

The Chemistry of Chemical Oxygen Demand

By John Stone

Chemical Oxygen Demand (COD) is a quick, inexpensive means to determine organics in water. COD samples are prepared with a closed-reflux digestion followed by analysis. Determinations can be made titrimetrically by several approved methods, or photometrically (colorimetrically) with EPA Method 410.4, Hach[®] Method 8000 and Standard Method 5520D. The COD chemistry reviewed here applies to colorimetric methods.

The first step is digestion. Concentrated sulfuric acid (H_2SO_4) provides the primary digestion catalyst. The secondary catalyst, Silver Sulfate (AgSO_4), assists oxidization of straight-chain hydrocarbons such as diesel fuel and motor oil. Heat from the digestion block (150°C) also acts as a catalyst.

During digestion the sample's organic carbon (C) material is oxidized with the hexavalent dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) found in potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$). The dichromate readily gives up oxygen (O_2) to bond with carbon atoms to create carbon dioxide (CO_2). The oxygen transaction from $\text{Cr}_2\text{O}_7^{2-}$ to CO_2 reduces the hexavalent $\text{Cr}_2\text{O}_7^{2-}$ ion to the trivalent Cr^{3+} ion. In essence a COD test determines the amount of carbon based materials by measuring the amount of oxygen the sample will react with. This oxygen transaction is the source of the test's name, *Chemical Oxygen Demand*.

Colorimetric analysis works because the two chromium ions absorb in the visible range but at different wavelengths. The dichromate ion does not absorb at the Cr^{3+} ion wavelength, and the Cr^{3+} ion absorbs only a small, correctable amount of the wavelength in the dichromate range. This slight interference is zeroed out in the calibration step.

The dichromate ion is visible at 420nm, and the Cr^{3+} ion around 600 – 620nm. Low range COD (<150 ppm) analysis measures the decrease in the oxidant, $\text{Cr}_2\text{O}_7^{2-}$. High range COD (<1,500 ppm) analysis measures the increase in Cr^{3+} . A spectrophotometer sends the correct wavelength through the sample cell to a detector that measures transmittance.

COD has two common error sources. First, the oxidation step does not distinguish between organic and inorganic carbons. Where carbons are available, oxidation will create Cr^{3+} ions. It's the organic carbon fraction of the sample that's sought after, and it's the organics that found the correlation basis for Biochemical Oxygen Demand (BOD) and Total Organic Carbon (TOC). Unfortunately unknown oxidizable inorganics introduce positive error, and skew

any attempt to directly substitute COD results for BOD or TOC. The more common interferent however, is chloride (Cl).

The origin of chloride is chlorine (Cl₂). Chlorine is a great oxidizer of organics to include micro organisms. This is why chlorine is a powerful disinfectant in water treatment. Cl₂ works well because the two Cl atoms share an electron, and readily receive two electrons to become two stable chloride ions (Cl⁻²). This electron grabbing oxidizes (or destroys) micro organisms, but adds many interferents to the COD sample.

The reaction between chloride and silver sulfate creates silver chloride (AgCl). The reduction of silver sulfate correspondingly reduces the activity needed to oxidize straight chain hydrocarbons, a negative interferent one would think. But the cloudiness of silver chloride precipitate causes a false positive absorbance value. Furthermore, the rigorous COD digestion can actually result in the reaction of dichromate with chloride to form chromic acid (and the elemental form of chlorine). Adding chlorine to the sample causes a positive interference.

Suffice it to say that all chloride interferences are overcome by complexing chloride with mercuric sulfate (HgSO₄). Chloride concentrations >2,000 mg/L cannot be corrected. High chloride samples must be run titrimetrically by EPA 410.3, *COD for Saline Waters*.

EPA approved COD methods for NPDES reporting:				
Method	Year	MDL mg/L	determinative technique	sample size ml
EPA 410.1	1971	>50	Titrimetric	50
EPA 410.2	1971	5 – 50	Titrimetric	50
EPA 410.3	1971	>250	Titrimetric	50
EPA 410.4	1978	3 – 900	Colorimetric (automated)	2.5
EPA 410.4	1978	20 – 900	Colorimetric (manual)	2.5
Hach 8000	1980	3 – 150	Colorimetric	2.0
Hach 8000	1980	20 – 1,500	Colorimetric	2.0
SM 5520 C	1998	<40 – >400	Titrimetric	2.5 – 10
SM 5520 D	1998	<90 – >900	Colorimetric	2.5 – 10

All colorimetric COD methods create hazardous wastes. These haz-wastes are silver, hexavalent chromium and mercuric sulfate. Mercuric sulfate can be eliminated from the digestion solution if the sample is positively chloride-free, but mercury-free digestions are not EPA approved for NPDES reporting. Hazardous wastes must be disposed of properly, but can be greatly reduced by use of a micro method.

Methods 410.4 and 8000 are micro colorimetric methods. They call for smaller sample sizes and reduced reagents. Both require sample homogenization prior to digestion. Analysts using Method 8000 employ commercially available digestion/analysis vials pre-filled with the necessary reagents. Quality vials are spectrally pure and include a specialized Teflon matrix liner that withstands the corrosive environment during the time between manufacture and use.