A Safe, No-Hassle Way To Measure Chemical Oxygen Demand

Many treatment facilities test for chemical oxygen demand on a regular basis. Some laboratory test methods can be time consuming and expose technicians to toxic chemicals. In addition, interference from components in the samples may affect the test results.

MilliporeSigma is a global leader in the life science industry and has produced test kits to measure numerous analytes. Water Online spoke with MilliporeSigma about advances in measuring chemical oxygen demand.

Why is the measurement of chemical oxygen demand (COD) important?

For most users, COD is important as an indicator of how much oxygen will be required to treat the incoming waste streams, which in turn drives the use of aeration equipment and ultimately electricity. Knowing what the COD levels are allows users to fine-tune their power usage and avoid excess energy bills. At a higher level, COD is also an essential measurement used to help determine how much impact discharged water will have on the receiving body. COD is commonly used as an estimator of biological oxygen demand (BOD) because the test is much simpler and more robust. In well-understood applications, the ratio of BOD to COD is established, and it's relatively simple to extrapolate a BOD concentration from a COD test.

What test methods are typically used to determine COD at water and wastewater laboratories?

The most common test method is the colorimetric analysis after oxidizing the COD with acid and using indicator compounds, such as hexavalent dichromate. In some instances, however, there are compounds that will interfere with the colorimetric analysis, and titration is required to determine COD levels.

Which components interfere with test results?

Depending on the composition of the water stream, there are a number of compounds that can interfere with COD testing when found in extremely high concentrations. Chromium, nitrite, sulfite, sodium nitrate, sodium sulfate, sodium phosphate, and chloride can all potentially impact accuracy when found in high enough concentrations. The most common interference, however, comes from chloride, as it can contribute to false high results when testing COD levels.

Are any test methods available for desalination plants or other laboratories needing to test seawater, brackish, or polluted waters with high chloride levels?

Historically, chloride levels in excess of 2,000 mg/L caused a great deal of trouble

for COD analysis. Seawater and brackish waters can exceed this limit by an order of magnitude, and some industrial processes can result in samples with chloride levels above 100,000 mg/L. Recognizing this problem in the industry, MilliporeSigma has developed a series of COD test kits that incorporate a chloride extraction step that ensures the interferences from high chloride content are eliminated and produce accurate test results.

Why does the chloride need to be removed/extracted from the samples to test for COD?

Chloride in any concentration interferes with the spectrophotometric analysis of COD. To compensate for this, most test kits require a pretreatment step of adding mercury sulfate to precipitate out the chloride. However, this only works up to 2,000 mg/L of chloride before the addition of more mercury sulfate compromises the accuracy of the test, as the final test requires a fairly precise ratio of water and sulfuric acid.

How is the chloride removed from the sample?

MilliporeSigma's patent pending chloride extraction process involves the use of sulfuric acid to create gaseous HCl (Hydrogen chloride), which is then captured by an HCl absorption tube and soda lime indicator. The process does require more time than conventional

photometric analysis of COD, but it is still less time consuming than a conventional titration test.

What items are needed for measuring COD in high chloride samples when using a COD cell test?

In addition to the COD test kit for high salinity applications, labs will need sulfuric acid with a certified low COD content, HCl absorption tubes, soda lime, flasks, and a magnetic stirrer with speed control. With the exception of the flasks and stirring apparatus, MilliporeSigma can provide labs with the remaining components necessary for the test.

Why is soda lime a better choice for absorption material than calcium hydroxide?

The use of soda lime instead of calcium hydroxide is recommended because soda lime offers better absorption capacity in this application and also prevents condensing water vapors from dripping back into the solution. This seemingly minor feature was observed to improve measurement accuracy.

What are the advantages of using a COD cell test vs. the open reflux and titration method?

Aside from the immediate benefit of requiring less time and less manual input from a technician, utilizing cell test kits reduces the amount of toxic chemicals used by a factor of 10 and the total waste volume by close to a factor of 20. Additionally, the cell test kits reduce the amount of exposure the lab technicians have to the toxic chemicals.

What are the benefits of using mercury-free COD cell tests?

In addition to the high salinity COD test kits discussed above, MilliporeSigma has developed a mercury-free COD test kit. In many parts of the world, mercury contamination is becoming a greater concern for lab technicians as well as regulatory agencies. By developing a mercury-free test kit, MilliporeSigma has created a colorimetric test method that can be used for rapid analysis of COD levels without worrying about mercury contamination or running afoul of regulatory requirements. ■