Oxygen Demand, Chemical, Mn III

For water and wastewater

Introduction

Chemical oxygen demand (COD) is defined as “a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.*” Trivalent manganese (Mn III) is a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to faint pink when it reacts with organic matter. Manganese III COD results are measured colorimetrically, and the color intensity is inversely proportional to the amount of COD in the sample.

The digestion time is 60 minutes, but can be extended when samples are difficult to completely oxidize. The reagent typically has an oxidation efficiency of about 80% for standards prepared from potassium acid phthalate and domestic wastewater samples. No oxygen demand test will oxidize all organic compounds with 100% efficiency. With non-typical samples, standards can be prepared from other reference materials. Studies have shown that the Mn III COD procedure correlates very well to biochemical oxygen demand (BOD) and dichromate COD tests.

Many COD reagents contain mercury, chromium and silver. The absence of these materials in the Mn III COD Reagent significantly minimizes the disposal cost and reduces exposure of the analyst to hazardous compounds.

Inorganic materials may interfere with the Mn III COD Reagent. Chloride is the most common interference and is removed by sample pretreatment with the Chloride Removal Cartridge. Ammonia interferes with the test when present with chloride. The interference is severe at high ammonia and chloride concentrations.

Chemical reactions

Trivalent manganese oxidizes organic materials in the sample to CO_2 and H_2O. In the process, manganese III is reduced to manganese II. The reaction occurring in the Mn III COD Reagent Vial is represented by the equation below:

$$2\ KC_8H_5O_4 + 30\ Mn_2(SO_4)_3 + 24\ H_2O \rightarrow 16\ CO_2 + 60\ MnSO_4 + 28\ H_2SO_4 + 2\ KHSO_4$$

Chemical oxygen demand results are usually expressed by the amount of oxygen consumed during the oxidation of organic matter.

When oxygen is used as the primary oxidant in the oxidation of potassium acid phthalate, the equation below describes the reaction:

$$KC_8H_5O_4 + 7.5\ O_2 \rightarrow 8\ CO_2 + 2\ H_2O + KOH$$

Seven and one-half molecules of oxygen ($O_{2)}$ consume one molecule of potassium acid phthalate (KHP). On a weight basis, the theoretical oxygen demand for KHP is 1.175 mg O_2 per mg KHP.

The interference from chloride is minimized by sample pre-treatment with the Chloride Removal Cartridge (CRC). The CRC contains a proprietary reagent to remove chloride from the sample solution. The flow rate through the CRC has been optimized for chloride removal, while at the same time minimizing any effect the CRC might have on other sample components.

* APHA Standard Methods for the Examination of Water and Wastewater, 19th ed., 1995

Suspended solids, which may contain oxidizable organic compounds, are filtered out of the sample with a glass fiber filter located in the upper part of the Chloride Removal Cartridge. After the sample has been filtered into a Mn III COD Reagent Vial, the glass fiber filter, along with any suspended solids present, is transferred into the COD Reagent Vial. The glass fiber filter is binder free and has no oxygen demand.

Comparability of the Mn III COD to other tests

For samples from a specific source, the Mn III COD results can be related empirically to BOD, dichromate COD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. The test can also be used to estimate dilutions for the five day BOD test. This will ensure reliable BOD data for pre-treatment and compliance monitoring. For samples with constant chloride concentrations, reliable correlations can be developed without the chloride removal pre-treatment.

Test oxidation efficiency

Different test methods may oxidize sample components with different efficiencies. The Mn III COD Reagent will oxidize KHP standards with about 80% efficiency. Many wastewater samples are also oxidized with 80% efficiency.

For example, an ASTM Wastewater Reference Sample was analyzed for COD using both the dichromate and Mn III COD. The dichromate COD result was 1018 mg/L and Mn III COD result was 1008 mg/L. These test results are comparable despite different oxidation efficiencies because the instrument calibration is based on KHP.

Correlation of test results

To demonstrate how to correlate the results between the two different tests, a glutamic acid standard was prepared to contain a theoretical chemical oxygen demand of 500 mg/L. The dichromate COD result was 506 mg/L and the Mn III COD result was 459 mg/L. To correlate the Mn III COD results with the dichromate COD, a correlation factor is determined.

$$\frac{\text{Cr COD}}{\text{Mn III COD}} = \frac{506\ \text{mg/L}}{459\ \text{mg/L}} = 1.102\ \text{(Correlation Factor)}$$

Mn III COD, mg/L ì 1.102 = Dichromate COD, mg/L

Calibrations based on reference materials other than KHP

It may be desirable for COD results to closely match the theoretical demand of the sample. Occasionally, samples contain a major component that is incompletely oxidized. In this situation, calibration standards can be prepared from known values of that sample component. In the example above, calibration standards would be prepared from glutamic acid.