



Reducing COD Testing Costs

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Oxygen demand testing is a staple of wastewater analysis. The oxygen demand of a wastewater indicates its potential impact on the stream or body of water receiving the wastewater. The higher the demand, the greater the potential impact. Two wet chemistry oxygen demand tests are basic to any wastewater testing laboratory operation: BOD, or biochemical oxygen demand, and COD, or chemical oxygen demand. BOD measures the oxygen demanded by microbes as they metabolize the contaminants in a wastewater under a standard set of conditions. The test measures the biologically degradable fraction of the contaminants in the wastewater. A more inclusive measure of oxygen demand is COD, which measures the oxygen equivalents required to chemically oxidize the wastewater contaminants under a different set of standard conditions. Generally, the COD of a wastewater is considered to measure all of the organics present (not just the biodegradable fraction); thus, it is broadly useful for wastewater treatment plant design and operations monitoring and where obtaining a carbon mass balance is important. COD is faster, more inclusive, and a more reproducible test than BOD. At the same time, COD bears a relatively constant relationship to BOD. These traits make COD quite useful for operational control of biological wastewater treatment plants.

The Open Reflux COD Test

The traditional open reflux (or macro) method of COD testing is based on

Method 5220, as specified in "Standard Methods for the Examination of Water and Wastewater (17th Edition)," EPA Method 410.1, or ASTM Method D1252. Each of these methods (and their variants) calls for the refluxing of a 50-milliliter (ml) sample of wastewater in 1 gram of mercuric sulfate, 75 ml of sulfuric acid reagent solution, and 25 ml of potassium dichromate reagent solution for two hours. This solution is then diluted to about twice its original volume and titrated to determine the excess potassium dichromate not consumed in the reaction. The used up (reduced) dichromate is determined, converted into oxygen equivalents, and expressed as a concentration of COD.

This method, while quite precise and reproducible, has several drawbacks:

1. Reagent use - it consumes large quantities of expensive reagents.
2. Labor use - it is labor-intensive and

requires a great deal of hands-on technician time.

3. Space and equipment use - the reflux glassware setup and hot plates are expensive and require a large amount of space.
4. Volatiles loss - because the apparatus is open to the atmosphere, volatiles are readily lost and acid fumes can be released.
5. Waste production - a significant quantity of hazardous and toxic waste chemicals is produced; mercury contamination is of particular concern.

The Micro-COD Method

The micro-COD method is based on Standard Methods 5220, EPA 410.4, and ASTM D125. While yielding precision and reproducibility similar to the macro method, the micro-COD method reduces the cost of the COD test significantly compared to the open reflux method. In the micro system, a much smaller sample of wastewater, typically 0.5 ml to 2.5 ml, is added to 7.5 ml of prepared standard reagent solution in a resealable vial. Volatile components are retained in the completely sealed vial, which is heated for two hours at 150°C in a simple, low-cost heater block. The disposable vial is of optical quality glass so that the sample can either be titrated or read directly in a calibrated spectrophotometer.

This method saves time and money, as shown in Figure 1. In fact, in side-by-side comparisons, the micro method saves in excess of 75 percent when compared to the open reflux approach. □

Figure 1.
Chemical Oxygen Demand Cost Comparison
Micro-COD Procedure vs. Open Reflux Procedure

Reagent Costs	Cost per COD Test	
	Open (Reflux)	Micro-COD Method
Sulfuric Acid	\$1.28	
Silver Sulfate	\$1.80	
Mercuric Sulfate	\$0.60	
Potassium Dichromate 0.25N	\$0.33	
Total Reagent Costs	\$4.01	\$1.08
Labor	\$3.20	\$0.60
Equipment (25 tests per week)	\$.23	\$0.12
Waste Disposal	\$0.90	\$0.06
Total Cost Per Sample Analyzed	\$8.33	\$1.86

NOTES:
(1) Open reflux procedure refers to Standard Methods of the Examination of Water and Wastewater Method 5220 (17th Ed.), EPA Method 410.1, or ASTM D1252
(2) accu-Test products are EPA-accepted as equivalent to approved procedures
(3) All costs calculated in U.S. dollars.