Potentiometric measurement of chemical oxygen demand

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Abstract

Measurement of the COD of an aqueous solution involves firstly digestion of a test sample with dichromate solution, and secondly measurement of the dichromate remaining either by titration by ferrous ammonium sulfate (FAS) to a color indicator endpoint, or via colorimetric determination using a spectrophotometer. In this paper, a potentiometric end-point determination (using FAS titrant) is proposed as a third option for measuring the dichromate remaining. The potentiometric method is based on the observation that the titration end point corresponds to a region of minimum redox buffer. That is, the end point to the titration is sharp and easily identified. Furthermore the platinum-calomel electrode system used in this method responds quickly to potential changes within the $(Fe2/Fe3+Cr2O7/Cr^{3+})$ solution producing stable readings. These factors allow rapid and accurate COD measurement. Furthermore the method is based firmly on theoretical considerations allowing extension into a region of low COD.

The method is applied to a broad spectrum of waste waters and dilutions of these, using both macro- and semi-macro techniques. Results are compared with data determined using colorimetric and color indicator end-point methods. It is shown that the potentiometric end-point titration (with FAS titrant) can be used with equal or better facility.

Introduction

Current practice is to use chemical oxygen demand (COD) as a system parameter both for process design and in the control of waste-water treatment works (Wentzel et al., 1995). The principal advantages of COD over biological oxygen demand (BOD) measurement, are the simplicity of procedure and the fact that the test can be completed very rapidly (within about 3 h).

The COD measurement procedure is based on the observation that under acidic conditions the dichromate ion $(Cr_2O_7^2)$ oxidises almost all organic materials $(C_xH_yO_z)$ to CO_2 and H_2O (Eq. 1).

$$C_xH_yO_z + kCr_2O_7^{2"} + kH^+ \Leftrightarrow xCO_2 + \frac{y + 8k}{2}H_2O + 2kCr^{3+} \quad (1)$$
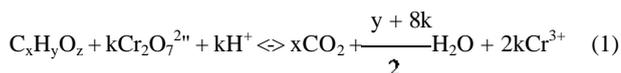
$$\text{where } k = \frac{2x}{3} + \frac{y}{6} - \frac{z}{3}$$

The test involves addition of an excess but known mass of dichromate to ensure complete oxidation of organic material in a digestion process. The COD is then estimated using any of the following routines (*Standard Methods*, 1992):

(a) measurement of dichromate $(Cr_2O_7^2)$ remaining via a colorimetric method;
(b) measurement of Cr^{3+} formed, again a colorimetric method;
(c) measurement of $Cr_2O_7^{2-}$ remaining via titration with a ferrous (Fe^{2+}) reagent FAS $(Fe(NH_4)_2(SO_4)_2 6H_2O)$ to a colorimetric end point using ferroin indicator (the classical procedure):

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \leftrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad (2)$$
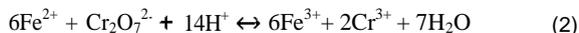
With regard to the colorimetric determinations (i.e. (a) and (b) above) the methods have a number of disadvantages. They require expensive equipment and are relatively time-consuming (the methods only can be applied after digested samples have cooled to room temperature). Furthermore they are affected by stratification in the digested solution (i.e. development of "Schlieren lines" - Messenger, 1981; Jones et al., 1985, Dasgupta and Petersen, 1990). Finally, turbidity interferes with accurate measurement - such turbidity may be present either in the raw samples or generated via precipitation on addition of silver catalyst during the digestion process (Moore et al., 1951; Bertram et al., 1958; Gaudy and Ramanatha, 1964; Messenger, 1981).

With regard to the titration method, disadvantages include use of a titrant $Fe(NH_4)_2(SO_4)6H_2O$ which degenerates with time and must thus be checked on a daily basis (Gaudy and Ramanatha, 1964). This, however, can be overcome by preparing the titrant using oxygen-free water and storing it in a CO_2 atmosphere (Cooke et al., 1951). Furthermore, problems may arise with estimation of the colorimetric end point to the titration. These include:

- masking the color change of the indicator due to presence of turbidity either in the raw sample or generated in the process of digestion (Gaudy and Ramanatha, 1964; Messenger, 1981), and
- an indeterminate error arising from the difference between the true end point to the titration and that reflected by the color change of the indicator used.

Comparing the two methods, colorimetric determination (of either Cr^{3+} or $Cr_2O_7^{2-}$ species) is considered to be faster than the titrimetric color indicator end-point method. Consequently it is preferred in waste-water treatment laboratories handling a large number of COD samples (greater than about 30) per day. Below this number, the colorimetric methods have no advantage over the titration approach. However, recognising that the titration method can be effected using significantly cheaper measurement apparatus, this method is to be preferred for small- to medium-size waste-water treatment laboratories (effecting less than about

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