



accu-Test™ Micro Chemical Oxygen Demand System Titration Method

Scope and Application

1.1 The Chemical Oxygen Demand (COD) test determines the quantity of oxygen required for oxidation of reduced species including organic matter in a water sample using a specific oxidizing agent, temperature and time of reaction.

1.2 Bioscience, Inc. offers prepackaged reagents for use in determining COD in the following ranges:

Low Range Twist-Cap COD Vials 5-150 mg/L COD *
Standard Range Twist-Cap COD Vials 20-900 mg/L COD *
High Range Twist-Cap COD Vials 100-4500 mg/L COD

These products are for use with the COD method described here. Samples with higher COD can be analyzed after dilution. When the chloride concentration of a sample exceeds 2000 mg/L, the sample may be analyzed after pretreatment with mercuric sulfate or after dilution. These same COD vials may be used with an appropriate spectrophotometer for colorimetric determination of COD⁹.

1.3 This COD method is designated as an approved alternate procedure for nationwide use. As an approved alternate procedure, this COD method is acceptable for use by any person required to use approved procedures under Section 304(g) of the Federal Water Pollution Control Act Amendments of 1972. Use Low Range or Standard Range reagents for NPDES reporting purposes. It is consistent with methods^{2,3,4} recognized by the vast majority of environmental analysts.

1.4 The titration method is used as an alternative to, or for comparison with, the spectrophotometric method. It can be used to avoid spectrophotometric interference problems (e.g. turbidity).

Summary of Method

2.1 Organic and inorganic compounds are oxidized in a sealed 10 ml borosilicate glass vessel (expendable vial) which contains premixed COD reagents. The titration method is theoretically capable of complexing up to 2000 mg/L of chloride.

- Available in mercury-containing form and in mercury-free form (for non-reporting test purposes of samples with low chloride and ammonia content).

Chlorides (<2000 mg/L) are complexed by pretreatment with mercuric sulfate. The reagents and catalysts used are in the same proportions as those used in the Standard Titrimetric Methods (3,4,5) with the exception of the normality of the dichromate oxidizing agent. For all samples the COD can be calculated by titrating the excess dichromate with ferrous ammonium sulfate (FAS), using a ferroin

indicator. The titration procedure is similar to the standard spectrophotometric method with respect to sample treatment and digestion.

Sampling and Preservation

- 3.1 Care must be taken to store COD vials in light-proof containers until use. The guaranteed shelf life of these products is twelve (12) months if stored in the dark and at room temperature.
- 3.2 Samples should be collected in glass bottles. Plastic containers may be used if the containers are known to contain no contaminants which would interfere with the test.
- 3.3 Samples containing active microorganisms should be analyzed as soon after collection as possible. Bottles containing materials which have settled to the bottom should be well-mixed (preferably homogenized) to permit samples of representative aliquots.
- 3.4 Samples which cannot be run immediately (within 5 hours) after collection should be preserved with a sufficient concentration of H₂SO₄ to lower the pH to below 2 and be refrigerated at 4 degrees Celsius until analysis can be performed.

Interferences

- 4.1 Any contamination of the sample with foreign organic matter will cause an error in the analysis.
 - 4.1.1 Water used for dilution and blanks should be as low in organic material as possible. Type II reagent grade water is recommended. All water used in any set of analyses should preferably be from the same batch or container.
 - 4.1.2 Any glassware used in sample preparation should be proven to be as free of organics as possible.
- 4.2 Volatile materials may be lost if the sample is mixed with reagents before sealing the vessel. To avoid this possibility, samples should be carefully added down the side of the vessel to effect the layering of samples over the denser reagents until after the vessel is sealed.

Chlorides are among the reduced species oxidized by dichromate and will cause erroneously high COD values if over 2000 mg/L Cl⁻ and not complexed. Therefore, sufficient mercuric sulfate is added to the reagents to complex chloride before the chloride reacts with the dichromate (for low chloride and ammonia samples mercury-free reagents are available).

Apparatus

- 5.1 Pre-mixed COD reagents in glass screw-capped vials.
 - Standard Range (20-900 mg/L COD) Vials, Part #174-318
 - Standard Range Mercury-free (20-900 mg/L COD) Vials, Part #185-252
 - Low Range (5-150 mg/L COD) Vials, Part #174-334
 - Low Range Mercury-free (5-150 mg/L COD) Vials, Part #185-240
 - High Range (100-4500 mg/L COD) Vials, Part #174-326
- 5.2 COD Reactor (heater block) capable of maintaining 150 ±2 degrees Celsius.

COD Reactor (15 Vials) ... Part #163-495 (110V) or 163-497 (220V)
COD Reactor (30 Vials) ... Part #163-496 (110V) or 163-498 (220V)

- 5.3 Class A 10 ml micro buret (scaled to 0.05 milliliters).
- 5.4 Magnetic stir bars and a magnetic stirrer.
- 5.5 125 ml Erlenmeyer flasks.

Reagents

- 6.1 Premixed reagents in twist-cap vials are specified in Section 5. These vessels contain all reagents and catalyst needed for the COD test except those required for chloride pretreatment when chloride exceeds 2000 mg/l.
- 6.2 Sulfuric Acid (95% H₂SO₄), for chloride pretreatment.
- 6.3 Mercuric Sulfate (HgSO₄), for chloride pretreatment.
- 6.4 Deionized or distilled water. Precautions should be taken to insure that water used in the test be low in organic matter, preferably containing less than 0.3 ppm organic carbon. Type II reagent water is recommended.
- 6.5 Deionized water should be used in the preparation of all standard solutions. Distilled water can be used if deionized water is not available.
- 6.6 Potassium Acid Phthalate (KHP): KOCOC₆H₄COOH, ACS primary standard grade.
 - 6.6.1 KHP Stock Solution: To obtain a 10 g/L COD stock solution, add 8.5034 g of potassium acid phthalate (KHP pre-dried to a constant weigh at 110 degrees Celsius) to a 1000 ml volumetric flask and dilute to 1000 ml using deionized water.
 - 6.6.2 COD Working Standards: Standard solutions from the above KHP can be run at several dilutions to establish sample concentration ranges. A procedural blank of the distilled water is required to be analyzed with other standards and samples for final calculation of COD.
- 6.7 Ferrous ammonium sulfate (FAS): FeSO₄(NH₄)₂SO₄ 6H₂O reagent grade. To prepare a stock concentrate solution with normality of about 0.10, weigh 39.0 g FAS and dissolve in deionized water, filling a 1000 ml volumetric flask 3/4 full. Then add 20 ml concentrated H₂SO₄ and fill to mark with water. Addition of H₂SO₄ causes the iron to remain in the ferrous state.

NOTE: If H₂SO₄ is not added, the solution will turn light brown indicating the presence of the ferric ion. In this case the solution will need to be prepared again.

 - 6.7.1 Dilute (as needed) this solution 1:1 with deionized water to obtain a 0.05 N titrant solution. This FAS solution is not stable and should be prepared weekly if usage rate is low.
 - 6.7.2 If Low Range vials are being analyzed or if greater precision is desired

for Standard Range vials, a 0.025 N FAS titrant can be prepared by one of the following methods: (1) dilute the resulting solution in Section 6.7.1 (0.05 N FAS) with deionized water 1:1 or (2) dissolve 7.5 g FAS to 1000 ml with 20 ml H₂SO₄ and deionized water to the mark.

6.8 Potassium Dichromate (K₂Cr₂O₇) Standard Solution (0.208 N).

The potassium dichromate should be placed in an aluminum weighing dish, then placed in an oven to drive off any moisture. The oven should be set at 110 degrees Celsius. Heating time should be two (2) hours. After heating, remove and place in a desiccator until it is at room temperature. Carefully and exactly, weigh 10.216 g of potassium dichromate into a suitable weighing dish which has been tared before adding the dichromate. Dissolve the dichromate with deionized water in approximately 400 ml, then quantitatively transfer to a 1000 ml volumetric flask and dilute to the mark. This solution is stable provided the solution is never left in an uncapped container.

6.9 Ferriin Indicator Solution.

This solution can be obtained already prepared as "Ferriin Indicator Solution." It can also be prepared by dissolving 1.485 g 1, 10-phenanthroline monohydrate and 0.695 g ferrous sulfate heptahydrate (FeSO₄·7H₂O) in a 100 ml volumetric flask with 40 ml deionized water. Dilute to the mark. This solution is stable and can be stored.

Procedure

7.1 Preheat COD reactor to 150 degrees Celsius.

7.2 This section describes procedures for pretreatment of high chlorides (>2000 mg/L). If pretreatment is not necessary, skip to Section 7.3.

NOTE: Samples should be diluted when possible to minimize chloride concentration. This procedure is preferred over the pretreatment method.

7.2.1 Place 30 ml of the sample into an Erlenmeyer flask.

7.2.2 Add 10 mg HgSO₄ for every milligram of chlorides present in the sample.

7.2.3 Carefully add 5 ml of 95% H₂SO₄ with stirring to the contents of the flask and mix thoroughly.

7.3 Remove screw cap from vial.

NOTE: Use of safety glasses is required.

7.4 For Standard Range and Low Range tests, carefully add 2.5 ml of sample (or standard solution) down the side of the vessel such that it forms a layer on top of the reagents. For High Range tests, add 0.5 ml of sample.

NOTE: Samples should be thoroughly homogenized and milled in a blender or similar device before adding the sample to the vessel.

7.5 Carefully reseal the screw cap.

- 7.6 Thoroughly mix the contents of the sealed vial by shaking.
- CAUTION:** The vessel will get very hot during mixing. Samples should be mixed either in racks or with use of insulated gloves. Appropriate clothing and eye protection should be worn.
- 7.7 Process standards and blanks exactly as the samples.
- 7.8 Place the vessel in a COD heater block capable of maintaining 150 +2 degrees Celsius for 2 hours. The 2-hour oxidation period is standard practice and is sufficient for complete oxidation of most compounds.
- 7.9 Mix vessel contents by shaking and allow to cool. If rapid cooling is desired, the vessels may be placed in a water bath. If crystals form during rapid cooling, discontinue and allow vessels to cool slowly in the room air.

Standardization of FAS Titrant

- 7.10.1 Pipet 1.00 ml of potassium dichromate standard solution into a 125 ml Erlenmeyer flask, containing a magnetic stir bar.
- 7.10.2 Add 20-50 ml distilled water and 2-3 drops of ferroin indicator.
- 7.10.3 Add 5 ml of concentrated H₂SO₄ down the side of the flask.
- 7.10.4 Place flask on magnetic stirrer directly under the buret valve.
- NOTE:** Make sure the buret is clean, free of crystal formation inside the barrel, stopcock area, and the tip of the buret. If crystal formation is noticed, rinse with distilled water to dissolve the crystals. All contact surfaces of the buret should be rinsed with each new FAS solution.
- 7.10.5 Start stirrer and rapidly titrate with FAS titrant to the end point (dark orange). (Color changes are typically yellow to green to blue to clear/gray to dark orange.)
- 7.10.6 Record the amount of titrant used.
- 7.10.7 Repeat steps 7.10.1 - 7.10.6 two (2) more times for a total of three (3) repetitions.

Analyzing Twist-Cap Vials

CAUTION: The use of protective eye wear, gloves and clothing is required.

- 7.11.1 Remove the screw cap.
- 7.11.2 Add stir bar and contents of the vial into a clean 125 ml Erlenmeyer flask. Rinse vial once or twice with distilled water into the flask.
- 7.11.3 Add approximately 40-50 ml distilled water and 2-3 drops of ferroin indicator.

7.11.4 Place flask on stirrer directly under buret valve. Start stirrer and quickly titrate to the end point (dark orange). Color changes are the same as before. (See Section 7.10.5.)

7.11.5 Record titrant amounts for each vial.

Calculation

8.1 Calculate the mean and standard deviation of the normality of the FAS using the values obtained from the titration of 1.00 ml of $K_2Cr_2O_7$ standard.

$$N(\text{FAS}) = \frac{N(K_2Cr_2O_7)}{\text{FAS volume (ml)}}$$

8.2 The measured COD must be multiplied by a dilution factor to correct for the dilution of the 30 ml sample if 5 ml of H_2SO_4 was added for complexing chlorides (per Section 7.2).

8.3 If a mathematical solution for the COD of samples is required, perform the following calculation:

$$\text{COD (mg/L)} = D \frac{(a-b)N \times 8,000}{S} \text{ where,}$$

D	=	Dilution factor
	=	1 if H_2SO_4 is not added for pretreatment
	=	$35/30 = 1.1667$ if 5 ml H_2SO_4 was added to a 30 ml sample
a	=	Milliliters of FAS required for titration of the blank
b	=	Milliliters of FAS required for titration of the sample
N	=	Normality of FAS
S	=	Milliliters of sample used

8.4 As an alternative, a linear regression may be applied to standard data sets and sample COD values derived accordingly.

Precision and Accuracy

9.1 After a thorough review and evaluation by the Environmental Protection Agency of the results of a comparability testing and other information submitted in accordance with Section 136.5, 40 CFR Part 136⁸, the EPA determined the Standard Range method to be a suitable alternate procedure to EPA Method 410.1¹. Precision of four replicates of each of 30 samples averaged $\pm 2.7\%$. The data submitted for this evaluation have been published by Messenger⁷. Reprints of this article are available from Bioscience, Inc. upon request.

9.2 A study of 60 synthetic samples containing KHP and sodium chloride analyzed by six laboratories produced a standard deviation of 11 mg/l at an average COD of 195 mg/l in the absence of chloride, and a standard deviation of 10 mg/l at an average COD of 208 mg/l when 100 mg/l chloride was present.

Bibliography

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