Review Paper

Relationship, importance, and development of analytical techniques: COD, BOD, and, TOC in water—An overview through time

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Abstract

Analytical techniques to measure organic matter in water, such as Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5), and Total Organic Carbon (TOC) are widely used. Modifications have been proposed to make them faster, more sensitive, and more environmentally friendly. The purpose of producing a review over some time is to show the changes made on the standardized methods of each of these techniques, and to highlight the relationship between them in the process of ascertaining organic matter in water. Modifications to techniques COD and BOD entail several factors that need to be considered, namely: time, miniaturization, sensitivity, use of environmentally friendly reagents. Changes to TOC are focused on detection systems. Despite the advantages obtained by the modified techniques, traditional methods continue to be widely used, in most cases due to the lack of standardization of the new methods.

Article Highlights

- A development perspective of each of the techniques is shown over the years
- The relation between COD, BOD and TOC is presented
- In COD, it was observed that modifications are related to the change of reagents looking for faster oxidation
- Changes in BOD focus on reducing response time and measuring the response to biodegradation
- TOC exhibited modifications in obtaining a more sensitive and precise response

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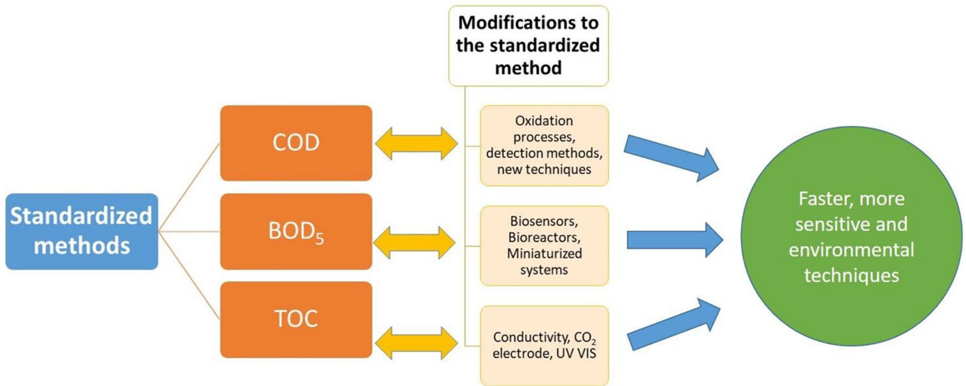
Graphic Abstract



Keywords Standardized method · Alternatives · Advanced oxidation · Biosensors · TOC in water

1 Introduction

Wastewater treatment requires continuous monitoring of pollutants, therefore, analyses criteria for this type of water have been established, i.e., temperature, fats and oils, sedimentable solids, pH, conductivity, inorganic ions concentration, etc. Organic matter determination represents one of the most significant challenges since it includes all carbonaceous compounds and some other elements, such as hydrogen, oxygen, and nitrogen. Thus, determining their presence and concentration requires a different kind of analysis, traditionally measured by two tests, Chemical Oxygen Demand (COD) (Federation W. E., & APH Association [26] – 5220) and Biochemical Oxygen Demand (BOD_5) (Federation W. E., & APH Association [26] – 5210). Nevertheless, currently the Total Organic Carbon (TOC) (Federation W. E., & APH Association [26] – 5310) analysis is being extensively more used than the other two [93].

COD is the standard analysis for measuring oxygen consumption during the decomposition of organic and oxidizing of inorganic matter, through oxidizing agents such as potassium dichromate in a short time (equivalent to hours). On the other hand, BOD_5 is the standard method for determining the concentration of oxygen demand required by microorganisms to decompose organic matter, which occurs in a minimum period of 5 days [71]. TOC is considered a potential alternative for COD and BOD, as it is faster, more precise, sensitive, and environmentally friendly [21].

Several authors have extensively studied the COD, $BOD_{5,}$ and TOC analyses in an attempt to improve standard protocols (Visco et al. [27, 39, 78] since they present some disadvantages such as the use of toxic reagents, waiting time, or the sensitivity of the response; hence, these analyses have been modified over time with the objective of optimizing them, and although those changes have not managed to replace the standardized methods, they may be considered as a possibility for ascertaining these parameters, so it is convenient to analyze the way they have evolved through time.

2 Relationship between the COD, BOD_5, and TOC Parameters to Determine Organic Matter In Water

COD and BOD_5 are routine analyses for wastewater. Respectively, each of them is the most accurate quantification of the amount of organic matter that can be oxidized utilizing chemical or biological processes. These techniques are closely related, and it is highly recommendable to use them together. The values obtained by COD are generally higher than those obtained by BOD_5 and depend on the type of water analyzed. The BOD_5/ COD ratio must be smaller or equal to 1.0. However, this proportion is only an indicator of the fraction of biodegradable organic matter present in wastewater [50, 71, 93].

Similarly, it is also possible to calculate BOD_5/TOC and TOC/COD. For example, Dubber and Gray [21] show that the BOD_5/TOC relationship for the influent is linear, this proportion was proposed initially by Eckenfelder [23], and it shows a decrease during water treatment that is explained by the generation of recalcitrant residues. Therefore, it is recommended to have at least the value of BOD_5 before performing a TOC analysis [5, 17], Lee et al. [49].

3 Chemical oxygen demand (COD)

Water pollution is a problem that affects society. Water treatment processes require covering some analytical parameters that allow finding out the initial and final degree of contamination. Of all the possible pollutants, organic matter is considered necessary, and this is why there are several techniques to find out the amount of organic matter present in water. Chemical Oxygen Demand (COD) is one of the fastest tests available to monitor water quality during treatment [9, 20].

COD represents the degree of contamination in water bodies due to organic matter. It is defined as the oxygen measure equivalent to the content of organic matter present in a sample that strong chemical oxidants, potassium permanganate or potassium dichromate, can oxidize. Each of these oxidants is used to calculate COD in different types of water: COD_{Mn} (COD Manganese) is utilized in determinations for slightly contaminated bodies of water. In contrast, COD_{Cr} (COD Chrome) is used in determinations of heavily contaminated water or wastewater due to the high oxidizing power of the reagent [52, 62].

3.1 Standardized method

In the standardized method described in International Standards, ISO 6060-[34] and ISO 15705–2002, organic matter (i.e., potassium biphthalate) is oxidized in the presence of potassium dichromate and sulfuric acid, in 2-h reflux at a temperature of 150 °C (open or closed). $HgSO_4$ are added to eliminate the presence of chloride ions and silver salts to catalyze the reaction.

In the "open reflux" procedure, the excess of dichromate can be measured by titrating the $K_2Cr_2O_7$ that was not reduced, using a solution of ferrous ammonium sulfate (Mohr's salt), with ferroin as an indicator [27, 52].

According to Li et al. [52], the initial reaction involves biphthalate, which reacts with dichromate:

$$2KC_8H_5O_4 + 10K_2Cr_2O_7 + 41H_2SO_4 \rightarrow 16CO_2 + 46H_2O + 10Cr_2(SO_4)_3 + 11K_2SO_4 \quad (1)$$

After this reaction, dichromate ($K_2Cr_2O_7$) is replaced by oxygen (O_2). After digestion (reflux), the excess of non-reduced dichromate is titrated with an iron solution (Fe^{2+}), according to the following reaction:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (2)$$

In the "closed reflux" procedure, the excess of dichromate is detected via spectrophotometric methods at a wavelength of 420 nm or the increase of trivalent chromium ions (Cr(III)) at a wavelength of 600 nm [59].

The methods above are reproducible and reliable, though they use expensive, highly corrosive, highly toxic reagents. In addition, using them involves other problems such as the interference and incomplete oxidation of volatile compounds. Therefore, it has been necessary to consider other alternatives for the modification of this technique. These new approaches are more environmentally friendly, and in some cases, they have reduced digestion time.

3.2 Modifications to the standardized method

Initially, the COD technique was improved in processes such as scaling [11]. Besides, the cost could be lowered, and the importance of adding silver salts (or not) was discussed [11, 19]. Moreover, the characteristics of COD allow us to divide it into different stages, all of which can be modified. That is the case of the elimination of interferences, other oxidation or digestion methods, the elimination of mercury, or the measurement of the response. Adding, new novel alternatives have emerged, e.g., the use of thermal biosensors [27, 52, 59].

Table 1 summarizes some papers related to the modifications to the standardized method reported since 2010. The modification kind was divided into a) standardized method, b) standardized method: oxidation processes, c) standardized method: detection methods, and d) new techniques.

The standardized method (5220D) uses the dichromate (Federation W. E., & APH Association [26] as oxidizing agent, which decomposes the greatest amount of organic matter, so the reaction is accelerated and interferences are avoided. A catalyst (Ag +) and $HgSO_4$ should be used together with the dichromate. Digestion is carried out by refluxing (150 °C). The excess of dichromate can be determined by titration or spectrophotometry, and using mercury salts to eliminate the interference caused by chlorine is needed. Dichromate is considered as the best oxidizing agent and the prepared solution is stable for a long time, the major problem that shows is the generation of highly toxic waste [12, 59].

Standard method scaling utilizes the same highly toxic reagents; nevertheless, a diminishing of volumes of reagent needed and the processing time of standardized technique allow minimizing the impact of waste generation. Also, costs are reduced while obtaining statistically comparable results.

However, the use of the same highly toxic reagents is a disadvantage for this technique, so some researchers have preferred to modify the standardized method using less toxic oxidizing reagents, such as the permanganate,

Table 1 Techniques used as alternatives for COD

Technique	Kind of modification	Linear range (mg L^{-1})	Detection limit (mg L^{-1})	References
Standardized method	Standardized method 5220D Closed reflux	NA	> 50	Federation W. E., & APH Association (2005)
	Scaling and cost reduction	30 – 600	NA	Carbajal-Palacios et al. [11]
Standardized method: oxidation processes	Advanced oxidation processes: photocatalysis	3.4 – 20	1.2	Akhoundzadeh et al. [2]
	Advanced oxidation processes: Fenton-like process	2.0 – 50	2.0	Esteves et al. [24]
	Oxidation with permanganate	20 – 500	~ 8	Kolb et al. [45]
Standardized method: detection methods	Fluorescence	1–100	0.9	Li & Song [51]
	Chemiluminescence	0.16 – 19.24	0.1	Yao et al. [90]
	Electrochemical detection: nanonickel sensor	10 – 1533	1.1	Jing et al. [36]
	Electrochemical sensor based on platinum nanoparticles	NA	1.83	Wu & Wu [84]
	Photocatalytic and electro photocatalytic detection	20 – 300	15	Wang et al. [80]
	Photochemiresistor sensor based on a Bismuth vanadate type semiconductor	0.20 – 19.9	0.05	Alves et al. [4]
New techniques	Thermal biosensors	5.0 – 3000	1.84	Yao et al. [92]

which is used to obtain a rapid and generalized approximation of the contamination level of water discharge [33, 86].

The amount of organic matter present in the sample is calculated by the time required for the permanganate ion to reduce, generating manganese dioxide. This compound catalyzes the decomposition of permanganate, thus increasing its consumption of organic matter. The process is carried out in hot acidic solutions but may not oxidize all organic matter, even requiring large volumes of sulfuric acid (E et al. [22]; Kolb et al. [45]).

As the drawback is using a strong oxidant coupled with toxic reagents, modifications to the standard technique begin to use advanced oxidation processes like photocatalysis and Fenton reaction that promote hydroxyl radicals ($^{\bullet}OH$) are generated, able to accelerate the decomposition of persistent (Li et al., [51]. Similar strategies can be used ($UV/H_2O_2/Fe^{2+}$), UV/H_2O_2/ultrasonic energy, UV/TiO_2, ZnO, ZnS, CdS WO_3, CeO_2, ZrO_2, O_3/UV, and, $O_3/H_2O_2/UV$ [2, 7, 12, 24, 52]. These techniques are more environmentally friendly, that avoids the use of toxic reagents. Nevertheless, the disadvantage of this kind of modification is that an approximation of the pollutant's concentration is required to identify the appropriate parameters, to name a few: exposure time to light and peroxide concentration [48, 61].

In addition to modifying the reagents of the original technique, other authors have preferred to work the detection method directly or indirectly by measuring the portion of organic matter in water with specific sensors, approaching the COD. Some of these detection methods include chemiluminescence (CL) and fluorescence; the first one is an environmentally friendly technique than when using it, Cr^{3+} is produced during COD reagents reaction, which is measured in the presence of a luminol-H_2O_2 mixture. The luminol-H_2O_2-Cr^{3+} reaction is measured with a photodiode detector developed to allow its instrumentation to be simple and monitoring can be online [30, 57, 75, 90].

On the other hand, fluorescence uses fluorescent chemical elements, such as Cerium (III) (Ce^{3+}). Its fluorescence intensity changes in response to the different concentrations of organic matter in the solution. As a result, the concentration of Ce^{3+} can indirectly determine COD. Nevertheless, it requires expensive equipment and reagents and is suitable only for slightly polluted waters (Li et al. [10, 51].

Other options for determinate COD are the electrochemical sensors, photocatalytic sensors, and the photo chemiresistor sensor. Wang et al. [80] proposed a highly sensitive electro photocatalytic detection method to determine COD in surface and lightly polluted water. The photogenerated electrons react with organic matter in a redox-type reaction. Also, an electrode is irradiated with UV light to generate electrons that will be transferred to a working electrode that produces an analytical signal, which may quantify COD values. For some authors, the disadvantages of this detection are the small specific surface areas and limited use of UV light to generate wide bands [63, 72, 82, 83].

Other techniques like thermal biosensors use sensors to monitor COD online at long-term in water samples. The biosensor measures the amount of heat generated during the oxidation of organic matter. The samples cross through a column with H_3IO_6 and generate a thermal signal to determine COD. These robust systems have a higher tolerance to interference, but oxidation may be incomplete, limiting its potential application [91, 92].

None of the modified techniques presented in Table 1 has been able to displace the standardized procedure; despite being cheaper or more sensitive, they do not offer the robustness of the standardized technique, which hinders its wide use in different types of wastewaters. These disadvantages are mainly the low capacity to achieve all the oxidation of organic matter as dichromate does. As a result, the elimination of chlorine interference in the samples is only accomplished using dichromate, mercury, and silver reagents [27, 52]. In the case of advanced oxidation processes, the diminishing or substitution of toxic compounds has been attained,however, larger amounts of reagents and prior knowledge of the possible contaminants present in the sample are required (Li et al. [7, 12, 51],Bri et al. [10, 48, 53, 61].

Methods focusing on the detection system have not yet been fully developed, as their only function is to make the final response more sensitive. Therefore, most do not directly modify the standard method; their applications aim to obtain the answer so that it can be more quickly detected and established, in some cases on online systems.

4 Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD_5) measures the amount of organic matter present in water that has the potential to be decomposed by a microbial consortium in 5 days. Nagel et al. [62] define BOD_5 as a measure of the organic contamination in the water that can be biologically degraded. It corresponds to the amount of oxygen present divided between the system's volume; it is usually expressed in milligrams of O_2 per liter.

The oxidation of organic matter is a biological process that requires the presence of microorganisms. Kono [46] expresses this process (4) as follows:

$$X_I + O_2 + C \rightarrow X_f + CO_2 + H_2O \quad (4)$$

where: X_i and X_f are the initial and final microbial populations; C is the organic matter present in the sample, which in contact with water and dissolved oxygen, is transformed into biomass, CO_2, and water.

4.1 Standardized method

In 1936, the American Public Health Association (2005) recognized BOD_5 as a standard method to estimate the biodegradability of compounds present in wastewater. The technique consists of placing the samples contaminated, possibly by organic matter in special bottles containing a mixture of previously aerated water, nutrients, and an unknown microbial inoculum, with approximately 105 cells/mL Patnik [60, 66]. First, the measurement of initial dissolved oxygen is carried out,then, the bottles are hermetically closed and incubated in darkness at 20 °C for 5 days. The determination of final dissolved oxygen according to ISO 5815: "Water quality determination of biochemical oxygen demand after the nth day (BODn)—Dilution and seeding method" is undertaken (1983).

This method aims to calculate the amount of dissolved oxygen consumed by the microorganisms; this oxygen is associated with the amount of oxidized organic matter. However, this technique presents practical problems related to response time (5 days), temperature or oxygen concentration. Besides, some compounds present in the sample may be toxic, whereas the concentration and conformation of the microbial inoculum could add a substantial variability in the results (> 20%) [15, 39, 42, 65].

Due to these drawbacks, different alternative techniques to carry out BOD analyses have been developed.

4.2 Alternatives for BOD_5 analyses

According to Jouanneau et al. [39], alternative methods for the standardized BOD_5 technique can be classified in the following areas: (i) biosensors with a redox mediator; (ii) biosensors based on bacterial bioluminescence; (iii) biosensors based on immobilized bacterial cells; (iv) microbial fuel cells; and, (v) bioreactors.

Table 2 shows the comparisons between various alternative techniques to ascertain BOD_5. Additionally, two more techniques are considered; measurement by fluorescence (a previously studied method, adding more recent applications), and miniaturized biological systems.

Modifications to the standard method include a decrease in the response time to achieve a faster test, and an increase in the sensitivity of the response to biodegradation. However, the disadvantages they present are the cost of sophisticated equipment compared with traditional standardized test kits, their maintenance, and the cost of special microbial inoculums [1, 37], Wang et al. [81] Costa et al. [18], which also present various problems such as the variation of the inoculum, the death, and replacement of the microorganisms in the cells, which generates short operational periods and the use of reagents that

Table 2 Comparison of the different techniques used as alternatives for BOD_5

Technique	Basis	Advantages	Disadvantages	Response time (media) (h)	References
Standardized method	The amount of dissolved oxygen is determined after 5 days, which allows calculating the amount of organic matter suitable for oxidization by biological processes	Accurate values are given It can be applied in field	Long analysis time Unknown and variable microbial inoculum Substantial variability in results	120 (5 days)	Jouanneau et al. [39] Federation, W. E., & APH Association [26]
Biosensors with a redox mediator	Electrochemical species are generated by biological processes, producing a signal that a detector can measure Biosensors use an electrode as a transducer This technique simulates the principle of the standardized method, but it substitutes O_2 with a redox-active synthetic mediator that acts as an electron transfer agent	Shorter analysis time (minutes or hours) The microbial inoculum (species and concentration) is known It needs a smaller work area	Expensive reagents and equipment are needed Microbial inoculum may not be viable for all kinds of wastewater	3.5	Pasco et al. [65] Trosok et al. [76] Jordan et al. [37] Jordan et al. [38] Khor et al. [40] Khor et al. [41]
Biosensors based on bacterial bioluminescence	Tests are based on redox reactions that induce the formation of reactive oxygen species. When these species react with luminol, they increase the chemiluminescence or bioluminescence signal (if working with bacterial strains with this characteristic)	Low-cost tests It predicts the potential biodegradability of pollutants Automated methods	It requires bioluminescent microbial inoculums It requires reagents that enhance chemiluminescence	1	Sakaguchi et al. [70] Yamashoji et al. [89] Cheng et al. [16] [18] Lopreside et al. [58]
Biosensors based on immobilized bacterial cells	They consist of a sensitive element (i.e., microorganisms) and a transducer. The microorganisms are immobilized on a membrane with an electrolyte, while the transducer detects changes in the electrolyte solution when organic matter is decomposed	Faster and easier tests Commercial versions of these tests are available High sensitivity Measurement in real-time	Short operational period of the biosensor Lysis of immobilized microorganisms occurs Large, high-cost sensors are needed	0.166	Pasco et al. [64] Villalobos et al. [77] Liu et al. [56] Yamashita et al. [88] Wang et al. [81]

Table 2 (continued)

Technique	Basis	Advantages	Disadvantages	Response time (media) (h)	References
Microbial fuel cells	It includes bio-electrochemical devices that contain an anode and a cathode. The anode usually keeps a concentration of microorganisms that can generate an electrochemical gradient since they oxidize the organic matter present in the sample. This oxidation results in a measurable electric current flow	Real-time response Online response	There are few reports of its application in the field	5	Chang et al. [15] Jouanneau et al. [39] Abrevaya et al. [1] Jiang et al. [35] Sonawane et al. [73]
Bioreactors	Bacteria are held in cells located inside the reactor, through which the effluent crosses. Once water is added, organic matter is decomposed, and a dissolved oxygen detector measures the concentration	The systems are continuous Direct measurement Commercial versions of these tests are available	It requires a large and exclusive work area Microbial inoculum generates variation in results	0.333	Jouanneau et al. [39] Li et al. [54] Liu et al. [55] Hu et al. [29] [67]
Fluorescence spectroscopy	The most common methods are the generation of excitation-emission matrices (EEM) and synchronous fluorescence spectra (SFS). BOD concentration can be estimated using the T peak in fluorescence, SFS, and the first derivative of the spectra	Quick techniques. Lower cost Highly sensitive and non-invasive It requires small amounts of water sample	Some reagents can cause interference with the biodegradability of organic matter	Real time	Hur et al. [31] Hur et al. [32] Bridgeman et al. [10] Kwak et al. [47] Xu et al. [87] Carstea et al. [13]
Miniaturized biological systems	Bacteria immobilized in microsystems (microchips) decompose organic matter, and the consumption of generated O_2 is measured by optical sensors attached to the walls	Reduction of response time Simultaneous measurements of different concentrations of organic load	Systems under development	Real-time	Recoules et al. [68] Recoules et al. [69] Xiao et al. [85]

accelerate the degradation of organic material to allow greater bioavailability [14, 37, 64].

Systems that modify the way to obtain the biodegradation response have opted to use more sensitive techniques such as fluorescence spectroscopy or optical sensors. In the first case, the results allow us to consider fluorescence spectroscopy as an alternative to ascertain BOD_5; albeit it is not applicable to optimize systems, since it is also a laborious and slow technique that can compromise the development of microorganisms with the reagents used [10, 13, 39]. On the other hand, optical sensors seem more promising in detecting the consumption of organic matter, but they are still under development, and at present, they are only reported in miniaturized systems [69].

5 Total Organic Carbon (TOC)

Unlike the techniques COD and BOD described above, Total Organic Carbon (TOC) is the most complete analysis if the objective is to detect all kinds of organic matter present in water: it measures the organic carbon present in all the dissolved compounds. Therefore, it approximates the carbon value of which organic pollutants are constituted (Federation, W. E., & APH Association, [26], however, this technique cannot replace COD or BOD, and it is considered as a complimentary analysis with great importance for water treatment.

To calculate how many carbon bonds there are in a water sample, it is necessary to break these bonds to convert the compounds into a more straightforward molecular form, one that could be quantitatively detected and measured as CO_2 (Federation, W. E., & APH Association, [26]. Methods capable of achieving a higher degree of conversion of organic matter into CO_2 employ high temperatures, catalysis, chemical oxidation, UV radiation, or combining several of these processes. Once CO_2 is released, it can be measured, resorting to various methods, e.g., titration, non-dispersive infrared (NDIR), or colorimetry [8], Visco et al., [79].

5.1 Standardized method: TOC in water

Federation, W. E., & APH Association [26] considers three methods to ascertain TOC, namely: (i 5310B, combustion at high temperatures; (ii 5310 C, oxidation with persulfate (Persulfate / UV and Heated-Persulfate Oxidation Method; and (iii 5310 D, wet oxidation. Table 3 shows the differences and applications of each one.

Table 3 Summary of the methods proposed by Federation, W. E., & APH Association [26] to ascertain TOC

Technique	Kind of sample	Principle	Minimum detectable concentration (mg TOC / L)
5310 B: Combustion at high temperatures	Samples require a diminishing of the particle size to flow through the hole of the syringes Samples with high levels of organic carbon	A homogenized and diluted sample reacts with an oxidative catalyst (cobalt oxide, platinum, or barium chromate). Organic carbon is oxidized and converted into CO_2, then transported by a carrier gas; it is finally analyzed by titration or non-dispersive infrared (NDIR)	1
5310 C: Oxidation with persulfate (Persulfate/UV and Heated-Persulfate Oxidation Method)	Samples with trace levels of organic carbon	Persulfate oxidizes organic carbon into CO_2; this process needs either heat or UV light. The produced CO_2 can be purged, dried, and transferred by a carrier gas to a non-dispersive infrared analyzer (NDIR). This can be titrated by colorimetry or separated from the liquid stream by a membrane to measure the change in conductivity that it produces	0.01
5310 D: Wet oxidation	Samples with different mixtures of sediments, seawater, brine, and wastewater with less than 0.1 mg TOC	The sample is acidified and purged, the inorganic carbon is removed and oxidized with persulfate in an autoclave at a 116–130 °C The resulting CO_2 is measured by NDIR	0.10

5.2 Alternatives for the analysis of TOC in water

The alternatives proposed by Federation, W. E., & APH Association [26] for the determination of TOC present different detection limits, which is a problem when other sample parameters are unknown, such as COD or BOD, because a possible detection limit for the unknown sample. In addition, special equipment and materials are required to perform these tests. Other analytical techniques have been developed to measure TOC, leading to more sensitive methods. Table 4 summarizes the investigations focused on the modifications applied to the standardized method to ascertain TOC in water. Most of the research focuses on the detection of CO_2, not on the oxidation process. The kind of samples that can be determined by each method are identified, and the detection limits for each one to make them comparable with the standardized methods shown in Table 3.

Being TOC a sensitive technique, it is challenging to accomplish a significant change in the methodology; this way, the applied modifications focus on different possibilities to detect the carbon present in the sample. However, prior treatments are required to accomplish the oxidation of all the organic matter present, and the levels of carbon detection are above those obtained through the standard technique, so they could hardly displace it; though, the use of various detection techniques allows their implementation in experimental laboratories as an alternative to traditional ones.

6 General discussion

The traditional techniques to determine COD and BOD are still widely used because they allow reliable results to be obtained. Despite the use of highly toxic reagents, COD is used because the reactions ensure the total oxidation of the raw material, unlike proposals where the change in oxidizing agents does not allow this type of reaction. The most current modifications suggest the use of more sophisticated equipment that may well be unfeasible if one considers the ease of obtaining and using a spectrophotometer necessary to carry out the technique.

On the other hand, the BOD, despite the very long response time, has not been able to be replaced by any other technique either because some require materials (including biological materials) that are difficult to maintain in the laboratories that could occupy them, so maintaining microbial cultures to BOD biosensors is not an easy task that can be compared with the ease that the traditional technique allows in this sense.

For its part, COT has been the only technique that has been able to be perfected over time, however, there was no change in the initial technique, only changes emerged in the detection method. The possibility of using more and more sophisticated equipment for this technique and not for the others can be explained in the acquisition of the equipment by the laboratories. When purchasing equipment with the modifications already preloaded, its use and maintenance is easier.

Due to the above, it is necessary to test the various alternative techniques, at least for COD and BOD, in different areas such as cost–benefit, validation, efficacy and sensitivity with the aim of proposing one as a substitute for the reference techniques.

7 Conclusions

Modifying the various analytical techniques reviewed in this summary focuses on reducing times, reagents, and waste generation and also searching for greater sensitivity.

COD presents a larger number of modifications than the other cases in all the different steps that it is necessary to carry out. The central point of most of these modifications is to diminish the use of highly toxic reagents or to change to others that may be more environmentally friendly. The biggest problem with several of the alternatives is their high cost and the time they require compared with the standardized method.

The analysis of BOD_5 methods shows there is unification in the systems, which allows them to be performed in situ or, in the best of cases, with an online identification of the results. Most of the studies reviewed focus on the use of microorganisms or biological systems, which can ascertain BOD in less than 1 day. They also focus on using equipment that could increase the sensitivity of the measurement of biodegradable organic matter.

On the other hand, only modifications in the detection systems are discussed in the analysis of TOC. These systems are expensive, but they have high sensitivity, so it was unnecessary to carry out further modifications.

In conclusion, it is preferable to highlight the importance of TOC and the possibility of using this technique as a complementary tool to verify the results obtained by other techniques.

It is essential to recognize the advance and evolution in the modifications of the standardized techniques; nevertheless, none of them has been able to displace traditional methodologies entirely.

Table 4 Alternative detection systems for the detection of Total Organic Carbon in water

Technique	Kind of sample	Principle	Minimum detectable concentration	References
Conductivity	Natural saline waters	It is used when oxidation is carried out with UV light. The generated CO_2 dissolves and then interacts with water ions, affecting conductivity	≥ 0.25 mg TOC/L	Visco et al., [78]
CO_2 electrode	Synthetic water and natural water Pretreatment required to remove total inorganic carbon	CO_2 diffuses from the sample to the internal solution of the electrode through a selective membrane. Due to its acidic nature, it produces a change in pH that is related to the CO_2 concentration	2×10^{-2} mol L^{-1} CO_2	Visco et al., [78] Visco et al., [79]
Reagent free ion chromatography (RF ™ -IC) and inductively coupled plasma atomic emission spectrometry (ICP-AES)	Synthetic water and natural water	The sample is introduced directly into the hot plasma without pre-oxidation, and the organic carbon is atomized. Then, carbon is measured by atomic emission spectrophotometry	0.5 mmol L^{-1} (RF™-IC) 0.1 mmol L^{-1} (ICP-AES)	[74] [28]
Infrared (TOC-VCSH) coupled to chemiluminescence detector (TNM-1 TN unit)	Environmental waters and purified waters	5310B method (19) is used for infrared, and by chemiluminescence, total nitrogen is determined. Both methods are coupled to generate simultaneous TOC and NT results	0.5–100 mg C/L	Fan et al., [25] bekiari et al., [6]
Ultraviolet–visible spectroscopy	Saline water and freshwater	Organic matter is determined at a wavelength of 250 – 300 nm. Then absorbance is analyzed with multiple linear regression models to estimate the TOC value and compare it with the traditional method	10–200 mg L^{-1}	Albrektienė et al., [3] Knapik et al. [44] Kim et al. [43]

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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References s

1. Abrevaya X, Sacco N, Bonetto M, Hilding-Ohlsson A, Cortón E (2015) Analytical applications of microbial fuel cells. Part I: biochemical oxygen demand. Biosens Bioelectron 63:580–590
2. Akhoundzadeh J, Costas M, Lavilla I, Chamsaz M, Bendicho C (2013) Miniaturized and green method for determination of chemical oxygen demand using UV-induced oxidation with hydrogen peroxide and single drop microextraction. Microchim Acta 180(11–12):1029–1036
3. Albrektienė R, Rimeika M, Zalieckienė E, Šaulys V, Zagorskis A (2012) Determination of organic matter by UV absorption in the ground water. J Environ Eng Landsc Manag 20(2):163–167
4. Alves NA, Olean-Oliveira A, Cardoso CX, Teixeira MF (2020) Photochemiresistor sensor development based on a bismuth vanadate type semiconductor for determination of chemical oxygen demand. ACS Appl Mater Interfaces 12(16):18723–18729
5. Aziz J, Tebbut T (1980) Significance of COD, BOD and TOC correlations in kinetic–models of biological oxication. Water Res 14(4):319–324
6. Bekiari V, Avramidis P (2014) Data quality in water analysis: validation of combustion-infrared and combustion-chemiluminescence methods for the simultaneous determination of total organic carbon (TOC) and total nitrogen (TN). Int J Environ Anal Chem 94(1):65–76
7. Bendicho C, Pena F, Costas M, Gil S, Lavilla I (2010) Photochemistry-based simple treatments as greener approaches for trace-element analysis and speciation. TrAC-Trends Anal Chem 29:681–691
8. Bisutti I, Hilke I, Raessler M (2004) Determination of total organic carbon—an overview of current methods. Trends Anal Chem 23(10–11):716–726
9. Boyles W (1997) The science of chemical oxygen demand. HACH Company
10. Bridgeman J, Baker J, Carliell-Marquet C, Carstea E (2013) Determination of changes in wastewater quality through a treatment works using fluorescence spectroscopy. Environ Technol 34(23):3069–3077
11. Carbajal-Palacios P, Balderas-Hernandez P, Ibañez J, Roa-Morales G (2014) Downscaling the chemical oxygen demand test. Environ Technol 35(11):1345–1349
12. Carbajal-Palacios P, Balderas-Hernández P, Ibañez J, Roa-Morales G (2012) Replacing dichromate with hydrogen peroxide in the chemical oxygen demand (COD) test. Water Sci Technol 66(5):1069–1073
13. Carstea E, Bridgeman J, Baker A, Reynolds D (2016) Fluorescence spectroscopy for wastewater monitoring: a review. Water Res 95:205–219
14. Catterall K, Zhao H, Pasco N, John R (2003) Development of a rapid ferricyanide-mediated assay for biochemical oxygen demand using a mixed microbial consortium. Anal Chem 75(11):2584–2590
15. Chang IS, Jang JK, Gil GC, Kim M, Kim HJ, Cho BW, Kim BH (2004) Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. Biosens Bioelectron 19(6):607–613
16. Cheng CY, Kuo JT, Lin YC, Liao YR, Chung YC (2010) Comparisons of *Vibrio fischeri, Photobacterium phosphoreum,* and recombinant luminescent using *Escherichia coli* as BOD measurement. J Environ Sci Health Part A 45(2):233–238
17. Choi D, Jung J, Yoon K, Lee K, Choi W, Lim S, Hwang T (2012) Estimation of TOC concentration using BOD, COD in runoff from paddy fields. J Korean Soc Water Environ 28(6):813–818
18. Costa SP, Cunha E, Azevedo AM, Pereira SA, Neves AF, Vilaranda AG, Saraiva ML (2018) Microfluidic chemiluminescence system with yeast *Saccharomyces cerevisiae* for rapid biochemical oxygen demand measurement. ACS Sustain Chem Eng 6(5):6094–6101
19. da Silva A, da Silva R, Camões M (2011) Optimization of the determination of chemical oxygen demand in wastewaters. Anal Chim Acta 699(2):161–169
20. Dedkov Y, Elizarova O, Kel´ina S (2000) Dicromate method for the determination of chemical oxygen demand. J Anal Chem 55(8):777–781
21. Dubber D, Gray N (2010) Replacement of Chemical Oxygen Demand (COD) with Total Organic Carbon (TOC) for monitoring wastewater treatment performance to minimize disposal of toxic analytical waste. J Environ Sci Health Part A 45:1595–1600
22. Ding T, Zhan SC, Yao FW, Wan HK (2013) Effect of chlorine concentration on determining cod by acid and alkaline potassium permanganate. Adv Mater Res 807–809:232–235

23. Eckenfelder WW (1980) Principles of water quality management. CBI Publishing Company.
24. Esteves LC, Oliveira TR, Souza EC Jr, Bomfeti CA, Gonçalves AM, Oliveira LC, Rodrigues JL (2015) A fast and environment-friendly method for determination of chemical oxygen demand by using the heterogeneous Fenton-like process (H2O2/Fe3− xCoxO4 nanoparticles) as an oxidant. Talanta 135:75–80
25. Fan SL, Qu F, Zhao L, Lin J (2006) Flow-injection analysis for the determination of total inorganic carbon and total organic carbon in water using the H_2O_2-luminol-uranine chemiluminescent reaction. Anal Bioanal Chem 386(7–8):2175–2182
26. Federation WE, Association APH (2005) Standard methods for the examination of water and wastewater. American Public Health Association (APHA), Washington
27. Geerdink R, van den Hurk R, Epema O (2017) Chemical Oxygen Demand: Historical perspectives and future challenges. Anal Chim Acta 961:1–11
28. Han B, Jiang X, Hou X, Zheng C (2014) Miniaturized dielectric barrier discharge carbon atomic emission spectrometry with online microwave-assisted oxidation for determination of total organic carbon. Anal Chem 86(13):6214–6219
29. Hu J, Li Y, Gao G, Xia S (2017) A mediated BOD biosensor based on immobilized *B. subtilis* on three-dimensional porous graphene-polypyrrole composite. Sensors 17(11):2594
30. Hu YG, Pang ZT, Yang ZY (2004) Simple chemical oxygen demand (COD) determination method by chemiluminescence. Shaanxi Chem Ind 5
31. Hur J, Kong D (2008) Use of synchronous fluorescence spectra to estimate biochemical oxygen demand (BOD) of urban rivers affected by treated sewage. Environ Technol 29(4):435–444
32. Hur J, Lee B, Lee T, Park D (2010) Estimation of biological oxygen demand and chemical oxygen demand for combined sewer systems using synchronous fluorescence spectra. Sensors 10(4):2460–2471
33. Ingols R, Murray P (1948) An oxygen consumed test for sewage. Water Sew Works 95(3):113–117
34. International Standard ISO 5815. (1983) Water quality determination of biochemical oxygen demand after n day (BODn)-Dilution and seeding method.
35. Jiang Y, Yang X, Liang P, Liu P, Huang X (2018) Microbial fuel cell sensors for water quality early warning systems: fundamentals, signal resolution, optimization and future challenges. Renew Sustain Energy Rev 81:292–305
36. Jing T, Zhou Y, Hao Q, Zhou Y, Mei S (2012) A nanonickel electrochemical sensor for sensitive determination of Chemical Oxygen Demand. Anal Methods 4(4):1155–1159
37. Jordan MA, Welsh DT, Teasdale PR, Catterall K, John R (2010) A ferricyanide-mediated activated sludge bioassay for fast determination of the biochemical oxygen demand of wastewaters. Water Res 44(20):5981–5988
38. Jordan M, Welsh T, John R, Catterall K, Teasdale P (2013) A sensitive ferricyanide-mediated biochemical oxygen demand assay for analysis of wastewater treatment plant influents and treated effluents. Water Res 47(2):841–849
39. Jouanneau S, Recoules L, Durand M, Boukabache A, Picot V, Primault Y, Thouand G (2014) Methods for assessing biochemical oxygen demand (BOD): a review. Water Res 49:62–82
40. Khor BH, Ismail, AK, Ahamad R, Shahir S (2014) Chromobacterium violaceum for rapid measurement of biochemical oxygen demand. J Teknol 69(1)
41. Khor B, Ismail A, Ahamad R, Shahir S (2015) A redox mediated UME biosensor using immobilized *Chromobacterium violaceum* strain R1 for rapid biochemical oxygen demand measurement. Electrochim Acta 176(1):777–783
42. Kim B, Chang I, Gil G, Park H (2003) Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. Biotech Lett 25(7):541–545
43. Kim C, Eom J, Jung S, Ji T (2016) Detection of organic compounds in water by an optical absorbance method. Sensors 16(1):61
44. Knapik H, Fernandes C, de Azevedo J, do Amaral Porto, M. (2014) Applicability of fluorescence and absorbance spectroscopy to estimate organic pollution in rivers. Environ Eng Sci 31(12):653–663
45. Kolb M, Bahadir M, Teichgräber B (2017) Determination of chemical oxygen demand (COD) using an alternative wet chemical method free of mercury and dichromate. Water Res 122:645–654
46. Kono T (1968) Kinetics of microbial cell growth. Biotechnol Bioeng 10(2):105–131
47. Kwak J, Khang B, Kim E, Kim H (2013) Estimation of biochemical oxygen demand based on dissolved organic carbon, UV absorption, and fluorescence measurements. J Chem 243769
48. Le G, Yang H, Yu X (2018) Improved UV/O_3 method for measuring the chemical oxygen demand. Water Sci Technol 77(5):1271–1279
49. Lee A, Nikraz H (2015) BOD: COD ratio as an indicator for river pollution. Int Proc Chem Biol Environ Eng 88(15):89–94
50. Lee J, Lee S, Yu S, Rhew D (2016) Relationships between water quality parameters in rivers and lakes: BOD 5, COD, NBOPs, and TOC. Environ Monit Assess 188(4):252
51. Li C, Song G (2009) Photocatalytic degradation of organic pollutants and detection of chemical oxygen demand by fluorescence methods. Sens Actuators B Chem 137(2):432–436
52. Li J, Luo G, He L, Xu J, Lyu J (2018) Analytical approaches for determining chemical oxygen demand in water bodies: a review. Crit Rev Anal Chem 48(1):47–65
53. Li S, Zheng F, Cai S, Liang W, Li Y (2013) A visible light assisted photocatalytic system for determination of chemical oxygen demand using 5-sulfosalicylic acid in situ surface modified titanium dioxide. Sens Actuators B Chem 188:280–285
54. Li Y, Sun J, Wang J, Bian C, Tong J, Li Y, Xia S (2016) A single-layer structured microbial sensor for fast detection of biochemical oxygen demand. Biochem Eng J 112:219–225
55. Liu C, Li Z, Jiang D, Jia J, Zhang Y, Chai Y, Cheng X, Dong S (2016) Demonstration study of biofilm reactor based rapid biochemical oxygen demand determination of surface water. Sens Bio-sens Res 8:8–13
56. Liu L, Bai L, Yu D, Zhai J, Dong S (2015) Biochemical oxygen demand measurement by mediator method in flow system. Talanta 138:36–39
57. Liu W, Zhang Z, Zhang Y (2008) Chemiluminescence micro-flow system for rapid determination of chemical oxygen demand in water. Microchim Acta 160(1–2):141–146
58. Lopreside A, Calabretta MM, Montali L, Zangheri M, Guardigli M, Mirasol, M, Michelini E (2020) Bioluminescence goes portable: recent advances in whole-cell and cell-free bioluminescence biosensors. Luminescence
59. Ma J (2017) Determination of chemical oxygen demand in aqueous samples with non-electrochemical methods. Trends Environ Anal Chem 14:37–43
60. Montes MF (2016) Biochemical oxygen demand. In: Finkl CW (ed.). Encyclopedia of Earth Sciences Series. pp 75–76. Springer, Netherlands.
61. Moreira F, Boaventura R, Brillas E, Vilar V (2017) Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. Appl Catal B 202:217–261
62. Nagel B, Dellweg H, Gierasch L (1992) Glossary for chemists of terms used in biotechnology (IUPAC recommendations 1992). Pure Appl Chem 64(1):143–168

63. Nurdin M, Zaeni A, Rammang E, Maulidiyah M, Wibowo D (2017) Reactor design development of chemical oxygen demand flow system and its application. Anal Bioanal Electrochem 9(3):480–494
64. Pasco N, Baronian K, Jeffries C, Webber J, Hay J (2004) MICREDOX®—development of a ferricyanide-mediated rapid biochemical oxygen demand method using an immobilised *Proteus vulgaris* biocomponent. Biosens Bioelectron 20(3):524–532
65. Pasco N, Baronian K, Jeffries K, Hay J (2000) Biochemical mediator demand–a novel rapid alternative for measuring biochemical oxygen demand. Appl Microbiol Biotechnol 53(5):613–618
66. Patnaik P (2010) Oxygen demand, biochemical. In: Patnaik P (ed.). Handbook of environmental analysis, pp 285–291, CRC Press
67. Pham T, Nguyen P, Van Nguyen T, Duong H (2019) Self-build packed-bed bioreactor for rapid and effective BOD estimation. Environ Sci Pollut Res 26(25):25656–25667
68. Recoules L, Jouanneau S, Thouand G, Gué A, Boukabache A (2018) A microsystem approach to measure the oxygen consumption of bacteria. Towards a precise evaluation of the BOD (Biological Oxygen Demand) parameter of wastewater. In: 5th international conference on environmental systems research (ICESR 2018), Brisbane, Australia
69. Recoules L, Jouanneau S, Thouand G, Gué AM, Boukabache A (2019) Towards a miniaturized device to evaluate the BOD parameter of wastwater. Int J Environ Sci Develop 10(6):178–182
70. Sakaguchi T, Kitagawa K, Ando T, Murakami Y, Morita Y, Yamamura A, Tamiya E (2003) A rapid BOD sensing system using luminescent recombinants of *Escherichia coli*. Biosens Bioelectron 19(2):115–121
71. Samudro G, Mangkoedihardjo S (2010) Review on BOD, COD and BOD/COD ratio: a triangle zone for toxic, biodegradable and stable levels. Int J Acad Res 2(4):235–239
72. Si H, Pan N, Zhang X, Liao J, Rumyantseva M, Gaskov A, Lin S (2019) A real-time on-line photoelectrochemical sensor toward chemical oxygen demand determination based on field-effect transitor using an extended gate with 3D TiO_2 nanotubes arrays. Sens Actuators B Chem 289:106–113
73. Sonawane JM, Ezugwu CI, Ghosh PC (2020) Microbial fuel cell-based biological oxygen demand sensors for monitoring wastewater: state-of-the-art and practical applications. ACS sens 5(8):2297–2316
74. Stefansson A, Gunnarsson I, Giroud N (2007) New methods for the direct determination of dissolved inorganic, organic and total carbon in natural waters by reagent-free™ Ion Chromatography and inductively coupled plasma atomic emission spectrometry. Anal Chim Acta 582(1):69–74
75. Su Y, Li X, Chen H, Lv Y, Hou X (2007) Rapid, sensitive and on-line measurement of chemical oxygen demand by novel optical method based on UV photolysis and chemiluminescence. Microchem J 87(1):56–61
76. Trosok S, Driscoll B, Luong J (2001) Mediated microbial biosensor using a novel yeast strain for wastewater BOD measurement. Appl Microbiol Biotechnol 56(3–4):550–554
77. Villalobos P, Acevedo C, Albornoz F, Sánchez E, Valdés E, Galindo R, Young M (2010) A BOD monitoring disposable reactor with alginate-entrapped bacteria. Bioprocess Biosyst Eng 33(8):961–970
78. Visco G, Bellanti F, Campanella L, Mazzela T, Nobili V (2005) Optimisation of a photochemical sensor for total organic carbon measurement. Ann di Chim J Anal Environ Cult Herit Chem 95(3–4):185–198
79. b)Visco, G., Campanella, L., Nobili, V. (2005) Organic carbons and TOC in waters: an overview of the international norm for its measurements. Microchem J 79:185–191
80. Wang C, Wu J, Wang P, Ao Y, Hou J, Qian J (2013) Photoelectrocatalytic determination of chemical oxygen demand under visible light using Cu2O-loaded TiO2 nanotube arrays electrode. Sens Actuators B Chem 181:1–8
81. Wang J, Li Y, Bianc C, Tong J, Fang Y, Xia S (2017) Ultramicroelectrode array modified with magnetically labeled *Bacillus subtilis*, palladium nanoparticles and reduced carboxy graphene for amperometric determination of biochemical oxygen demand. Microchim Acta 184(3):763–771
82. Wang X, Zhang S, Wang H, Yu H, Wang H, Zhang S, Peng F (2015) Visible light photoelectrochemical properties of hydrogenated TiO_2 nanorod film and its application in the detection of chemical oxygen demand. RSC Adv 5(93):76315–76320
83. Wibowo D, Ruslan M, Nurdin M (2017) Determination of COD based on photoelectrocatalysis of $FeTiO_3$.TiO_2/Ti electrode. In: IOP conference series: materials science and engineering. Surabaya, East Java: Institute of Physics Publishing.
84. Wu C, Wu K (2013) Preparation of electrochemical sensor based on morphology-controlled platinum nanoparticles for determination of chemical oxygen demand. Chin J Anal Chem 41(5):704–708
85. Xiao N, Wu R, Huang JJ, Selvaganapathy PR (2020) Development of a xurographically fabricated miniaturized low-cost, high-performance microbial fuel cell and its application for sensing biological oxygen demand. Sens Actuators B Chem 304:127432
86. Xu X, Thomson N (2008) Estimation of the maximum consumption of permanganate by aquifer solids using a modified chemical oxygen demand test. J Environ Eng 134(5):353–361
87. Xu Z, Xu Y (2015) Rapid field estimation of biochemical oxygen demand in a subtropical eutrophic urban lake with chlorophyll a fluorescence. Environ monit Assess 1–14
88. Yamashita T (2016) A novel open-type biosensor for the in-situ monitoring of biochemical oxygen demand in an aerobic environment. Sci Rep 6(1):1–9
89. Yamashoji S, Asakawa A, Kawasaki S, Kawamoto S (2004) Chemiluminescent assay for detection of viable microorganisms. Anal Biochem 333(2):303–308
90. Yao H, Wu B, Qu H, Cheng Y (2009) A high throughput chemiluminescence method for determination of chemical oxygen demand in waters. Anal Chim Acta 633(1):76–80
91. Yao N, Liu Z, Chen Y, Zhou Y, Xie B (2015) A novel thermal sensor for the sensitive measurement of chemical oxygen demand. Sensors 15(8):20501–20510
92. Yao N, Wang J, Zhou Y (2014) Rapid determination of the chemical oxygen demand of water using a thermal biosensor. Sensors 14(6):9949–9960
93. Zaher K, Hammam G (2014) Correlation between biochemical oxygen demand and chemical oxygen demand for various wastewater treatment plants in Egypt to obtain the biodegradability indices. Int J Sci Basic Appl Res IJSBAR 13(1):42–48

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