ENVIRONMENTAL PROBLEMS
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Chemical Oxygen Demand

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Abstract—New instrumental methods and tendencies of development of direct potentiometric determination of the chemical oxygen demand in the framework of the standard technique are considered.

In view of the increasing contamination of water, both the number of analyses made and that of studies of the analytical capacity of methods for determining the quality of water of various kinds are steadily growing [1–4]. The main parameter in the case in question is the oxygen concentration maintaining the normal ecological situation in water reservoirs. However, it is insufficient to determine only this parameter. The main task consists in monitoring the concentrations of substances (reducing agents of mostly organic nature) that can disturb the oxygen balance of water reservoirs, which leads to environmental disasters [1–4]. This problem has been solved by developing two integrated techniques for determining the parameters "biological oxygen demand" (BOD) and "chemical oxygen demand" (COD): in both cases, the total concentration of substances that can be oxidized, biologically or chemically, to inorganic final products is determined [3–6].

In the COD method, the results obtained are recalculated to the oxygen concentration (oxidizing agent, mg O_2 per liter).

Determination of BOD is a complicated analytical procedure requiring a high skill of analysts.[1] Two main difficulties have been noted [2, 5]: the necessity for introduction of a bacterial microflora and biogenic elements into a sample and the long duration of analysis. In practice, results obtained after incubation for five days (BOD_5) are most frequently used, but complete biochemical oxidation by oxygen may require 20–25 days. Even with substances chosen as reference for determination of BOD, the deviation from the cal-

culated values is ±5 rel. %, and the reproducibility in the case of real wastewater is ±15–20 rel. % [5].

The introduction of such a parameter as COD into the analytical practice made it possible to obviate the above difficulties. The standard procedure involves boiling of a sample (2 h) in an 8 M H_2SO_4 solution, with introduction of $K_2Cr_2O_7$ and Ag_2SO_4 as catalysts and mercury salts for binding of chlorides. The unreacted $Cr_2O_7^{2-}$ is removed by titration with Mohr's salt. The standard procedure for determining COD makes it possible to achieve in many cases the required extent of oxidation, e.g., in analyses of household sewage (90–100% relative to the theoretically calculated values). In some cases, however, it is inefficient, which is primarily determined by the composition of water being studied. The COD method is inapplicable to water containing (upon dilution) more than 2 g l^{-1} chlorides.

Some countries use their own conditions of COD determination. For example, Japanese scientists believe that it sufficient to make analysis only for easily oxidizable components, which represent an immediate danger to the state of water reservoirs [2]. In this approach, $KMnO_4$ is chosen as an oxidizing agent and the conditions of analysis (temperature, acidity, and duration) are considerably milder. It is noteworthy that use of integral parameters is always rather difficult, because not only general principles are to be standardized, but also all details of the analytical procedure.

The method of direct potentiometric determination of COD (without sample titration) and the necessary apparatus were suggested in [7–9].[2]

The aim of this study was to reveal the most important issues associated with application of direct po-

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[1] The parameter BOD corresponds to a greater extent to the natural conditions of oxidation of organic substances in water (according to the commonly accepted procedure, its determination resembles the process used in aerotanks in treatment of wastewater with activated sludge).
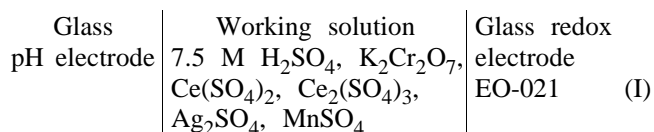
Table 1. Potentiometric determination of COD in solutions of oxalic, tartaric, and phthalic acids

COD_{preset}, mg O_2/l	ΔE_{calc}, mV	COD_{exp}, mg O_2/l	Δ,* %
60	6.0	68	+13.3
120	11.3	116	–3.3
400	30.9	408	+2.0
600	41.9	584	–2.7
1200	69.4	1188	–1.0

* $\Delta = [(COD_{exp} - COD_{preset})/COD_{preset}] \times 100\%$.

tentiometry to determination of COD and to analyze the tendencies of development of new instrumental techniques for COD monitoring.

The voltaic cell developed in [7–9] can be represented as follows:

Glass pH electrode	Working solution 7.5 M H_2SO_4, $K_2Cr_2O_7$, $Ce(SO_4)_2$, $Ce_2(SO_4)_3$, Ag_2SO_4, $MnSO_4$	Glass redox electrode EO-021	(I)

The potentiometric determination of COD was made possible by use of new electrode systems. In voltaic cell I, having no liquid interface, the glass pH electrode is used as a reference [10], because the concentration of H_2SO_4 is high and constant, the electrochemically reversible metallic contact to the inner side of the glass membrane (LiSn alloy) ensures stable operation of the electrode at temperatures higher than 100°C, and the internal resistance of the electrode at 130°C does not exceed 300 kΩ.

The choice of a glass redox electrode (membrane made of electron-conducting titanosilicate glass) as an indicator, instead of the traditional platinum, gold, or iridium electrode, is due to the high selectivity of such electrode to the redox system $Ce^{4+/3+}$ (compared to components of other systems present in the working solution). The electrochemical reversibility of the voltaic cell as a whole made it possible to calculate the concentration dependence of the electromotive force on the solution composition in accordance with the Nernst equation. Severe difficulties in the development of cell I were encountered in choosing the composition of the working solution, because the system $Cr^{6+/3+}$ is not reversible on the known redox electrodes, including glass electrodes of the EO-021 type, owing to low exchange currents. This difficulty could be overcome by introducing the components of the $Ce^{4+/3+}$ redox system and minor amounts of $MnSO_4$

(catalyst of homo- and heterogeneous reactions of electron exchange) into the working solution.

The potentiometric COD analyzer comprises the following three basic units [7–9]: cell made of a heat-resistant glass (equipped with a reflux condenser), in which an indicator electrode, a reference, and a heater in a quartz sheath are placed; measuring unit[3]; and power source.

The range of COD measurements was from 30 to 1300 mg l^{-1}. The following formula was used in calculations (mg l^{-1}):

$$[COD_{pot}] = \frac{(A-1)[Ce^{4+}][Ce^{3+}] \times 8 \times 10^6}{A[Ce^{3+}] + [Ce^{4+}]V_s}, \qquad (1)$$

where $A = 10^{(E_1 - E_2)/\theta}$; $E_1 - E_2$, difference of the successive values of the electromotive force (mV) of cell I before and after introduction of a sample under study into the working solution; $\theta = 2.3RT/F = 79.2$ mV at 128°C; V_s, sample volume commonly equal to 5 or 10 ml.

The concentrations $[Ce^{3+}]$ and $[Ce^{4+}]$ (g-equiv l^{-1}) were found by calibrating the working solution. Oxalic acid or, as recommended in the standard method, potassium biphthalate was used in calibration [6, 7].

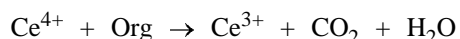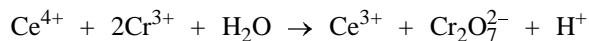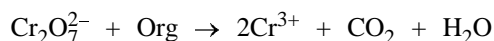The principal results of the study performed are as follows.

(1) The conditions of COD determination close to those in the standard method as regards the concentration of $K_2Cr_2O_7$ and H_2SO_4 (and, consequently, as regards the boiling point of the working solution, too) could be created in the working solution. It proved to be possible to diminish by an order of magnitude the concentration of silver, $[Ag^+]$ [8, 9]. The concentration of cerium(IV, III) sulfates was chosen in such a way that just these system determined the redox buffer capacity of the working solution. The initial $[Ce(IV)] : [Ce(III)]$ ratio in the working solution was $3.5 \times 10^{-3} : 0.5 \times 10^{-3}$. The correctness and accuracy of potentiometric determinations of COD in the range 60–1200 mg O_2/l are shown in Table 1 for model solutions of oxalic, tartaric, and phthalic acids. It is known that these acids are 100% oxidized to CO_2 and H_2O in the standard method.

(2) The formal potential of the $Ce^{4+/3+}$ system is approximately 120 mV higher than that of the $Cr^{6+/3+}$

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[3] As measuring devices can be used digital voltmeters, pH-meters–millivoltmeters, or specially developed automated microprocessor devices (manufactured by LEK, Ekoniks, Ekoniks-Ekspert, etc.).

system. Such a difference is sufficient for ensuring virtually complete oxidation of chromium(III) with cerium(IV). From the standpoint of thermodynamics, it is easier to achieve complete oxidation of organic substances with the cerium system, and this system should be preferred in monitoring of COD. However, the specific features of oxidation reactions and of their kinetics were found to be the key factor. It was shown on model solutions that both a faster rate and a higher extent of oxidation can be achieved with $Cr_2O_7^{2-}$ (combined with a catalyst common in these cases, Ag^+). Therefore, the suggested mixture of oxidizing agents played an important part and provided close agreement between the results furnished by chemical and potentiometric methods for determining COD [7, 8] (Table 2).

The mechanism of oxidation of the total organic substance (Org) can be written as

$$Cr_2O_7^{2-} + Org \rightarrow 2Cr^{3+} + CO_2 + H_2O$$

$$Ce^{4+} + Org \rightarrow Ce^{3+} + CO_2 + H_2O \qquad (2)$$

$$Ce^{4+} + 2Cr^{3+} + H_2O \rightarrow Ce^{3+} + Cr_2O_7^{2-} + H^+$$

$$Ce^{4+} + Org \rightarrow Ce^{3+} + CO_2 + H_2O$$

System of equations (2) illustrates the assertion that only Ce(IV) is consumed in the course of the oxidation, irrespective of the actual relative amounts in which Ce(IV) and $Cr_2O_7^{2-}$ are involved in oxidation.

(3) The potentiometric technique obviates the problem of strict regulation of the analysis duration (more than 2 h in the standard method). After a sample is introduced into the working solution and boiling starts (2–3 min), it becomes possible to record the variation of the emf of the voltaic cell and, consequently, to monitor the oxidation rate. Figure 1 shows the dependences E–τ, measured both in the calibration of the working solution (successive introduction of two equal amounts of oxalic acid) and in experiments with model (working) solutions containing phenol, soluble cellulose, or isoamyl alcohol. In the latter case, no 100% oxidation is observed, and making the determination time any longer has no effect on the result obtained. On the whole, the determination time decreases dramatically in potentiometric determination of COD. For example, an analysis for COD of water before and after biological treatment took 50 an 20 min, respectively, at a water treatment plant[4] and 20 and 10 min at sewage treatment works.[5]

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[4] Belyi Island, St. Petersburg.
[5] Sarov, Nizhni Novgorod oblast.

Table 2. COD values in wastewater. Standard and potentiometric methods

Wastewater	Sample no.	COD$_{stand}$	COD$_{potent}$	Δ,* %
		mg O$_2$/l		
Industrial before treatment	1	150	140	–7
	2	170	170	0
	3	420	400	–5
	4	600	600	0
Household (St. Petersburg) before treatment	5	325	265	–18
	6	285	295	4
	7	180	155	–14
	8	220	215	–2
after treatment	9	43	36	–16
	10	41	52	27
	11	45	57	27

* $\Delta = [(COD_{potent} - COD_{stand})/COD_{stand}] \times 100\%$.

In both cases, the COD of water delivered to treatment was $180-400$ mg l^{-1}. Permanent control measurements by the standard method demonstrated that the difference between the COD values obtained by the two methods (standard and potentiometric) does not exceed, on the average, 8 rel. % in the range in question [11, 12].

(4) The possibility of monitoring of the kinetic parameters of the oxidation in analysis for COD is largely associated with the correct choice of the EO-021 electrode as indicator in cell I. The difference in behavior between these and platinum electrodes was the most clearly manifested in those cases when samples contained chlorides and bromides, but it was also
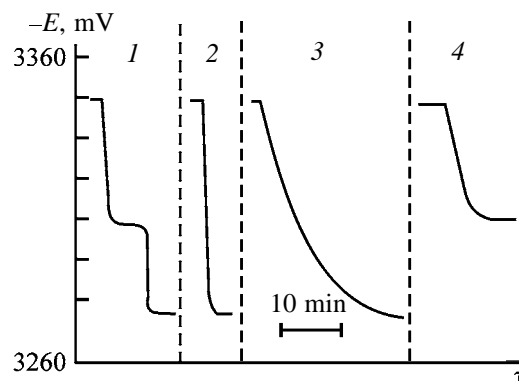

Fig. 1. Kinetic curves of oxidation of various organic substances in the working solution. (E) Potential and (τ) time; the same for Fig. 2. (*1*) Oxalic acid (calibration), (*2*) phenol, (*3*) cellulose (soluble), and (*4*) isoamyl alcohol.
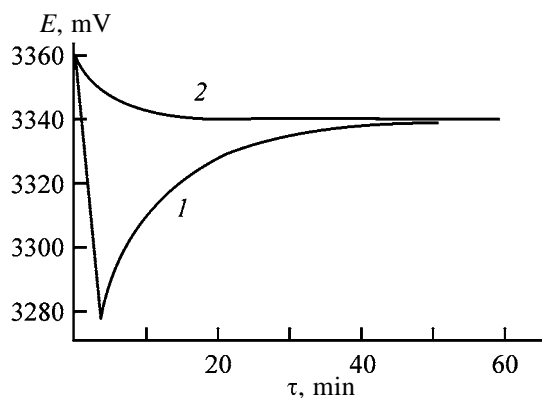
E, mV

Fig. 2. Comparison of the selectivities of (*1*) Pt and (*2*) glass redoxmetric electrodes in oxidation of a mixture of chlorides and bromides in the working solution.

observed for solutions exhibiting a noticeable electro-chemical activity on platinum. Figure 2 illustrates the difference in the properties of the indicator electrodes. Among the large number of determinations performed with cell (I), not a single case of violation of the reversibility of glass redox electrodes was recorded, which confirms their high selectivity toward the $Ce^{4+/3+}$ system [9, 12].

The possibility of differentiation of the contribution from difficultly and readily oxidizable substances to the COD value is an important advantage of the poten-tiometric method. The interpretation of kinetic depen-dences is strongly facilitated by the fact that the con-centration of $Cr_2O_7^{2-}$ remains constant in the course of analysis (see paragraph 2).

(5) For particular cases,[6] the existence of a stable correlation between BOD_5 and COD_{potent} was estab-lished.

In the last 15 years, more than a hundred reports and patents reflecting the tendencies of development of the generalized COD parameter have been pub-lished. These publications emphasize the importance of using this parameter for monitoring of the composi-tion of potable, natural, process, and wastewater and for control over industrial processes for which COD is a key parameter. Conventionally, the main areas of research, most important in the authors' opinion, can be formulated as follows: choice of oxidizing agents, new methods and apparatus, and relationship between COD and other parameters that characterize the quality of water.

Choice of an oxidizing agent. In view of the im-portant role of cerium salts in the above-discussed

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[6] Household sewage in St. Petersburg and Kharkov, wastewater of a poultry plant and a brewery.

"cocktail" for potentiometric determination of COD, the studies [13–16] in which use of cerium salts was continued should be mentioned first. Ce(IV) was used as an oxidizing agent in analyses of river water and industrial sewage under comparatively mild condi-tions as regards the concentration of the acid and tem-perature, i.e., in determination of readily oxidizable components that present an immediate hazard to the state of water reservoirs. According to Japanese regulations [13, 14], the procedures suggested can compete with the permanganate method. The main advantage of the cerimetric technique for determina-tion of COD consists in its insensitivity to presence of very high concentrations of chlorides (up to $30\,000$ mg l^{-1}) in the samples, which eliminates the necessity of using mercury [13, 14]. The capabilities of the direct potentiometry were not used in these studies, and the loss of cerium(IV) in the course of oxidation was monitored spectrophotometrically.

At the same time, manganese salts started to be used extensively in new techniques as catalysts for homogeneous oxidation with potassium dichromate, instead of silver sulfate in the standard procedure [17]. An even more important step in the improvement of parameters of COD determination was made in [18]: it was suggested to replace $K_2Cr_2O_7$ as oxidizing agent with Mn(III), with no silver salt required in this case as catalyst. Also, the problem of elimination of mercury from the process was solved by preliminary removal of chlorides by treating a sample with sodium bismuthate. It was established for model solutions and wastewater of varied origin that the time of determina-tion of COD at 150°C does not exceed 60 min. The procedure for removal of chlorides by preliminary treatment of a sample with sodium bismuthate (or, more precisely, with an adsorbent based on this com-pound) was also studied in [19].

Noteworthy among other solutions of interest are use of granulated titanium and Fenton's reagent as oxidation catalyst and coulometric determination of COD in an alkaline medium with a copper anode [20]. Coulometric generation of oxidizing agents [Ce(IV), Cl_2, BrO^-] for COD determination was also studied in [21].

New methods and apparatus. The aim of studies in this field has been to make the analysis time shorter and the determination threshold lower as compared to the standard method. Studies employing the micro-wave technology for sample heating and new analyti-cal techniques based on flow-through and flow-injec-tion methods (FIM) of analysis have been the focus of attention in recent years.

Microwave heaters have been used in experiments devoted to COD determination under nearly standard conditions [22–25]. Water samples were placed both in sealed and in open cells. In all cases, it was possible to substantially diminish the time of analysis both by raising the temperature of the oxidation and by using spectrophotometric techniques to determine the loss of Cr(IV) or gain of Cr(III). For sealed Teflon cells with a sample volume of 0.5–2.0 ml and microwave heating, the analysis time decreased to 7 min at a COD of the samples of less than 1000 mg l^{-1} [25]. It may be assumed that application of the microwave technology in analysis for COD will be developing fast in the future.

The use of modern technology was excellently demonstrated in a study of Beltra *et al*. [26], who employed microwave heating, spectrophotometric determination of the reaction rate from the accumulation of Cr(III) (absorption at λ = 590 nm), and automated computer processing of the results obtained. Such parameters as the concentrations of an acid and silver and determination time were varied by a specially designed program. Analyzers of this kind will extend the field of research and will make it possible to find the optimal modes of analysis for samples of particular compositions.

Versions of flow-through and flow-injection methods (FIM) have been used under mild conditions of COD determination at a relatively low acidity and temperature [with $KMnO_4$ and Ce(IV) as oxidizing agents] [15, 27–31]. Only in [29], COD could be determined by FIM under standard conditions. It was also possible, in all of these studies, to diminish the determination time to 10 min and avoid introduction of Hg(II) to mask chlorides in samples. At present, it is difficult to assess the extent to which FIM-based analyzers can be widely used in determining COD.

The new approach to COD determination was also implemented in [30, 31], where a thin-layer flow-through electrochemical cell was used in combination with coulometric generation of reagents. The adequacy of analyses was achieved [30] owing to formation of highly active ozone or OH· radicals. A lead dioxide electrode served as an anode, and a platinum or titanium plate, as a cathode. Ozone was also used as an oxidizing agent in [32, 33]. The indubitable interest in these studies is due to use of ozone chemiluminescence in monitoring the sample composition.

The enhanced capabilities of the relatively fast and reliable instrumental determinations of COD and the accumulation of data obtained by various methods promoted investigations aimed to gain deeper insight into the contribution of various substances and processes to the COD values of water of various kinds, and primarily wastewater. The interest in distinguishing the contributions of readily and difficultly oxidizable components, obtaining the kinetic data as an advantage of the potentiometric determination of COD, and different approaches to the choice of standard techniques were already mentioned above. The contributions of different kinds of substances and the approach to modeling of water-treatment processes were the subject of [34–37]. The closest attention is focused on gaining insight into the process of biological purification of wastewater [35]. The problem was analyzed from the seemingly opposite standpoint, by calculating the COD values from parameters of UV absorption spectra of organic compounds [38].

Relationship between COD and other parameters. Directly to in-depth studies of the problem are adjacent investigations in which relationships between parameters characterizing the extent of contamination of water are analyzed. In [39, 40], correlations between the total organic carbon (TOC) and COD were discussed; in [40], [TOC]/[COD] ratios of 0.91 were obtained for some kinds of wastewater. Of particular interest for paper-making is the paper by Bristol *et al*. [41]. Although empirical ratios [TOC]/[COD] or [COD]/[BOD] are known for wastewater of this industry, the [TOC]/[COD] ratio was very important both by itself and as regards its fluctuations, which made it possible to use this ratio as a contamination indicator. A classification of wastewater by the [TOC]/[COD] ratio has been suggested.

The existence of a stable correlation between COD and BOD has long been known in food industries, with the preference given to the first of these parameters in analyses of wastewater [42]. Now, the number of studies of this kind is growing because the main substances contained in sewage and process features of various industries became known. Of interest are the data reported in [43]: the [BOD]/[COD] ratio in wastewater formed in manufacture of various compounds is 0.97 for glucose and phthalate, 0.87 for near beer and ice-cream, and 0.93 in processing of fruits and vegetables. It is noteworthy that use of COD as a process parameter requires another approach to the problem of standardization of determinations.

CONCLUSIONS

(1) The standard chemical method for determining the chemical oxygen demand has become poorly applicable to monitoring the contamination of water,

primarily because of the toxicity of the reagents involved and due to the comparatively long time of determination. The steep rise in the number of analyses performed made this problem more acute.

(2) Analysis of tendencies in the development of new techniques and analyzers of the chemical oxygen demand, operating on electrochemical and spectrophotometric principles, including flow-through and flow-injection variants, made it possible to conclude that new devices will provide in the nearest future analysis durations shorter than 15 min and a detection limit of 10 mg l^{-1}.

(3) The results obtained in the last decade when studying the kinetics of oxidation with oxygen of substances dissolved in water revealed the key role of the chemical oxygen demand. This quantity is already being used as a parameter of new technologies in biological treatment of wastewater; in food, pulp-and-paper, and other industries; and in environmental monitoring.

ACKNOWLEDGMENTS

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