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# Oxygen Demand, Chemical

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For wastewater

Reactor Digestion Using Potassium  
Dichromate Method

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## Introduction

The Dichromate Chemical Oxygen Demand (COD) test measures the oxygen equivalent of the amount of organic matter oxidizable by potassium dichromate in a 50% sulfuric acid solution.

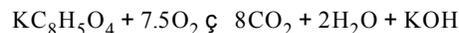
Generally, a silver compound is added as a catalyst to promote the oxidation of certain classes of organics, and a mercuric compound may be added to reduce interference from the oxidation of chloride ions by the dichromate. End products are carbon dioxide, water, and various states of the chromium ion.

After the oxidation step is completed, the amount of dichromate consumed is determined titrimetrically or colorimetrically. Either the amount of reduced chromium (chromic ion), or the amount of unreacted dichromate, can be measured. If the latter method is chosen, the analyst must know the precise amount of dichromate added.

## Chemical reactions

In the oxidation of organic materials by dichromate in sulfuric acid, most of the carbon is converted to carbon dioxide while any hydrogen present in the organic compound is converted to water. Other elements also may be oxidized.

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.

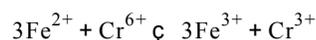


Seven and one-half molecules of oxygen ( $\text{O}_2$ ) consume one molecule of potassium acid phthalate (KHP). On a weight basis, the theoretical oxygen demand for KHP is 1.175 mg  $\text{O}_2$  per mg KHP.

There are two basic methods, titrimetric and colorimetric, for determining the amount of chromium in a particular valence state. There are several variations of each method.

When titration is used in the measurement process, the amount of  $\text{Cr}^{6+}$  left is determined. It is done in one of two ways; in both cases, the precise initial amount of  $\text{Cr}^{6+}$  ion must be known. This is necessary because one must be able to subtract the final  $\text{Cr}^{6+}$  level from the initial level to yield the amount that was reduced to  $\text{Cr}^{3+}$ . This difference is used to calculate the COD. The initial amount is known either through calculation, because primary standard grade potassium dichromate is readily available, or by testing the bulk solution before running the individual tests.

The final amount of dichromate is most commonly determined by direct titration using ferrous ammonium sulfate as the titrant and "ferroin" (1,10-phenanthroline ferrous sulfate) as the indicator. The  $\text{Fe}^{2+}$  in the titrant reacts with the chromic ions:



1,10-phenanthroline forms an intense color with  $\text{Fe}^{2+}$  but no color with  $\text{Fe}^{3+}$ . When reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  is complete,  $\text{Fe}^{2+}$  reacts to form the ferroin complex and the solution color changes sharply from greenish-blue to orange-brown, signaling the end point. The end point also can be detected potentiometrically.

The colorimetric determination has several advantages over titration. Colorimetric determination is quicker and easier to run, and does not require additional reagents. In the Reactor Digestion Method, the digestion vials can be checked during the digestion process while they are hot to determine when no further oxidation is taking place, resulting in a shorter digestion time. When using the Reactor Digestion Method the spectrophotometer is set at 420 nm or 365 nm for the low ranges, and 620 nm for the high ranges. Low range measurement determines the remaining yellow  $\text{Cr}^{6+}$ . High range measurement determines the amount of green  $\text{Cr}^{3+}$  produced.