

Methods of Assessment of the Fractional Distribution of Organic Substances in Natural Waters: A Membrane–Oxythermographic Method

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Received March 24, 2017; in final form, November 1, 2017

Abstract—A review of methods for the assessment of the fractional distribution of organic substances in natural waters is presented. The problem is usually solved by combining methods of separation into fractions with those of the quantitative determination of substances in the fractions obtained. There is also an original approach based on a combination of methods of membrane filtration and oxythermography; an example of using this approach is presented.

Keywords: organic substance, fractions, integrated index, high-temperature combustion, oxidation, membrane filtration

DOI: 10.1134/S1061934818060126

Data on the fractional distribution of organic substance (OS), i.e., on dimensional characteristics identical to particle size distribution are necessary for fulfilling a number of tasks, in particular, tasks of the migration of substances in natural waters, because each OS fraction differently binds metals into complexes, which affects the migration of substances [1]. As a rule, the major part of OSs in natural waters of the northern region are substances of humic origin, i.e., high-molecular OSs [2]. We put forward the problem of the comparative characterization of the known methods of study of the fractional distribution of humic substances (HSs) of natural waters. This task is not simple, because the exact formulas of these substances are unknown and all data provided in the literature are only hypothetical [3–10]. From the viewpoint of analytical chemistry, gaining information about the fractional distribution of OSs must consist in the consecutive solution of two problems: separations of a test substance into fractions and the determination of the amount of this substance in the fractions obtained. The method ensuring the simultaneous solution of these problems today is unknown; therefore, we will consider groups of methods of OS separation and determination separately.

METHODS OF THE SEPARATION OF ORGANIC SUBSTANCES OF NATURAL WATERS

Several methods of OS separation are used. The most widely used method is gel-permeation chroma-

tography (gel filtration), which ensures the estimation of mainly the molecular weight distribution. This method was first used by Posner in 1963 [11]. The method is based on the separation of substances using gels (most often dextran-based gels, sephadex, are used with granule size depending on the size of the studied molecules). The principle of the method is simple: a chromatography column is packed with a swollen gel and equilibrated with a corresponding solvent. Large molecules, which do not penetrate sieve pores, pass between the gel particles, whereas small molecules get stuck between them and move at a lower speed [12] (Fig. 1).

It was noted in [13] that, for high-molecular polymers like HSs, which are the prevailing OSs of natural waters of the northern region [14], the applicability of the method is limited by the time of attainment of an equilibrium and the trend of polymers to swell, complicating the extraction. In this connection, the results of analysis of the same HS sample under various conditions (pH and ionic strengths of the mobile phase and sample, gel type, high or low pressure in the column, ion composition of the eluting buffer and sample, sample concentration, etc.) are often contradictory, and sometimes mutually exclusive.

Hydrophilic gels (dextrane, polymethacrylate) contain residual amounts of carboxyl groups, whose ionization leads to the formation of a negative charge on gel particles. For this reason, polyanions of humic acids are excluded because of stronger ion exclusion. As a result, the eluted volume of the substance to be

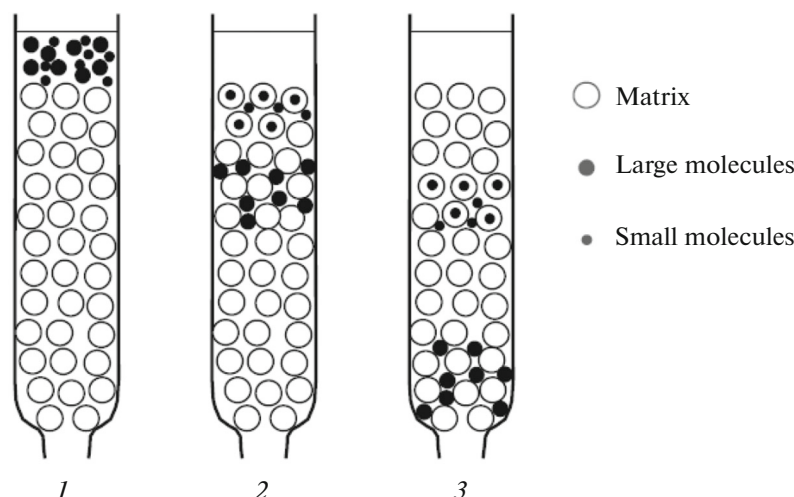


Fig. 1. Separation of substances by gel filtration: (1) mixture introduction into the column, (2) beginning of fractionation, (3) beginning of elution of fraction of the largest molecules from the column.

determined is much smaller, than that in the absence of this effect, which leads to the overestimation of the found molecular weight. If the analyte is highly charged, the eluted volume can be equal to the dead volume of the column. Specific adsorption is due to the formation of hydrophobic or hydrogen bonds between the analyte and the gel matrix. As a result, the eluted volume of the analyte significantly increases and can exceed the total volume of the column, which leads to the underestimation of the found molecular weight. To suppress nonexclusion effects, analysts use eluent modification. The effects of superexclusion are eliminated by increasing ionic strength and selecting optimum pH [15]. Among the drawbacks of gel-permeation chromatography are also its long duration and high requirements to chemical reactants, sometimes very expensive.

Examples of using capillary electrophoresis based on the separation of macromolecules by their electric charge, size (or molecular weight), and spatial configuration are also known [13]. The basic possibility of the electrophoretic separation of HSs by their charge was shown, but the works were so far of research character. Attempts at analyzing products of exclusion chromatography by electrophoresis were made, but no correlation between the chromatographic profile and electrophoretic zones of HSs was found [13].

In the study of the distribution of OSs of natural waters into fractions for geochemical purposes (in connection with the ability of the majority of trace elements to form migration species with organic substances), substances were separated into fractions by ultrafiltration or dialysis, followed by the determination of total organic carbon (C_{org}) [16, 17].

Common filtration under a pressure of up to 2 atm ensures the separation of particles larger than 10 μm

from the liquid. Ultrafiltration offers a possibility of separating particles of the diameter $5 \times 10^{-7} - 10^{-5}$ cm. In this case, pressure from 2 to 10 atm is necessary. Ultrafiltration ensures the separation of colloidal solutions and solutions of high-molecular compounds, for which the membrane is impermeable, from electrolyte solutions [18].

The method of dialysis is based on different diffusion rates of substances through a membrane under the influence of a concentration gradient. In dialysis, molecules of a dissolved substance pass through a membrane and colloidal particles capable to penetrating through the membrane remain after it as a purified colloidal solution. Separation by dialysis takes rather long time. Electrodialysis, using a difference in electric potentials on both sides of the membrane, can accelerate the separation [19].

The separation method is selected depending on the problem posed and the nature of the studied substance.

METHODS OF DETERMINATION OF THE CONCENTRATION OF ORGANIC SUBSTANCES

The determination of the concentration of an organic substance in natural water represents a complex task, because the composition of organic substances decomposing in water gradually changes. An additional difficulty is that natural oxidation processes can hardly be reproduced in the laboratory. As a rule, analysts use methods of gas and liquid chromatography, which possess the necessary selectivity and sensitivity. However, their wide use is complicated by the high cost of equipment and the need in sample preparation, and also by strict requirements to personnel qualification. In addition, the number of individual

Table 1. Total carbon components [23]

Full name	Abbreviation	Description
Inorganic carbon	IC	Carbonate, hydrocarbonate, and dissolved CO ₂
Total organic carbon	TOC	Carbon atoms in organic molecules bound with a covalent bond
Purgeable organic carbon	POC	TOC fraction extracted from an aqueous solution on purging gas under certain conditions (other name – volatile organic carbon, VOC)
Nonpurgeable organic carbon	NPOC	TOC fraction not separated on purging gas
Dissolved organic carbon	DOC	TOC fraction not retained on a filter with pore diameter 0.45 μm
Nondissolved organic carbon	NDOC	TOC fraction retained on a filter with pore diameter 0.45 μm

substances practically determined in surface waters is limited, because waters contain a very great number of various organic compounds. The multicomponent nature of the test sample hinders gaining solid and reliable information. Among the important factors are the cost and labor intensity of the simultaneous determination of a great number of organic compounds. In this connection, integrated indices are determined, such as biochemical (BOD) and chemical oxygen demand (COD), permanganate oxidizability (PO), and total organic carbon. These indices ensure the estimation of the concentration level of organic substance in the sample [20].

The integrated index is a rough estimate of the total concentration of a group of similar substances present in the studied sample and forming the total analytical signal [21], expressed in terms of a standard substance. As was noted above, the integrated index C_{org} is quite often determined in fractions obtained by ultrafiltration or dialysis. However, it is believed [22] that oxidizability indices COD, PO, and BOD give more information for the ecological evaluation of the state of a water reservoir compared to C_{org} , because they allow judgments about the necessary amount of oxygen for the utilization of pollutants coming to natural water media. In other words, the values of PO, BOD, and COD characterize potential needs in oxygen of water media in which organic substances were found. In the assessment of the impact of sewage waters on natural water reservoirs, these indices are necessary for comparing the needs in oxygen and typical potentials of an ecosystem of a water basin to replace oxygen losses and thus to predict the consequences of water pollution.

Let us consider methods ensuring the determination of integrated indices of the concentration of organic substances.

Methods of the determination of total organic carbon. As was noted previously, the concentration of OSs is most often estimated by the determination of total organic carbon (TOC) present in the sample. The value of TOC is part of total carbon. It includes a number of components that can be estimated separately depending on the task (Table 1). For the determination of organic carbon, complex molecules must

be decomposed into separate carbon-containing fragments and then transferred to simple molecular forms, whose concentrations can be determined quantitatively. There are numerous laboratory modifications of methods for the determination of TOC. The most widespread methods are reduced to the dry or wet combustion of organic substances in a water sample in the presence of catalysts and to the determination of the amount of the formed carbon dioxide. Inorganic carbon present in water must also be determined and its amount is subtracted from total carbon.

Several methods are known for the oxidation of carbon-containing substances to carbon dioxide [23]. To completely oxidize carbon-containing substances to CO₂ and H₂O, analysts most often use catalysts (Pt, Cu, Co, Ir, and their oxides or alloys) in the gas phase at 680–950°C. A flow of liquid, being a water sample, is sent to a reaction tube filled with a catalyst. The carbon dioxide formed is determined by a detector. These may be spectrophotometry systems, heat conductivity detectors, flame ionization detectors, inductively coupled plasma atomic emission spectrometry (ICP AES), gravimetry, and also acid and base titration. The main problem arising in the determination of TOC by high-temperature combustion is associated with the difficulties of temperature control at the oxidation stage, which leads to the deterioration of the reproducibility of the results. Among the drawbacks of these methods are also (1) the presence of long-term memory effects; (2) the blocking of a sampling needle in the work with highly concentrated salt solutions or samples containing suspended solid substances; (3) the high level of background due to the release of carbon from the catalyst and some other parts of the system; (4) low yield of the oxidized product; and (5) mechanical problems due to the sudden expansion of the gas flow at the entrance to a high-temperature column.

All this has led to the invention of other oxidation methods, such as UV irradiation, oxidation by persulfates and chromic acid, gamma irradiation and irradiation by electron beams, and also direct determination by ICP AES [24]. TOC can also be determined by treating a sample with ozone with the formation of hydroxyl radicals; however, this can be done with a

special device, for which only one version is present in the market.

The most widespread procedure consists in the UV irradiation of a test solution (200–400 nm) for the decomposition of organic substances with the formation of radicals, followed by the determination of the formed CO_2 by conductivity measurements. In this case, some ionic compounds other than H^+ and HSO_3^{3-} can affect conductivity measurements. The catalysts are TiO_2 and persulfate as dilute suspensions in water. TOC is determined by the difference of the values of conductivity of the irradiated and nonirradiated samples.

The method of photodecomposition is inapplicable to the analysis of heat-resistant nonpurgeable organic compounds. This problem is solved using the method of “dry” oxidation [25], which consists in the complete evaporation of water from the sample. It is natural that this process results in losses even moderately volatile substances.

Methods of the determination of BOD, PO, and COD indices. BOD, PO, and COD indices are related to the value known as oxidizability. Oxidizability characterizes the concentration of organic and mineral substances oxidized by a strong chemical oxidant in water under certain conditions. Organic substances formed in a water reservoir and arriving from outside are quite different in nature and chemical properties, including their stability to the action of different oxidants [26].

Biochemical oxygen demand is the amount of oxygen in milligrams necessary for the oxidation of organic substances found in one liter of water under aerobic conditions as a result of biological processes occurring in water [27]. The drawbacks of the method based on the determination of BOD are the long duration of the analysis, the inadequacy of the results of analysis to the state of the water system because of an increase in the rate of biooxidation, effect of inhibitors of the nitrification process on some redox processes in the system. In addition, some organic compounds (such as substituted aromatic hydrocarbons) are not oxidized biochemically because of the lack of corresponding bacteria as in the nature. For these reasons, below we will not consider the BOD index.

Permanganatny oxidizability. The method of permanganate oxidation (the Kubel method) used previously is unsuitable for the analysis of natural waters, because permanganate is an insufficiently strong oxidant. It oxidizes organic substances incompletely, and many of them are not oxidized at all.

Chemical oxygen demand. We will consider the COD index in more detail. The theoretical value of COD is the amount of oxygen (or an oxidant in terms of oxygen) in mg/L necessary for the complete oxidation of organic substances contained in the sample, when carbon, hydrogen, sulfur, phosphorus, and other elements (except for nitrogen) present in the

organic substance are oxidized to CO_2 , H_2O , P_2O_5 , SO_3 , and nitrogen is converted into an ammonium salt. In this case, oxygen present in the oxidized organic substances is involved into the oxidation process, and part of hydrogen from these compounds passes to the composition of the ammonium salt (3 atoms per each nitrogen atom) [26]. Various methods of the determination of COD in water samples are used in practice.

Iodate method. The iodate method, historically proposed by Bazyakina in 1948 for estimating the total concentration of organic substances in a sample, was the first method of the determination of COD. The efficiency of the oxidation of organic substances by the iodate ion is rather high; however, this method has drawbacks. One should use a precisely weighed portion of potassium iodate and, in the course of analysis, one should maintain the temperature of the reaction mixture with a high precision to prevent the decomposition of potassium iodate. The method possesses low sensitivity; therefore, in the analysis of pure waters, one should evaporate large volumes of water and volatile organic substances may be lost.

Classical method (boiling with reflux condenser). A sample is placed in a flask and the flask is connect with a reflux condenser. Then oxidation is performed by the reaction of an oxidant with the water sample. The most suitable oxidant now is potassium dichromate; however, one can also use some other substances, for example, cerium(IV) persulfate. Several solutions were proposed to optimize the rate and accuracy of the method. Thus, an increase in the rate of reaction is attained using a catalyst. It was proved that the addition of silver sulfate significantly reduced the time necessary for the complete oxidation of OSs. As for the accuracy of the method, the presence of inorganic substances oxidized by dichromate (mainly chlorides) in water samples can lead to the overestimation of COD values. It was found that the addition of HgSO_4 favors the elimination of the negative effect of chlorides, because mercury forms very stable chloride complexes.

To increase the oxidative ability of the dichromate, sulfuric acid is added on boiling, usually within 2 h. After cooling the mixture and washing the condenser with distilled water, the unreduced dichromate is titrated with the Mohr salt using ferroin sulfate as an indicator. The titration end-point is determined by the change of indicator color from blue-green to reddish brown. The value of COD (mg O/L) is calculated as the ratio:

$$\text{COD} = \frac{8000(a - b)cf}{V_{\text{sample}}},$$

where a is the volume of titrating solution consumed for the titration of the blank sample, mL; b is the volume of titrating solution consumed for the titration of the working sample, mL; c is the concentration of the

titrating solution, mol-equiv/L; f is correlation coefficient of the titrating solution; 8000 is equivalent mass of O_2 , mg O_2 /equiv; V_{sample} is volume of the analyzed water sample, mL.

Semimicro method (dichromate method). The principle of this method the same as of boiling with a reflux condenser. In this case, analysts use various cultural test tubes with fluoroplastic covers. The samples and four reagents listed above are placed in test tubes. In addition, blank solutions (reagents with distilled water) are prepared. All test tubes are install in a heating block or in a furnace at 150°C for 2 h. After this time, the unreduced excess of dichromate is titrated with a standard solution of the Mohr salt in the presence of ferroin as an indicator.

Boiling in closed test tubes is more efficient than the classical method in the oxidation of volatile OSs, because the contact of the last ones with the oxidant is not so long. In addition, the closed method is more economical, because an analysis requires only 2 mL of a sample and the total volume of the mixture is 5 mL. This means that the amount of the sample and reagents is 20 times lower than that necessary for the implementation of the method of boiling with a reflux condenser. In addition, the considered method ensures the best protection against possible pollutions and the simultaneous analysis of a great number of samples (for example, using a furnace for 2 h, one can decompose 40–50 samples). The limits of detection are of about 3 and 5 mg O/L for the semimicro method and classical method, respectively [23].

Other methods of discrete analysis. Several versions of the semimicro method are known. Thus, titration can be replaced by the spectrophotometric determination of chromium(IV), the so-called “calorimetric method of closed boiling” [28]. Several modifications of the two above methods were also described. They ensure (1) the reduction of the amounts of reagents, (2) an increase in the productivity of analysis, (3) an increase in the efficiency of the oxidation stage. The main restriction of traditional methods (open and closed boiling) is the long duration of the decomposition stage, which takes 2–3 h.

It is known that microwave [28] and ultrasonic [29] irradiation increases the rate of chemical reactions. The optimization of parameters affecting the irradiation process allowed the reduction of the duration of the decomposition stage from 3 h to 2 min. A combination of both types of irradiation for the simultaneous and direct irradiation of water samples had a synergistic effect in the determination of COD. The patented system [30] considerably (to 1 min) reduced the time of decomposition and increased the recovery of the organic substance for pure pyridine to 75%.

Methods of flow-injection analysis (FIA). In the determination of COD by FIA methods, the decomposition and detection steps are performed in an on-line mode. The concentration of an analyte in a liquid

flow is determined continuously. Small volumes of samples and reagents are introduced into the system in certain points. Several schemes were developed especially for the determination of COD.

The first attempt at the development of a FIA system for the determination of COD was made in 1980 [31]. The method involved heating in a thermostatically controlled bath (water, oil, or polyethylene glycol) with a submerged fluoroplastic capillary of the length 20–50 m. Using a system of connecting devices, the reagents were mixed in a uniform flow simultaneously with the introduction of a certain sample volume into the carrier flow via injection valves. At the sample exit from the bath, absorbance was measured in a flow cell at wave lengths depending on the used oxidant. This methodology included the application of potassium permanganate [31], cerium(IV) [32], and dichromate [33] as oxidants.

A number of FIA systems with the microwave heating of samples were proposed for the determination of COD [34]. The decomposition stage was slightly accelerated in comparison with that in the previously proposed systems. A completely automated microwave unit for the rapid determination of COD was described quite recently [35]. The method is applicable in the concentration range from 0 to 15000 mg O/L; interferences due to the presence of the chloride ion can be eliminated at its concentration up to 8000 mg/L.

A flow-injection scheme for the determination of COD in fresh water, including a device for UV photo-oxidation, was described in [36]. The reduction of the absorbance of the permanganate ion after the oxidation of organic compounds was detected at 524 nm at a rate of input 30 samples per hour. The use of UV irradiation excluded the need in high-temperature oxidation. The proposed system ensured the analysis of 50 samples per hour; the linear dynamic range was from 50 to 10000 mg O/L. Methods of the flow-injection determination of COD possess a number of advantages over the traditional ones. These are (1) the higher productivity of analysis, (2) simplified methodology, (3) better precision, and (4) expanded dynamic range.

Therefore, the methods described above are based on the same principle, oxidation of organic substances with different oxidants; the character and versions of the stages of analysis are determined by its duration. The most complete oxidation of the organic material is attained using thermal methods of analyte combustion. We can draw a conclusion that the optimum method is the thermal oxidation (combustion) of an organic material to carbon dioxide and water with obtaining a quantitative oxidizability index as a result. This method is the most rapid. We will consider it below.

Oxythermography method. *Principle of the method and its instrumental provision.* The oxythermography method is based on measurements of the consumption

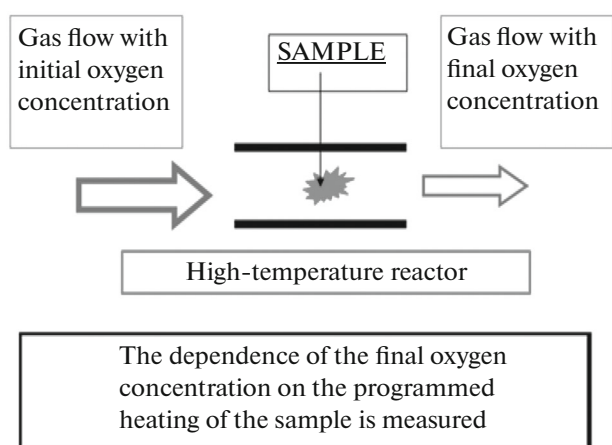


Fig. 2. Principle of operation of the device for the determination of COD.

of oxygen in a flow of a binary gas mixture of oxygen with an inert gas (argon) in the exhaustive oxidation of a test sample in a thermoreactor with temperature rise in accordance with a certain preset law. Strictly speaking, we measure the oxidizability of an analyzed sample, i.e., an index similar to COD. The method was developed by Zuev in 1998 and patented [37]. The formation of the method was preceded by the works [38–44], in which the authors proposed the concept of “thermal oxygen demand” (TOD), the instrumental basis of the method was developed, and prospects of its use for the study of water samples were shown.

It is known that the thermooxidative destruction of organic substances is determined by their chemical structure and temperature of the reaction system. The quantitative measure of thermooxidative destruction in the method under consideration is the consumption of oxygen. The method is similar to thermogravimetry, in which analysts measure the mass loss of a substance as a result of its thermodestruction on programmed heating. In the method of oxythermography, an analyst measures the loss of oxygen in a binary mixture consumed for the formation of volatile gases (CO_2 , H_2O , etc.) in the programmed heating of a sample. The method of oxythermography can be also compared with methods of absorption spectrometry. In absorption spectrometry, the intensity of electromagnetic radiation is decreased through the absorption of radiation by a sample and, in a method of oxythermography, the concentration of oxygen is decreased through the oxidation of a sample in the course of its programmed heating. The principle of oxythermography is illustrated by Fig. 2.

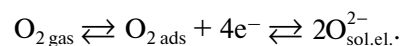
A device was developed for the implementation of the method. It allows (1) the creation of a flow of a binary mixture of oxygen with an inert gas with a controlled concentration of oxygen; (2) purging of the analyzed sample with this mixture; (3) programmed heating of the sample to a high temperature (about

800–900°C); (4) complete oxidation of organic substances (through the use of a catalyst); (5) recording of the concentration of oxygen in the flow of a binary mixture leaving the reactor.

The detector of oxygen is a high-temperature solid-electrolyte cell (HSEC) based on zirconium dioxide and possessing oxygen-ion conductivity. The binary mixture leaving the reactor enters the HSEC, which continuously records the concentration of oxygen in it. It records current passing through the cell, which is proportional to the concentration of oxygen in the binary mixture. The conditions of registration are determined by the value of voltage applied to HSEC electrodes.

An oxygen mixture with argon is prepared with a dosing HSEC, in which oxygen is introduced from the atmosphere into an inert gas. The current passing through the HSEC determines the flow of oxygen introduced into the mixture [45]. Argon is also purified of residual oxygen using a purifying HSEC. In this case, the polarity of the potential applied to the cell electrodes changes to reverse polarity; as a result, oxygen is released from argon to the atmosphere. Therefore, the high-temperature solid-electrolyte cell is used as a detector of oxygen, dosing unit of oxygen, and for the purification of argon of oxygen.

Solid electrolytes based on zirconium dioxide belong to binary compounds in which high ionic conductivity is due to impurity disordering. Such electrolytes contain oxygen vacancies, which determine their conductivity and selectivity to oxygen anions. In detecting molecular oxygen with an HSEC, the key point is a triple point. The following reversible reaction proceeds in its vicinity:



This reaction is a source of oxygen ions in the solid electrolyte.

Oxygen ions can move through anion vacancies in the solid electrolyte; however, because of the high activation barrier, sufficient mobility and ionic conductivity appear at temperatures about 700–1000°C. The range of working temperatures of the cells is from 700 to 1300°C [45].

The solid electrolysis cell is reversible and can be used as an oxygen pump for the creation of a constant concentration of oxygen in a gas flow. In this case, using an electric current source, one creates current of through the cell, under the influence of which oxygen moves from the SEC cathode to the anode. As current through the cell is equivalent to the amount of the oxygen passed through the cell in a gas flow, a stable concentration of oxygen will be created [45].

The excessive pressure of an inert gas supplied to the device, which determines the flow rates of the gas the device, is chosen experimentally; it remained constant and equal to 0.4 bars.

The analyzed sample is introduced into the reactor using boat made of an inert material through the gas-dynamic gate created by a countercurrent of pure argon. Water is evaporated in a flow of argon and does not affect the concentration of oxygen in the inner flow of a binary mixture. The boat then moves to the high-temperature section of the reactor in a flow of a binary mixture, where the sample is completely oxidized. For the complete oxidation of volatile organic substance, an afterburner (platinum catalyst) is placed at the end of the reactor.

The boat is introduced into the high-temperature reactor following a certain preset algorithm, which is called profile. The profile is the dependence of the boat position in the reactor on time. In other words, the researcher chooses certain temperature and time necessary for the complete oxidation of the organic substance. It is also necessary to set the values of current (I) through the dosing cell and voltage across the registering cell (U).

According to the Faraday law, the partial pressure of oxygen in the gas flow after the dosing cell is determined by the equation:

$$P = P_0 + \frac{IV_m}{4Fv}$$

where P_0 is the initial partial pressure of oxygen in argon; I is current passing through the cell, A; V_m is the molar volume of oxygen under normal conditions, m^3 ; F is the Faraday constant, C/mol; and v is gas flow rate through the cell, cm^3/s .

Voltage on the registering HSEC determines the conditions of oxygen registration in the flow at the exit from the reactor. The result of analysis is an oxythermogram, the dependence of current on time on heating the sample. The value of registration in each time point characterizes the concentration of oxygen in the binary mixture leaving the reactor. In the course of analysis, the value of current is displayed on a computer monitor.

The amount of oxygen consumed for the oxidation of an organic substance in a unit sample volume is proportional to the square G^T of the negative peak. This value, according to the Faraday law, is determined by the equation:

$$G^T = \frac{1}{V_{\text{sample}}} \int_{T_1}^{T_2} (A/nF)(I_0 - I(t))dt,$$

where I_0 is background ionic current of oxygen before the introduction of the sample; $I(t)$ is the ionic current of oxygen at time point t , (A/nF) is the electrochemical equivalent of oxygen, and V_{sample} is the volume of water sample.

The oxythermograph is controlled with a specially developed software, which allows the setting and maintaining of the temperature of the reactor and heaters for the work of HSEC. The boat with the sam-

ple was introduced into the reactor with a step engine, which was controlled by a computer in accordance with the preset dependence path length–time. This allows thermoprogrammed heating, which is well reproduced under the conditions of repeated measurements. The software allows the researcher to set current through the dosing HSEC and, correspondingly, to create a binary gas mixture and also to set the potential and measure current through the registering HSEC. Processes leading to the consumption (or release) of oxygen on heating a sample, are displayed on a computer monitor as a kinetic curve (current through the registering SEC–time).

The software contains algorithms of the determination of the baseline (initial concentration of oxygen), calculations of the area of negative peak of oxygen consumption, and calculations of COD by this area on the assumption of the complete oxidation of the organic substance, complete (i.e. without the “loss” of oxygen, incomplete trapping of oxygen by the cell) registration of the amount of oxygen consumed for this oxidation according to the Faraday law [46].

Determination limit for oxygen. To estimate of the minimum amount of oxygen that can be recorded within about 50 s, we selected analytical signal as a dependence of current (registering SEC) on time in the introduction of an empty boat into an inert gas flow passing through the reactor. In this dependence, we choose a time interval in which oxygen was absorbed. Then we found the average value of current the standard deviation. The application of the 3σ -test allowed us to determine by the minimum amount of oxygen that can be registered within the time ~ 50 s (duration of absorption peak). The estimate of the minimum registered amount of oxygen was 1.6×10^{-8} .

Amount of oxygen in the mixture oxygen–inert gas necessary for the complete oxidation of OSs in the sample. Before sample injection into the flow of a binary mixture with a dosing cell, one should create a concentration of oxygen sufficient for the oxidation of organic substances in the sample. According to the Faraday law, in the gas flow with flow rate v at ion current I , a gas mixture with a constant concentration of oxygen (c_{O_2}) formed:

$$c_{\text{O}_2} = I/(n/A)Fv,$$

where I is current, $A F$ is the Faraday constant, C/mol; A/n is the electrochemical equivalent of oxygen; v is gas flow rate through the cell, cm^3/s .

The concentration of oxygen in the binary mixture c_{O_2} necessary for the complete oxidation of organic substances in the sample can be calculated by the equation

$$c_{\text{O}_2} = (V_{\text{sample}} \text{COD}_{\text{theor}})/(vt_{\text{oxid}}),$$

where V_{sample} is sample volume, L; $\text{COD}_{\text{theor}}$ is the amount of oxygen consumed for the complete oxidation of OSs in a unit volume of the sample, calculated

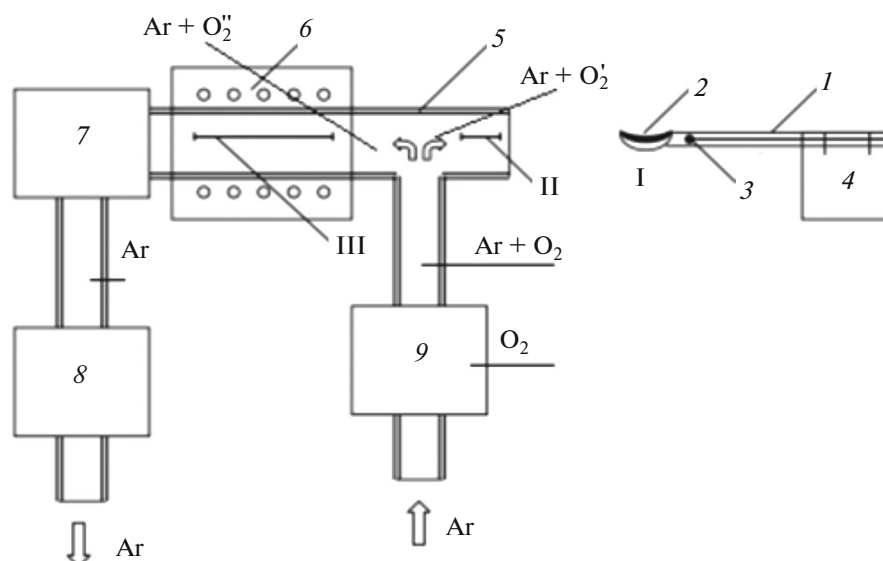


Fig. 3. Scheme of the distribution of gas flows in the first version of the device implementing the principle of oxythermography. (1) boat; (2) sample container; (3) thermocouple inside the quartz boat; (4) system of boat transport; (5) quartz reactor; (6) high-temperature heater; (7) oxygen sensor (HSEC); (8) activator of gas flow; (9) block of oxygen introduction into argon from air (HSEC); (I) boat position for sample introduction; (II) boat position in solvent distillation; (III) area of registering thermooxidative spectrum.

in accordance with the determination of COD, mg O/L; v is gas flow rate through the cell, cm^3/s , t_{oxid} is oxidation time.

Thus, for a sample volume of $10 \mu\text{L}$ with $\text{COD} = 10 \text{ mg O/L}$, 10^{-4} mg of O_2 is necessary. At a volume flow rate of $1 \text{ cm}^3/\text{s}$ and oxidation time of about 10 s, the necessary concentration of oxygen in the flow is of about $10^{-5} \text{ mg O/cm}^3$, or 10^{-2} mg O/L . The concentration of oxygen in technical argon may be significantly higher.

Scheme of the distribution of gas flows in an oxythermograph. A block diagram of an instrument (oxythermograph) is shown in Fig. 3. It is the first version of the setup on which the first studies by the oxythermography method was started. A tube by which an oxygen mixture with argon is fed is connected to a high-temperature reactor with an open entrance. This mixture is divided into two flows. One of them is used to create a gas-dynamic gate, preventing the ingress of air to the reactor. The other flow arrives at the high-temperature reactor. A catalyst for the recombination of volatile organic substances and an oxygen sensor are placed at the exit from the reactor. The boat with the sample is introduced into the reactor through a gas-dynamic gate following the preset program. The temperature in the reactor is non-uniform; therefore, entering different parts of the reactor, the sample is heated to different temperatures. Thus programmed heating of sample is carried out. The sample temperature is constantly registered with a thermocouple.

As was found in the of studies, on the evaporation of a sample of distilled water, the partial pressure of

oxygen in the binary mixture in the reactor changed, which was due to an increase in the partial pressure of water vapors in the mixture of oxygen with argon. This change significantly affected the registration of oxygen by the sensor placed in the end of the reactor. To eliminate the dilution of the binary mixture with water vapors on sample evaporation, a new gas scheme of the oxythermographic installation was developed. In this version, we used an oxidation scheme based on the creation of an inner contour of the flow of the binary mixture of oxygen with an inert gas in the high-temperature reactor (Fig. 4).

The arrows show the directions of gas flows of pure argon and the mixture of argon with oxygen. Water in this case is evaporated in the flow of purified argon and has virtually no effect on the partial concentration of oxygen in the inner gas contour. This became possible through the use of two inputs of gas flow into the high-temperature reactor. Through one input, the binary mixture arrived at the central part of the reactor and argon for the creation of a gas-dynamic gate preventing the ingress of atmospheric air into the reactor arrives through the other input. The flow of the binary mixture in this case arrived only at the high-temperature part of the reactor, forming an inner contour. This eliminates changes in the concentration of oxygen in the flow of binary mixture through its dilution with water vapors.

To verify the oxythermography method, we investigated samples of natural water and compared the results obtained by the standard dichromate method and by the method of oxythermography. Results are

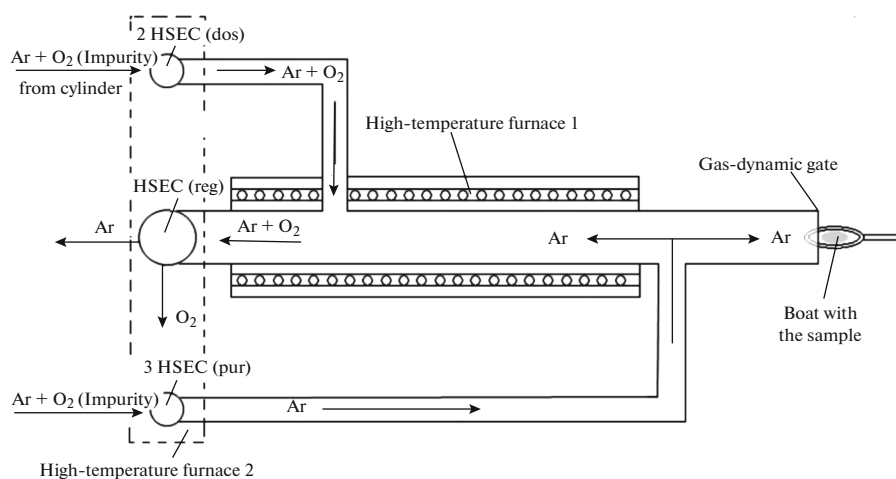


Fig. 4. Scheme of the distribution of gas flows in the new version of oxythermograph.

summarized in Table 2. It can be seen that, within the error, the results are quite comparable. The error of the determination of COD by oxythermography, which is actually determined only by the error of the dosing pipette (3.0% of 10 μ L), was much lower, which points to the advantages of this method.

COMBINED MEMBRANE– OXYTHERMOGRAPHIC METHOD OF THE STUDY OF THE FRACTIONAL DISTRIBUTION OF ORGANIC SUBSTANCES

A combined membrane–oxythermography method was proposed for study of the distribution of OSs by fractions [47]. The scheme of the method is shown in Fig. 5.

Organic substances were separated by the ultrafiltration method. A one-step membrane cell was used, pressure was no more than 3 atm. Membranes with consecutively decreasing pore sizes, 0.22 μ m; 500, 200, and 100 kDa, were used with a compressor for maintaining pressure and a magnetic stirrer for stirring the solution. If pore size must be expressed in terms of length, it was conditionally accepted that membranes with pore size of 500 kDa had linear size of 50 nm, 200 kDa = 20 nm, and 100 kDa = 10 nm. Organic substances in the obtained fractions were determined by oxythermography. For each fraction, the value of an integrated COD index was obtained.

Among the advantages of oxythermography that allowed this method to occupy its place in this combination are the small volume of the sample (volume of each fraction is no more than 1 mL) and its rapidity (below 10 min for one determination). The whole experiment can be performed within one working day, which excludes the need in the storage of samples; no wastes are obtained.

To prevent the ingress of OSs from the filter material (made of a mixture of cellulose acetate and aro-

matic polysulfonamide), membranes were prepared using ultrasound [48]. Ultrasonic cleaning is widely used because of the cavitation phenomenon, the formation of bubbles at a high pressure on the liquid medium, their growth and reduction. The efficiency and sufficiency of the application of this way of membrane preparation was also studied.

CHANGE OF THE DISTRIBUTION OF ORGANIC SUBSTANCES IN THE VOLGA WATER INTO FRACTIONS WITHIN HYDROLOGICAL YEAR AND IN DUMPING THROUGH A DAM

As a sample for the assessment of the potentials of the method, we chose water from the Volga River near Dubna. The chemical composition of the Volga water in this area was studied for many years. In this place, the Volga River is the lower pond of the Ivan'kovskoe Reservoir. The composition of water in the lower pond of the reservoir depends on the composition of water in the reservoir; however, it changes on dumping water through the dam of Ivan'kovskaya hydroelectric power station. According to our observations, on passing water through the dam, concentrations of virtually all hydrochemical components increase, and concentrations of many trace elements, on the contrary, considerably decrease [49]. To answer the question what is

Table 2. Results (c_{av} , mg O/L) of COD measurements in natural water samples by (I) dichromate method and (II) oxythermography

Sample	Method I (FERD* 14.1:2.100-97)	Method II
1	18 \pm 4	21 \pm 3
2	34 \pm 8	33 \pm 3
3	36 \pm 9	28 \pm 5

* Federal Environmental Regulatory Document.

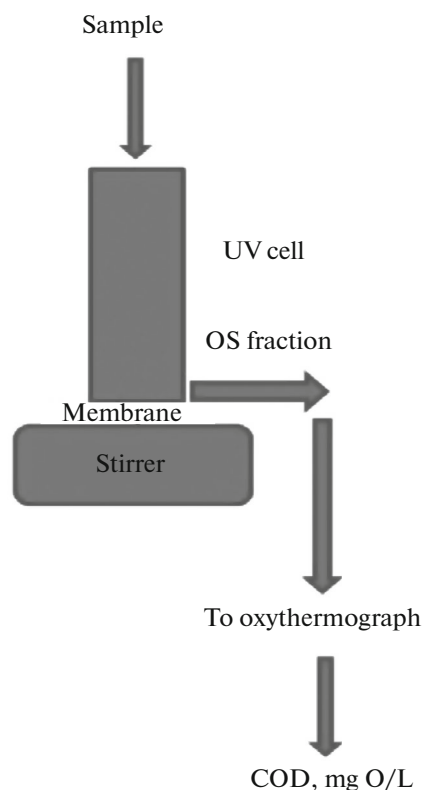


Fig. 5. Scheme of study of the distribution of OSs over fractions.

the reason for the decrease in concentration, we performed the fractional determination of trace elements in water by membrane fractionation. We analyzed water samples taken within spring high water, when dumping of water through the dam attained a maximum [50].

It was found that, after dumping, many elements pass into suspended forms. This is most clearly seen on an example of cadmium, which in the reservoir occurred completely in the dissolved state, presumable as ions and hydroxo ions (Cd^{2+} , CdOH^+). After dumping, cadmium was present at all suspended fractions as insoluble oxide and carbonate, which precipitated near the dam.

The behavior of cadmium can be explained by the change of redox conditions on dumping. The precipitation of other trace elements was, probably, caused by their coprecipitation in the coagulation of the organic substance on dumping water through the dam. To confirm this assumption, information on the change of the distribution of OSs over fractions is necessary.

The results of the study of the distribution of OSs of water over fractions and its change within the year in the main phases of the hydrological regime of the river, winter and summer low-water periods (low water level in the river), in the spring high water, and in

autumn homothermy (when equal temperature and, corresponding, water density within the whole thickness of the river is observed) are presented below. As can be seen in Fig. 6, the fractional distribution of OSs slightly changes with time. This points to the prevalence of different OS components of the Volga water, humic and fulvic acids, at different stages. Let us note that one can only estimate the prevalence of one or another fractional size of OSs; however, these data help to draw conclusions about the further migration of OSs in the water medium. Thus, the fraction with the particle size 10–20 nm prevails in summer, and, in the winter low-water season, in the delivery of river underground waters, organic substance with particle size of 20–50 nm dominates in water.

Change in the distribution of OSs over fractions in the maximum dumping of water from the reservoir through the dam of the Ivan'kovskaya hydroelectric power station in spring high water is of special interest. In this time, samples were selected in two places, in the Ivan'kovskoe Reservoir closely near the dam and immediately after the dumping of water through the dam.

It can be seen in Fig. 7 that the fractional distribution of the organic substance changes. Whereas soluble form up to 10 nm in size dominates in the reservoir, suspended species larger than 20 nm dominate after dumping. We can suppose that, in the further travel downflow the river, this organic substance will precipitate on the bottom. This confirms our hypothesis that the dissolved organic substance, like other components of river water, on dumping passes into the suspended form, which probably leads to their coprecipitation.

In autumn, within homothermy, all fractions are balances with a small prevalence of the dissolved form (Fig. 8).

In 2017, the study was continued. The simultaneous measurements of the fractional distribution of OSs and metals in the main phases of the hydrological mode of the river were performed. The fractions were separated by the method described above; COD in the obtained fractions was determined by oxythermography and metals, on an ICAP-6500 plasma spectrometer (Duo, England).

The period of the maximum consumption of water on dumping through the dam of the hydroelectric power station in spring high water was of special interest. It should be noted that, as we also supposed, we observed the trend to the transformation of the fractional distribution of both OSs and metals towards the formation of larger fractions (Fig. 9).

The data showed obtained demonstrated wide possibilities of the method of oxythermography in the study of the fractional distribution of OSs in natural waters.

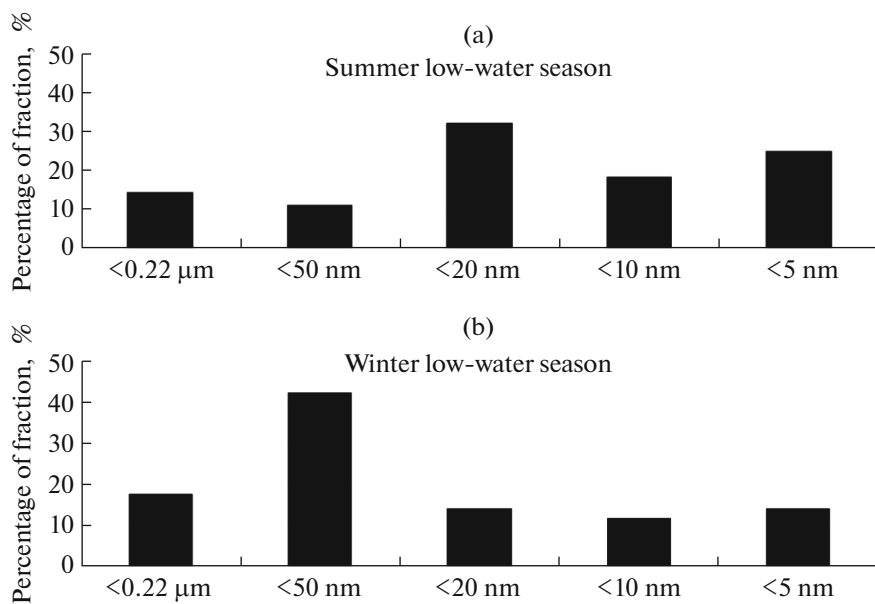


Fig. 6. Transformation of the fractional distribution of the organic substance in Volga water in summer and winter low-water seasons.

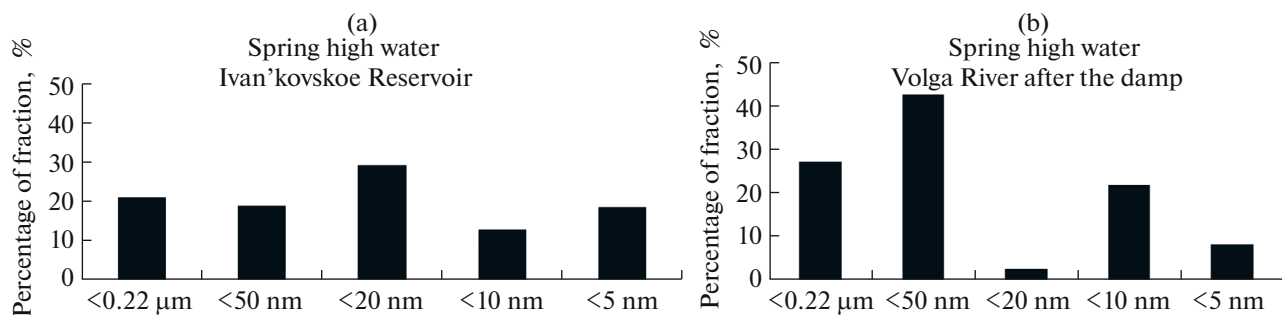


Fig. 7. Transformation of the fractional distribution of the organic substance in Volga water on dumping through the dam in spring high water.

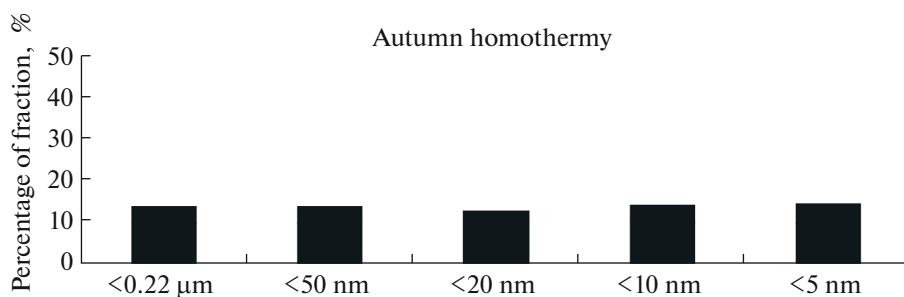


Fig. 8. Transformation of the fractional distribution of the organic substance in Volga water in the autumn homothermy.

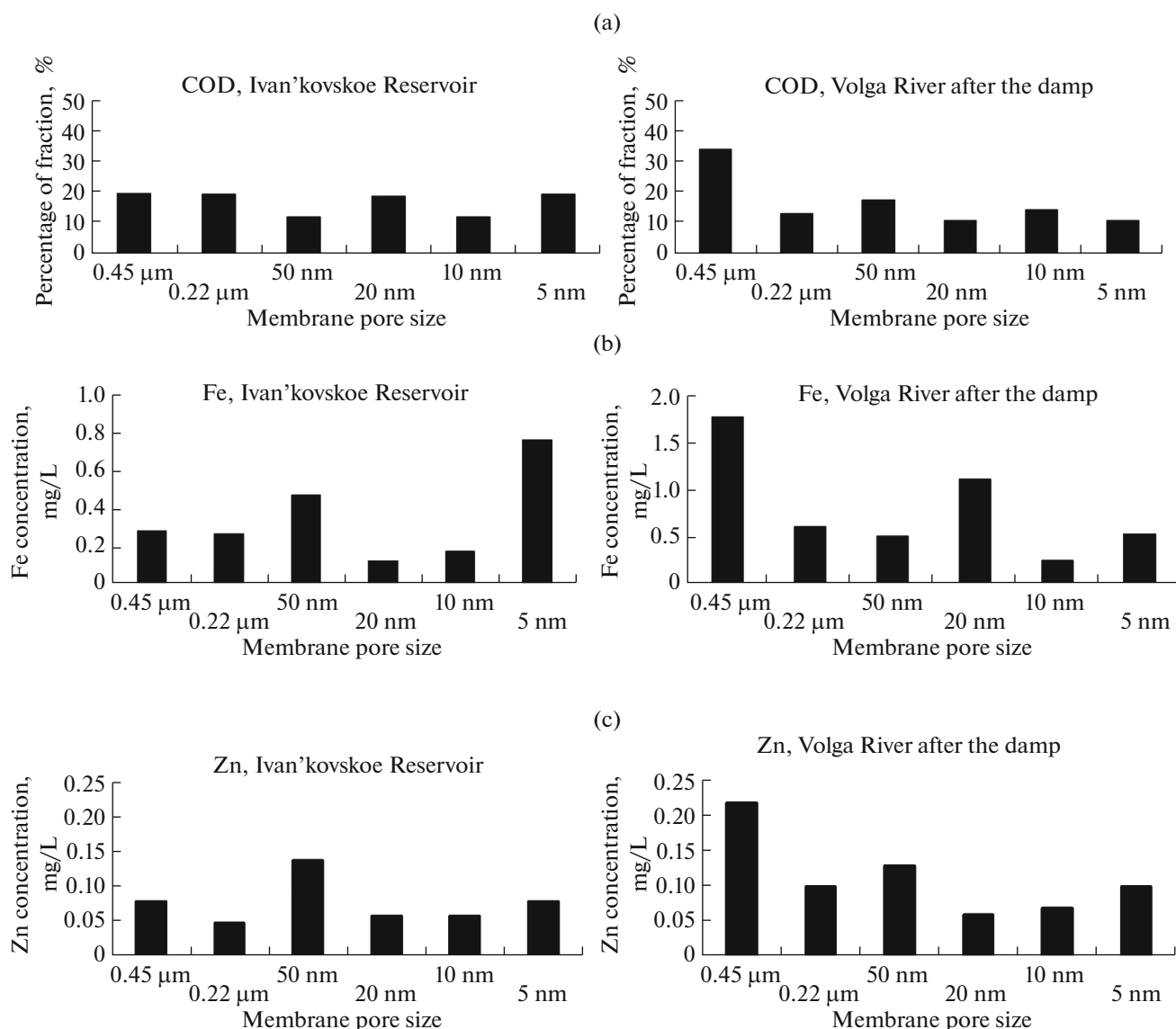


Fig. 9. Transformation of the fractional distribution of (a) organic substance, trace elements (b) Fe and (c) Zn in Volga water on dumping through the dam in the spring high water of 2017.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation of Basic Research, project no. 16-33-00864.

The development of the membrane-oxythermographic method was carried out under the government contract no. 0137-2018-0020 for the development of new instruments for the spectrometric analysis of environmental samples.

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Translated by E. Rykova