



Review

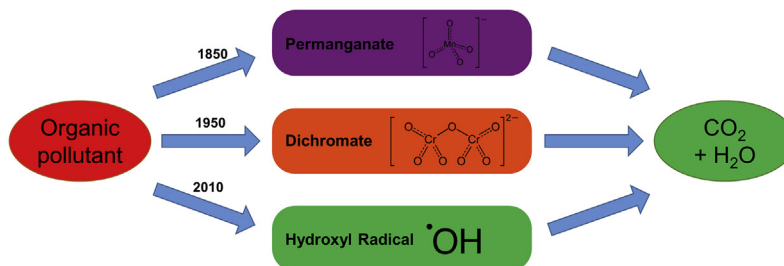
Chemical oxygen demand: Historical perspectives and future challenges

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HIGHLIGHTS

- A historical view of the development of the COD determination is presented.
- Dichromate has survived in standard quantitative procedures.
- COD procedures burden the environment with hazardous chemicals like mercury.
- Electro- or photo oxidative methods show potential as replacements for COD methods.

GRAPHICAL ABSTRACT



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ABSTRACT

Determining the chemical oxygen demand (COD) is challenging because of the chemicals that are used in the current methods. There is an urgent need to determine the pollution in surface waters from (heavy) industry via a simple, reliable and fast method. However, the current procedures use hazardous chemicals, such as mercury, to suppress chloride interferences. This challenge has not been resolved.

The introduction of modern detection techniques, such as chemiluminescence and oxidation procedures, e.g., microwave and ultrasound dissolution, has not resulted in a breakthrough. Currently, the applicability of mercury-free methods is limited to samples with a chloride content of approximately 3000 mg/L. New electro- and photo-oxidative methods show potential as replacements for the standard COD methods that require toxic reagents, but further research is still needed.

In this paper, a historical view of the development of chemical oxygen demand determination methods is presented. Critical notes on and outlines of the development of the first through the current procedures are discussed. In addition, the Dutch situation is presented as an example to other countries in their “struggle” to establish a COD procedure with two basic qualities, reliability and environmental friendliness.

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1. Introduction

ISO 6060 states that the accepted definition of COD (chemical oxygen demand) is the mass concentration of oxygen that is equivalent to the amount of dichromate consumed by dissolved and suspended matter when a (water or sludge) sample is treated with that oxidant under defined conditions [1].

The earliest methods to determine COD were developed approximately 150 years ago and involved the observation of colour changes of a permanganate solution mixed with water samples [2]. The earliest attempts to examine the oxygen consumption caused by pollution in water and wastewater used a permanganate test.

The first attempts to use dichromate to oxidize organic matter were during the period from 1925 to 1930 and were not very promising. In 1949, Moore et al. [3] applied the dichromate procedure to wastewater analysis. Quantitative oxidation of compounds was obtained by refluxing the sample for 2 h with dichromate in a 50% sulphuric acid solution at 145–150 °C. Using this procedure, approximately 90% of the organic matter present and most of the chloride were oxidized, but a correction was required for the chloride [3]. In 1951, Moore et al. [4] introduced a small amount of silver sulphate to a mixture to catalyse the oxidation, and this resulted in nearly quantitative results even with several relatively inert compounds, such as carboxylic acids and aliphatic alcohols.

In 1963, Dobbs et al. [5] demonstrated that chloride oxidation during COD digestion was reduced substantially by the addition of mercuric sulphate to the sulphuric acid/dichromate reagent, which meant that a separate chloride determination was no longer necessary.

Chloride is the most common interference in a COD analysis. It is oxidized in acidic solutions by dichromate, but it is not oxidized by natural processes in the environment [2]. Additives such as HgSO₄, AgNO₃ and Cr(III), or their combinations, will minimize chloride interference but not completely remove it [6]. At high temperatures, the masking of chloride is insufficient even with mercury sulphate. Additionally, these additives create additional hazardous

developed that do not require toxic reagents. These new methods are based on either electrocatalytic [9–15] or photocatalytic [16–23] oxidation principles. Although some of the methods have great potential, none of the methods have been widely adopted. Recently, photoelectrocatalytic COD determination using TiO₂ was introduced, and it may have a great future for dissolved COD. In the commercially available PeCOD[®] system, the chloride tolerance is approximately 350 mg L⁻¹, and some authors [17,24] report a chloride tolerance up to approximately 2000 mg L⁻¹ with a modified system.

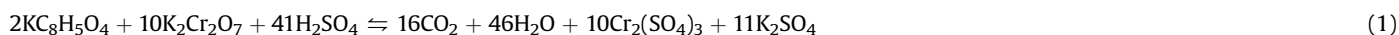
As outlined above, the current COD determination methods are not satisfactory because of the use of highly toxic substances such as Cr(VI), Hg and Ag. This is true even when considering the possibility of strongly reducing or completely recycling the spent chemicals. In the literature, there are few procedures that advocate an environmentally friendly method for COD determination, and the chance of successfully introducing such a method is slim as long as the use of the current COD methods are embedded in legislation and taxation.

2. Chemical and analytical background

In this section, the chemistry behind the analytical procedures will be described. For details on the conditions used in standard COD analysis, refer to the standard procedures, e.g., ISO 6060 [1]. It is important to note that the conditions have a large impact on the respective methods, but that falls outside of the scope of this review.

2.1. Equations

In the standard COD determination method, an oxidant (Cr₂O₇²⁻), a catalyst (Ag⁺) and sulphuric acid are added to an aqueous sample that is then heated for 2 h. Potassium hydrogen phthalate is often used to represent organic material when procedures are tested. The conversion of potassium hydrogen phthalate by dichromate is as follows:



wastes [7].

Although COD methods that replace mercury with AgNO₃ and/or Cr(III) have been proposed, they cannot be used for samples with variable salt loads [8]. Furthermore, silver ions are toxic and expensive, and the addition of Cr(III) precludes colorimetric detection. Therefore, mercury containing COD reagents continue to prevail.

In recent years, some new “green” COD methods have been

When dichromate is replaced by oxygen, the equation becomes:



Eqs. (1) and (2) show that each mole of Cr₂O₇²⁻ oxidizes the amount of potassium hydrogen phthalate that is equivalent to 1.5 mol of O₂.

The excess dichromate is determined via titration with ferrous

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