (ΔH) reactions converting organic substance into the compounds of small energy: water and carbon dioxide. During synthesis a part of organic substance is converted into new biomass.

As seen from given equations, all metabolism processes exploit oxygen, the energy emerging in the organism either comes loose in the form of heat, or is employed for synthesizing new compounds, or becomes heat during the mechanical operation. Applying a thermodynamic approach, it can be stated that the amount of released heat is an index of energy demand. To estimate this index, direct and indirect calorimetry methods are used (*Brandt B. et al., 2004*). On the other hand, no processes take place without oxygen, thus according to the general amount of oxygen demand, it is possible to judge about the used and released amounts of energy. Having the experimental data about the demanded oxygen amount or the released heat amount, it would be possible to calculate the thermodynamic potential of the system in which all reactions take place simultaneously. One more index indicating the course of processes could be the amount of carbon participating in metabolism.

Oxygen concentration in the analyzed systems is to be estimated by evaluating living conditions of hydrobiontes, intensity of production and destruction processes of organic substances, and self-purification or condition of an ecosystem.

The oxygen amount in the system is indicated as a conditional impurity index, because the less oxygen in the system - the more organic waste whose oxidation demands oxygen. Formation of organic substances composition in ecosystems is highly influenced by a number of factors, most significant of them being the production and transformation processes of organic substances in the ecosystem, access of organic substances into the system. In ecosystems, organic substances exist in dissolved, colloidal and suspended particles forms.

To estimate the quantity of organic substances in water systems, a number of different analysis methods are applied. They may be divided into the methods for estimating the general quantity of organic substances involving those with similar properties, and the methods for estimating the amount of a particular organic substance or its one component (e.g. oxygen). The amount of oxygen dissolved in the system is quantitatively expressed by the amount of oxygen (mg/l) equivalent to that of the consumed oxidizer. To estimate the concentration of organic substances in the system indirectly, various methods may be applied (according to the quantity of microorganisms or to the other biological, chemical, or physical indices).

The methods of estimating water system parameters presented below are selected as suitable to achieve the aim of this research. Analysis of the methods has been carried out following the survey of the scientific literature concerned and has been experimentally verified.

Quality of various water systems is analyzed by means of indirect methods and special indices are found which assist in evaluating the total of the organic substances to be oxidized in the system. These are chemical oxidation methods for determining the amount of oxygen equivalent to that of a strong oxidizer demanded for oxidizing organic substances. Conventionally, the quantity of organic substances in the system is estimated by applying biochemical oxygen demand (BOD) and chemical oxygen demand (COD) methods.

2.1. Chemical oxygen demand (COD)

COD is the oxygen mass concentration equivalent to the amount of bichromate which is demanded to oxidize fully dissolved and suspended substances when a substrate solution sample is treated with this oxidizer under definite conditions (*ISO 6060-1989; Lietuvos..., 2006*). During this process, carbon, hydrogen, sulphur and phosphorous present in organic substances are oxidized up to CO_2 , H_2O , SO_3 , P_2O_5 , respectively, and nitrogen turns into ammonium salts. Oxygen which was in organic compounds participates in the oxidation reaction (*Unifikuoti..., 1994*). The obtained COD values make up 95-98% of the COD theoretical values. A standard error in a 50-600 mg O_2/l concentration interval does not exceed 10% (*Unifikuoti..., 1994*). The experiment lasts for 4 hours, excluding the preliminary period. Estimating COD in the system, more sorts of organic substances may be detected (*Hyunook K. et al., 2007*).

2.2. Biochemical oxygen demand (BOD)

BOD in n days (BOD_n) is the concentration of dissolved oxygen mass needed to oxidize organic and/or inorganic substrate solution impurities biologically under strictly defined aerobic conditions (n - incubation of 5 or 7 days).

A treated analyzed substrate solution sample is diluted with different amounts of dilution water saturated with dissolved oxygen and seeded with aerobic microorganisms by a nitrification inhibitor. The sample is incubated at 20°C in the dark, in fully filled up and corked up bottles for a definite period of 5 or 7 days. The concentration of dissolved oxygen is measured before and after incubation. The demanded oxygen amount for a liter of a sample is calculated (ISO 5815-1:2003; Lietuvos..., 2007).

The obtained results do not include the amount of oxygen demanded for nitrification, i.e. for ammonium salts oxidation up to nitrites, later - to nitrates. The oxidation rate depends on a number of other factors, such as temperature, quantity of microorganisms, their activity, oxygen concentration, toxicity of impurities, etc., therefore oxygen demand is to be estimated under the strictly standardized conditions. Only in this way the comparative results are obtained (Unifikuoti..., 1994). Error of this method comes up to 20% depending on the analyzed BOD value (usually the greater the value - the smaller the error). The experiment lasts up to 8 days.

2.3. Estimation of dehydrogenase catalytic activity

Biological toxicity of chemical compounds in natural systems is estimated according to enzyme dehydrogenase activity (Buckteeg W. et al., 1979). Dehydrogenase accelerates the process of hydrogen separation from a substrate (donor) and its transfer to another substrate (acceptor). Enzyme is of a protein origin and is exceptionally sensitive to bio-contamination. Dehydrogenase responds to the concentration changes of chemical impurities known for their toxicity, therefore the changes in enzyme activity enable specialists to make quick decision about contamination of the analyzed natural systems by toxic materials. On the other hand, in water ecosystems a direct dependence of non-toxic organic substances concentration on dehydrogenase activity has been estimated (Buckteeg W. et al., 1979).

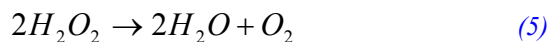
The essence of the method estimating dehydrogenase activity lies in potency of chemical indicators to change color when passing from an oxidized state to a reduced one. In this case, a

hydrogen ion acceptor serves as an indicator. It accepts a hydrogen ion which is carried from an oxidized substrate by enzyme dehydrogenase. The most selective indicator for this enzyme is methyl blue which begins to change blue into colorless at the start of an oxidation-reduction reaction. The reaction rate is proportional to the indicator color change (Buckteeg W. et al., 1979).

Later, a number of scientists improved the method developed by German scientists W. Buckteeg and H. Thiele (Кривицкая Л.С. et al., 1981; Роговская Ц.И. et al., 1980) by suggesting to estimate dehydrogenase activity with Tumberg tubes or common tubes, and also to replace an indicator - methyl blue by 2,3,5-triphenyltetrazole chloride. Actually, the essence of this method has remained unchanged. Accuracy of the method depends on the nature of impurities, whereas it may not suit to some of them. In addition, this method is insufficiently objective. An experiment lasts for about 3 hours.

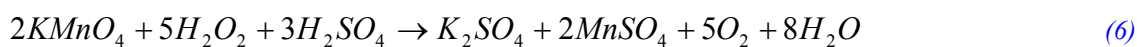
2.4. Estimation of catalase catalytic activity

Out of all enzymes, oxireductases and hydrolases have a strongest effect on decomposition of contaminants. Oxireductases are divided into dehydrogenases and oxidases. Among oxidases the most prevailing are peroxidases, polyphenoloxidases and catalases. By means of catalases the aerobic cells combat an impact of noxious peroxide H₂O₂. According to Equation (5) H₂O₂ affected by catalase splits into:



The quality of a water system can be evaluated according to catalase activity (maximum catalase activity is in the zones with high BOD and a great quantity of germs). The physiological state of ecosystem biocenoses (e.g. active sludge) can be evaluated according to catalase activity (Тимофеева С.С., 1987a; Тимофеева С.С., 1987b; Тимофеева С.С., 1984; Негода Л.Л. et al., 1986).

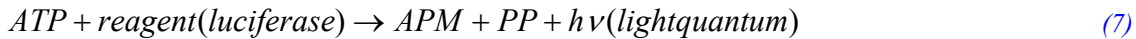
To determine catalytic activity of ecosystem biocenose or substrate solution, a titrimetry method is recommended. Its essence is as follows: an accurate amount of H₂O₂ is added to an analyzed sample, after some time the amount of non-dissolved H₂O₂ is estimated by titrating it with potassium permanganate KMnO₄ according to Equation (6) (Тимофеева С.С., 1987a):



This method is selective only for some organic substances occurring in the cells of vegetable and animal origin. The experiment lasts for about 4 hours.

2.5. Bioluminescencic water parameter research method

A bioluminescent research method of ecosystems quality is based on estimation of a general amount of adenosinetriphosphate ATP alongside with two comparative analyses, namely, one with a clean system, the other - with relatively contaminated (e.g. analyzed water ecosystem). In this case, ATP serves as an indicator indicating the total quantity of organic substances and microorganisms in the analyzed solution. By means of this method, a general amount of ATP and a conditional luminescence change



The glow intensity is measured by a lumitester. Data are recorded by RLU (or $\log/10$ RLU) - by relative light units. RLU is proportional to the ATP amount in an analyzed medium and is directly proportional to medium contamination with non-toxic biological substances. Time for making this experiment is 10 minutes, but it not suitable to the mixture of various organic and non-organic substances.

2.6. Total organic carbon (TOC)

Total organic carbon (TOC) is the amount of dissolved or suspended carbon (including cyanates, elemental carbon and thiocyanates) bound into organic compounds estimated by a standard laboratory analysis. This method does not estimate the origin of organic compounds. It estimates the concentration of organic carbon in drinking-water, groundwater, surface-water and wastewater. The range of estimated concentration is from 0.3 to 1000 mg/l. The TOC concentrations being higher, they can be estimated by diluting the sample.

The whole organic carbon present in the substrate solution is oxidized up to carbon dioxide by subjecting it to an appropriate oxidizer under ultraviolet UV rays (gamma and X-rays may also be used). The UV method, when an oxidizer is oxygen, is applied to estimate TOC in a substrate solution with low concentrations of carbon.

The amount of carbon dioxide formed during oxidation is estimated either directly or after reduction of organic compounds.

The final carbon dioxide amount emerging after oxidation can be estimated by several different procedures, for example, infrared IR rays spectrometry, titration, thermal and electric conductivity, calorimetry, CO₂ sensitive sensors or flame ionization.

The amount of non-organic carbon is removed by acidifying and precipitating the solution or it is estimated separately (ISO 8245-1999; LST ISO

between clean and analyzed ecosystems are estimated (Official..., 2009).

A bioluminescence method is applied both to the environmental express-check-up of industrial regions, agricultural complexes and to the estimation of wastewater treatment plants efficiency.

ATP is a substance present in all animal and vegetable origin cells, also in germs, mushrooms and other microorganisms. Its concentration in living cells is about 0.4 mM. ATP is used as a qualitative indicator estimating the existence of cells in the analyzed medium. The essence of this research is characterized by the following reaction (7):

8245:2003). Application of the method including preparing of a sample takes up to 24 hours.

3. Methodology of evaluating a water systems condition estimation method

Applying a comparative analysis method (Staniškis J.K., et al. 2005) for evaluation of the fast, reliable, low-cost, efficient estimation of water quality analysis parameters described in Section 2, the methodology has been developed, comparative parameters have been formulated, their evaluation scale has been set up and given below.

To evaluate the efficiency of systems quality indices estimation, the comparative analysis of measuring methods of the parameters of all - natural and anthropogenic systems has been carried out. Two comparative parameters are selected for each of these aspects (chosen comparative parameters are given in brackets):

1. technologic (with respect to raw materials (reagents), time for analysis of a sample, input);
2. legal (with respect to unification/standardization, potential to coordinate with an international law);
3. consumer's (with respect to reliability(error) and sample analysis rate);
4. scientific (with respect to potential to evaluate the system state and to employ the state parameters for the system control).

Comparative parameters of each method are evaluated according to the scale of 10 points: 1 point is the lowest (worst) evaluation, 5 points - average evaluation, 10 points - the highest (best) evaluation. The points are characterized according to the selected comparative parameters in Table 1.

When the points of comparative parameters are allotted to each selected method according to the scale in Table 1, the sum is obtained. The greater the sum, the more suitable the method is for efficient, fast, low-cost and sufficiently reliable estimation of the parameters of water systems state.

Table 1. Points of evaluation scale according to comparative parameters of water systems state estimation methods

Comparative parameter of water system state estimation methods	Evaluation scale point		
	1-4	5-7	8-10
Input of raw materials (reagents)	susceptible to reagents	reagents needed	no reagents
Input of time for sample's analysis	susceptible	medium susceptible	very fast
Unification/standardization of method	non-unified/ non-standardized	tried to be applied	unified/ standardized
Potential to coordinate with international law	no potential	potential exists	can be coordinated
Reliability of results (error)	$\geq 20\%$	10-20%	$\leq 10\%$
Rate of analyzed sample up to reliable results	longer than 2 h	less than 2 h	less than 1 h
Potential to evaluate the system state	no potential	potential exists	serviceable
Potential to apply the state parameters to the system control	no potential	potential exists	serviceable

4. Experimental results

In open natural systems the basic part of substrate consists of protein, fat, carbohydrate, urine, cellulose, organic acids. A complicated oxidation process of organic substances is affected by many factors. For this reason a steady experimental system is developed. During the experiment and activated sludge adaptation, with a view to obtain reliable results, a fixed nourishing substrate solution is used which is made of the substances of the following concentrations (Aravinthan, V. et al., 2001): glucose $C_6H_{12}O_6$ - 150 mg/l, yeast suspension $C_5H_2O_2N$ - 150 mg/l, sodium acetate CH_3COONa - 150 mg/l, ammonium chloride NH_4Cl - 90 mg/l, potassium dihydrophosphate KH_2PO_4 - 42 mg/l, potassium hydrophosphate K_2HPO_4 - 42 mg/l, potassium chloride KCl - 60 mg/l, sodium chloride $NaCl$ - 30 mg/l, magnesium sulphate $MgSO_4$ - 18 mg/l and sodium hydrocarbonate $NaHCO_3$ - 720 mg/l. All these substances were diluted in 1 liter distilled water.

After adaptation, activated sludge was supplied with the solution of the same substrate. To examine the water system alterations due to pollution, we additionally put the polluting substance - potassium chloride KCl into separate containers and increased its concentration from 0.746 to 14.92 g/l, i.e., from 0.01 mol/l to 0.2 mol/l (chloride ions concentration from 355 to 7100 mg/l).

To evaluate reliability of indices, the rate of performance, and a potential to calculate thermodynamic alterations in the system, the following indices were measured: BODs, CODs, the amount of dehydrogenase, bioluminescence and TOC before and after clean-up. During the experiment three parallel measurements of all parameters were made and here the averages of calculated parameters are presented. Knowing that reliability of BOD index was low, its average was calculated from five dilutions and three repeats, i.e. from fifteen samples. Measurement data are presented in Table 2.

Table 2. Alterations of BOD, COD dehydrogenase amount, bioluminescence and TOC averages before and after cleaning

Estimated parameter	Chlorides ions concentration, mg Cl/l									
	0.0		355.0		2662.5		5325.0		7100.0	
	Before	After	Before	After	Before	After	Before	After	Before	After
BOD, mgO ₂ /l	196.1	10.6	220.4	10.6	292.6	64.4	386.6	127.1	458.6	259.9
COD, mgO ₂ /l	335.3	21.6	376.9	21.7	500.4	110.2	660.5	217.3	784.3	444.5
Dehydrogenase amount	0.619	0.625	0.645	0.645	0.629	0.643	0.640	2.323	1.572	0.050
Bioluminescence, RLU	720.5	564.5	667.0	557.5	417.5	221.0	373.6	173.7	296.6	61.4
TOC, mg/l	187.2	5.7	182.6	25.1	179.8	27.1	180.6	10.7	179.9	7.5

5. Discussion on experimental results

To evaluate thermodynamic parameters of any system and to write them in balancing equations, the alterations between two states of mass, energy or entropy are to be calculated from the research results. The equations of the state set up in either open natural or closed water system, when the system accumulates stable structures due to interchanges with the medium, make it possible to decide about the course of processes and predict the possibilities of achieving the

balance of the system. It is of great importance when one system has either to flow into the other or they have to be blended, because in this case the fast and quite reliable estimation of the quality of parameters of a new system is its first requirement. To find a relevant method an experiment has been made with a closed system using an artificial substrate solution whose composition is close to the indicated generalized equations.

Calculation of energy accumulation in the agitated sludge system is done calculating theoretical

calorific capacity of nourishing medium which was steady during the experiment according to Formula (8) (Бикбулатов Э.С., 1982):

$$K = 2.326 \cdot \left[145 \cdot C + 610 \cdot \left(H_2 - \frac{1}{8} \cdot O_2 \right) + 40 \cdot S + 10 \cdot N \right], \text{ kJ/kg} \quad (8)$$

here:

- C - carbon portion in total composition of organic structures, weight %;
- H₂ - hydrogen portion in total composition of organic structures, weight %;
- O₂ - oxygen portion in total composition of organic structures, weight %;
- S - sulphur portion in total composition of organic structures, weight %;

N - nitrogen portion in total composition of organic structures, weight %.

Twelve litres of substrate solution have been prepared for the experiment. Composition and quantity in per cent of their weight of organic structures (substrate) in the artificial substrate solution are given in Table 3.

Table 3. Composition and quantity (in weight per cent) of organic substances in 1 litre of artificial substrate solution

Organic substances in artificial substrate solution			Quantity of chemical elements in organic substance, mg				
Name	quantity, mg	molar mass	C	H ₂	O ₂	S	N
Glucose C ₆ H ₁₂ O ₆	150	180	60.00	10.00	80.00	0.00	0.00
Yeast C ₅ H ₂ O ₂ N	150	108	83.33	2.78	44.44	0.00	19.44
Sodium acetate CH ₃ COONa	150	82	43.90	5.49	58.54	0.00	0.00
Total:	450	370	187.23	18.27	182.98	0.00	19.44
Weight per cent:	100	-	41.61	4.06	40.66	0.00	4.32

Theoretical calorific capacity of 1 gram of organic substances calculated according to Formula (8) is equal to:

$$K = 2.326 \cdot \left[145 \cdot 41.61 + 610 \cdot \left(4.06 - \frac{1}{8} \cdot 40.66 \right) + 40 \cdot 0 + 10 \cdot 4.32 \right] = 12683.5 \text{ J/g.}$$

Putting 0.45 g of organic substances into 1 litre distilled water, theoretical calorific capacity of this artificially made substrate solution should be:

$K = 12683.5 \cdot 0.45 = 5707.6 \text{ J}$ or 1364.1 cal per litre of the artificial solution. In this way, its calorific capacity should be 1.36 kcal.

In order to check reliability of this calculation method, we referred to some experimental works done by other researchers. We calculated the energy value according to the formula presented by Russian scientists (Бикбулатов Э.С., 1982; Дзюбан А.Н., 1999), when substrate in the substrate solution was fully oxidized by potassium bichromate, and then we obtained:

$$26.05 \cdot (4 \cdot C + H - 2 \cdot O)$$

then

$$26.05 \cdot (4 \cdot 13 + 17 - 2 \cdot 10) = 49 \cdot 26.05 = 1276.5 \text{ kcal/mol.}$$

Since one litre of substrate solution contains 0.00122 mol of organic substances, its calorific capacity will be 1.55 kcal.

After checking this calculation by two methods, the obtained result is almost the same (error is about 10%).

According to the literature on this subject (Бикбулатов Э.С., 1982; Дзюбан А.Н., 1999), the dependence of BOD on the amount of carbon is expressed by Equation (9):

$$BDS = 4.76 \cdot C - 1.19,$$

here:

C - carbon portion in the total composition of organic substances in weight %.

Then the theoretical calculated BOD of artificial substrate solution should be 196.9 mg O₂/l.

Whereas, referring to the same special literature we find that COD theoretical value is expressed by Dependence (10) on carbon, hydrogen, nitrogen and oxygen in an initial compound:

$$ChDS = (4 \cdot n \cdot C + n \cdot H - 2 \cdot n \cdot N - 3 \cdot n \cdot O) \cdot 8$$

here:

n - quantity of atoms in carbon, hydrogen, nitrogen and oxygen in an initial compound.

Calculation of theoretical COD of artificial substrate solution yields 296.0 mg O₂/l.

Comparison of experimental data (see Table 2 BOD and COD values before cleaning, when chloride concentration is 0.0 mg Cl⁻/l) with the theoretical ones indicates that they are sufficiently close to each other. However, the experimental data obtained after cleaning and the values estimated before and after cleaning at high chlorides concentrations (varying from 355 to 7100 mg Cl⁻/l during experiment) do not agree with the theoretical data. It shows that these methods are not selective when estimating organic and non-organic pollution and they do not suit when biological processes (catabolism and anabolism) in the system are suppressed by chlorides.

Applying the algorithm of estimating thermodynamic potential in water systems, from the differences between the initial and final states according to the COD index in the substrate solution before cleaning and after it, we find Gibbs energy alterations during oxidation, catabolism and anabolism processes. Calculation data are given in Table 4. Presented calculations indicate that internal

energy demand for separating organic substances rises till the concentration of chlorides reaches 0.15 mol, after that the system becomes unstable and has insufficient energy to neutralize organic substances.

Employing the substrate obtained due to oxidation in the inanimate nature, biological oxidation in a cell during an anabolism process differs in its substrates oxidation during which the releasing energy is accumulated in macro-energetic compounds and specific chemical linkage which is catalyzed by enzymes, and then the energy releases when hydrogen oxidizes to water, not when carbon oxidizes to carbon dioxide which occurs when organic substances are burning in the air. These energy alterations should be indicated by other measured parameters, such as dehydrogenase and catalase indices displaying an increase in toxic substances concentration. The experimental data (see Table 2) indicate that the substrate concentrate solution of one and a half moll in one litre of distilled water produces a significant dehydrogenase alteration after cleaning, whereas in the substrate concentration solution of two molls, this index produces no alterations at all. It allows us to think that this method is unsuitable to the systems with high concentrations of pollutants.

Table 4. Alterations of potential energy in cleaning system (before and after cleaning), kcal/l

	Chlorides ions concentration, mg Cl ⁻ /l									
	0.0		355.0		2662.5		5325.0		7100.0	
	Before	After	Before	After	Before	After	Before	After	Before	After
Alteration of potential energy	1693.7	91.5	1903.9	91.8	2527.5	556.5	3338.8	1097.7	3961.2	2245.1

Catalytic activity of catalase has not been estimated in the experiment, because this method is analogous to the catalytic activity estimation of dehydrogenase in which only a different enzyme was used.

During the catalytic activity estimation of both dehydrogenase and catalase, the release of enzymes is being suppressed by chlorides.

When the adenosinetriphosphate (ATP) amount in the examined medium is estimated by a bioluminescence method, and it is proportional to the medium pollution by its non-toxic biological substances, it is evident that with an increase in BOD before and after cleaning, bioluminescence decreases after the first chlorides concentration, and then a sudden fall occurs to 2662.5 mg Cl⁻/l concentration. The study performed by this method indicates that it does not reflect the real situation in the cleaned substrate, because chlorides block the method and do not display how much substrate is left uncleaned at different concentrations of chlorides.

Theoretically, the standard TOC method is most suitable for estimating the water system state, but during the experiment the research has been carried on by the UV method which strongly constricts the carbon concentration range likely to be estimated. The laboratory in which the experiment was made had no equipment for estimating large substrate TOC

concentrations. For this reason, the TOC estimation method was rejected as unsuitable for the water system state estimation.

6. Evaluation of water system state estimation methods

Following the evaluation scale of comparative parameters given in Table 1, each method of water system state estimation described in Section 2 is evaluated. Evaluation points and their sum are given in Table 5. The motives for choosing particular points are given below the Table.

During this experimental work we have estimated that deficiency in the COD method is that during its application all organic substances including a part of inorganic are oxidized, negatively affecting reliability of results (evaluated by 6 points). The method is susceptible to the input of reagents (2 points) and time, both laboratory (3 points) and complete period from sampling till final results (3 points.). Its advantage lies in unification and recognition all over the world (10 points), coordination with the international law standards (10 points), and also it is suitable, with some errors, to evaluate the water system state (5 points) and application of the state parameters to the system

control (4 points). According to the suggested methodology this method received 43 points.

Deficiency in the BOD method is its low reliability of results because its errors may reach 20% (3points). The method is susceptible to the input of reagents (4 points) and time, both laboratory work (3 points) and the whole period of obtaining final results - 7 days (1 point). It is also unsuitable to estimate the

water system state parameters because it does not correlate with the fixed carbon amount in an organic medium (3 points), thus it cannot be applied to control the state parameters (3 points). Its advantage is that it is unified and recognized all over the world (10 points), correlated with the international law standards (10 points). The method is evaluated by 37 points.

Table 5. Evaluation of water system state estimation methods in points and their sum

Water system state estimation method	Evaluation of comparative parameters in points								Total of points
	Raw materials (reagents) input	Input of time for sample's analysis	Method's unification/standardization	Potential to coordinate with international law	Reliability of results (error)	Rate of sample's analysis up to reliable results	Potential to evaluate the system state	Potential to apply the state parameters for system control	
COD	2	3	10	10	6	3	5	4	43
BOD	4	3	10	10	3	1	3	3	37
Dehydrogenase catalytic activity	7	6	6	6	3	4	4	5	41
Catalase catalytic activity	7	6	6	6	3	4	4	5	41
Bioluminescencic ecosystems quality analysis	7	7	4	6	4	8	4	6	46
TOC	4	3	5	8	6	3	3	3	35

Evaluation of dehydrogenase and catalase catalytic activity estimation methods is analogous. Deficiency in these methods lies in their limited application (6 points), however there is a possibility to coordinate them with the international law standards (6 points), also low reliability of their results because they are obtained by indirect measurements. Their error is about 20% (3 points). Both methods are not very susceptible to the input of reagents (7 points) and time, for laboratory performance (6 points) and for the whole estimation period (4 points). They are not suitable to estimating the water system state because they do not correlate with the fixed carbon amount in the organic medium (4 points), thus they cannot be applied to the control of the water system state (5 points). Both methods are evaluated by 41 points each.

Deficiency in the bioluminescencic water parameters analysis method is that it is not widely applied (4 points), but there is a possibility to coordinate it with the international law (6 points). Reliability of its results is rather low because the results are obtained by indirect measurements. The method can be applied to estimate organic pollution evaluating microbiological pollution of the examined solution. The error of this method reaches 20-25% (4 points). The method is little susceptible to the input of reagents (7 points) and time - for laboratory performance (7 points) for the whole results estimation period (8 points). This method cannot be used for evaluation of the water system state and does not correlate with the fixed carbon amount in the

organic medium (4 points), nevertheless it can be used in the control of the water state system (6 points). Its evaluation is 46 points.

The TOC method is susceptible to the input of reagents (4 points) and time, for laboratory experiment (3 points) and for the whole estimation performance (3 points). Its advantage is unification and recognition all over the world, but it is unsuitable for experimental work because it is applied to estimate the substrate solutions of small concentrations of carbon (5 points). It is coordinated with the international law standards (8 points) and reliability of its results is high - with high TOC concentrations the error does not reach 10 % (6 points), (actually, at small TOC concentrations, less than 5 mg/l, the error may be even 25%). The organic carbon amount estimated in the organic medium by this method has a poor correlation with the water system state parameters (3 points), for this reason by means of it there is a slight possibility to apply the state parameters to the system control (3 points). Evaluation is 35 points.

7. Conclusions

1. The experiment deals with comparison of the following measuring methods of water systems states: COD, BOD, dehydrogenase and catalase catalytic activity estimation, bioluminescencic ecosystems quality research, and TOC. All these methods at greater chlorides concentrations

- (from 0.15 mol Cl⁻/l) make bigger than 20% errors and do not display the examined water system state. COD and BOD methods do not suit because chlorides suppress the system metabolism, dehydrogenase and catalase catalytic activity estimation methods also do not suit because chlorides suppress release of enzymes, bioluminescensic ecosystems quality examination does not suit because chlorides are blocking the method itself, while TOC fails for a particular experiment because of too small fixed carbon concentrations.
- After calculation of the system energy alterations, it has been determined that increasing the pollutants concentration from 0.01 to 0.2 mol Cl⁻/l, the potential energy alteration can be calculated only by applying a COD index. The other methods fail to be selective; they do not display thermodynamic alterations and do not offer any possibility to calculate the potential energy.
 - The analyzed methods do not suit for evaluation of the water system thermodynamic state, for this reason it is expedient to adapt the method which would enable specialists to measure energy alterations in the system.

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Vandens sistemų būklės įvertinimo metodų analizė

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Vandens ekosistemų būklė daro įtaką nuolat gamtoje vykstantys procesai. Medžiagų ir energijos judėjimas šioje sistemoje formuoja naują dinaminę pusiausvyrą, kuri keičia pačios sistemos parametrus. Medžiagos sistemoje juda ratu iš vienos grandies į kitą, o energija juda kryptingai. Todėl tikslinga metabolizmo procese nustatyti termodinaminės prigimties parametrus: masę, energiją, entropiją, entalpiją ir jų pernešimus.

Organinių medžiagų produkcijos ir destrukcijos procesų intensyvumui, termodinaminiam stabilumui, savaiminiam ekosistemos apšilumui arba jos būsenai daro įtaką sistemoje esančio deguonies koncentracija. Energijos, kurios reikia biosintezės reakcijoms, judėjimui, medžiagų pernešimui, ląstelė gauna oksiduodama maisto medžiagas. Oksidacijos-redukcijos reakcijų metu išsiskirianti energija sunaudojama ląstelės statybos procesams palaikyti. Deguonies koncentracijos kitimu paremta ir vandens ekosistemose esančių organinių cheminių priemonių kokybinė ir kiekybinė analizė. Sistemoje esančių maistinių medžiagų koncentracija vertinama netiesioginiu būdu pagal BDS ir ChDS parametrus, kurie imlūs laiko atžvilgiu ir ne visada patikimi.

Dėl šios priežasties ieškomi efektyvūs, greiti ir pigūs metodai, kurie leistų kontroliuoti parametrus, neišleisti blogai išvalytų nuotekų, valdyti nuotekų valymo įrenginių technologinį procesą ir t. t.

Darbe nagrinėjami egzistuojantys vandens ekosistemų kokybės parametrų nustatymo metodai, jie tarpusavyje palyginami pagal eksperimento metu gautus rezultatus lyginamosios analizės metodu. Suformulavus lyginamuosius parametrus technologiniu, teisiniu, vartotojo ir moksliniu požiūriais ir sudarius jų įvertinimo skalę, metodai įvertinti pagal sistemos būklės nustatymo greitį. Atlikus vandens sistemų būsenos įvertinimo metodų analizę, nustatyta, kad visi šiuo metu egzistuojantys metodai, pagrįsti cheminių, fizikinių ir biologinių parametrų nustatymu, dėl įvairių priežasčių nėra tinkami tam, kad būtų greitai nustatyta vandens sistemos būklė. Publikacijos autoriai rekomenduoja vandens sistemų būklę įvertinti taikant metodą, pagrįstą termodinaminį parametrų prigimtimi.