Lab **Matters**

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Understanding Chemical Oxygen Demand (COD)

Introduction – COD is a slightly different category of test. There is no one COD atom or molecule. You can't hold COD in your hand and point to it. It is also not necessarily a specific method defined parameter. It is simply a definition. COD is the amount of oxygen consumed when **all** materials present in a sample are fully oxidized. Note the distinction between this and the other oxygen demand test (BOD). COD is when all materials are fully chemically oxidized; BOD is only that material which is oxidized by (occasionally uncooperative) bacteria over a period of 5 days. Any method that is capable of oxidizing compounds and allows the amount of oxidation to be measured could theoretically be used to determine COD. The dichromate ion ($Cr_2O_7^{2-}$) has proven itself to be best suited for general purpose COD and is required in all approved methods.

Approved Methods – There are only two major distinctions in approved methods for COD

Titrimetric –

- EPA 410.3 (contains instructions for overcoming chloride in excess of 2000 mg/L)
- SM5220 C
- ASTM D1252-95, 00(A)
- USGS I-3560-85

Photometric –

- EPA 410.4 (does not contain provisions for low-level determinations)
- SM5220 D
- ASTM D1252-95, 00(B)
- USGS I-3561-85

Method Summary – An aliquot of the sample is digested for two hours at 150°C in the presence of dichromate and sulfuric acid. The resulting solution is titrated to a colored endpoint with ferroin indicator or read on a spectrophotometer at an appropriate wavelength.

What You Should Know – There are few listed interferences with the COD methods. The most common one encountered is the chloride ion, although any halogen will function the same way. Chloride is an interesting problem in that it can be both a positive and negative interference. It will react with the silver ion to precipitate out silver chloride. This will inhibit the ability of the silver to catalyze the oxidation of certain compounds, leading to low results. However the chloride will react with the dichromate to form elemental chlorine. This registers in the test as oxidation and will form a positive interference in the results, not to mention a poisonous gas in your digestate.

Several inorganic species are listed as interferences as well, namely nitrite and reduced metals. These are only interferences if one is looking solely for the organic portion of the oxygen demand.

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Typically, the test is used to determine the total oxygen depletion due to the constituents in the water in order to judge if it poses a hazard to aquatic life. Often, it is presumed that the organic portion makes the largest contribution. However, it does not matter to the fish whether they are asphyxiating because the oxygen is bound to some organic molecule or large concentrations of ferrous iron. Therefore, these particular species are only an interferent if you are interested in the organic contribution.

Many analysts read through COD methods and wonder if they can accurately run the test without a few of the chemicals specified in the digestion mix. This is done in an attempt to reduce the hazardous waste generated and reduce the cost of the test by eliminating the more expensive chemicals. The most common question is the elimination of mercuric sulfate. This reagent is added to the mix in order to complex any free chloride ions. Standard Methods contains instructions that the mercuric sulfate can be reduced or eliminated completely if the amount of chloride in solution is negligible. The EPA does not allow a modification of the reagents used for reporting purposes. You must use all specified reagents in the COD vial. There are further scientific grounds for keeping your vials consistent with one another. The presence or absence of different ions in solution will have an effect on the optical density of the solution. This can lead to slight discrepancies in the absorbance in the colorimetric methods. If you omit the mercuric sulfate in your standards knowing that you prepared them from pure stock but have to use it in some of your samples due to chloride presence you can have a slightly different response between the two. The other request is to eliminate the silver sulfate in the digestion mix. This is more often a cost issue, but the silver also contributes to the hazardous nature of the waste. The silver helps serves as a catalyst to promote the oxidation of some of the more difficult organic species. Leaving this reagent out of the mix will often lead to incomplete digestion and a low bias in the reported COD. The same two lines of reason with EPA acceptance and optical density also apply here. Always remember, even if you have managed to eliminate the mercury or silver salts in your COD waste, the chromium and sulfuric acid components will still leave it classified as hazardous.

When using SM5220 D, you are given the option of preparing a slightly different digestion solution to more accurately analyze low levels of COD. This digestion solution will end up more of a pale yellow than the orange/brown of the normal range digestion solution. This color difference is due to using 1/10 of the potassium dichromate salt. There is one other important difference to know when analyzing low-level COD. The calibration curve does not follow normal procedures. Instead of blanking your spectrophotometer on a color developed aliquot of reagent water you will blank out on reagent water only. The slope of your calibration curve will end up negative, sloping down from left to right as the concentration increases. The differences in the slopes of these curves arise from what is actually being measured. The normal range COD digestion is read at 600 nm and is proportional to the *increase* in the chromic ion (Cr^{3+}), which causes the digestion solution to move towards a green shade as the COD concentration increases. The low range COD digestion is read at 420 nm and is proportional to the *decrease* in the dichromate ion ($Cr_2O_7^{2-}$), which causes the solution to move towards a colorless/pale blue shade as the COD concentration increases. Your digested zero COD standard will have a higher absorbance than your digested 100 mg/L COD standard. Yes, it is counter-intuitive, but it is also correct.

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Method Procedure

Note – This is not intended to be a standalone method and does not address all safety or quality control aspects that may be required. Please consult your local regulations to comply with all requirements.

1. Collect your sample in the appropriate size container and preserve with the appropriate volume of sulfuric acid.
2. Properly label enough prepared COD vials (without mercury for non-regulatory samples) for all samples and standards to be digested.
3. Turn on your COD reactor and ensure it is set to 150°C.
4. Homogenize your sample by mixing or shaking. Aliquot 2 mL of sample or standard into each vial and replace the cap.
   Caution – the tubes and solutions inside will become very hot upon addition of samples/standards, handle them carefully.
5. Once the reactor is at the proper temperature, place the vials containing samples/standards in the reactor and set the timer for two hours.
6. After two hours remove the vials from the reactor and allow them to cool to room temperature. **Caution – do not accelerate the cooling of the vials via any means. Rapid thermal changes can cause the vials to crack and hazardous spills to occur. Once digested, do not open the vials without proper ventilation and protection. High pressure buildup of potentially toxic gases may be present.** If participating in the COD disposal program, do not open the vials after digestion for any reason.
7. Set your spectrophotometer to the appropriate wavelength and read the absorbance.

We all like things that make life easier. Was this document helpful? Or do you…disagree with something?

Have something to add? Contact me at DavidS@envexp.com to let me know what you think.