Method 410.3: Chemical Oxygen Demand (Titrimetric, High Level for Saline Waters) by Titration

METHOD #: 410.3   (Editorial Revision 1978)

TITLE: Chemical Oxygen Demand (Titrimetric, High
                             Level For Saline Waters)

ANALYTE: COD Chemical Oxygen Demand

INSTRUMENTATION: Titration

STORET No.   00340

1.0   Scope and Application

       1.1   When the chloride level exceeds 1000 mg/L the minimum accepted value for the
              COD will be 250 mg/L. COD levels which fall below this value are highly
              questionable because of the high chloride correction which must be made.

2.0   Summary of Method

       2.1   Organic and oxidizable inorganic substances in an aqueous sample are oxidized
              by potassium dichromate solution in 50 percent (by volume) sulfuric acid
              solution. The excess dichromate is titrated with standard ferrous ammonium
              sulfate using orthophenanthroline ferrous complex (ferroin) as an indicator.

3.0   Sample Handling and Preservation

       3.1   Collect the samples in glass bottles, if possible. Use of plastic containers is
              permissible if it is known that no organic contaminants are present in the
              containers.
       3.2   Biologically active samples should be tested as soon as possible. Samples
              containing settleable material should be well mixed, preferably homogenized, to
              permit removal of representative aliquots.
       3.3   Samples should be preserved with sulfuric acid to a pH < 2 and maintained at
              4°C until analysis.

4.0   Interferences

       4.1   Traces of organic material either from the glassware or atmosphere may cause a
              gross, positive error.
              4.1.1   Extreme care should be exercised to avoid inclusion of organic materials
                       in the distilled water used for reagent preparation or sample dilution.
              4.1.2   Glassware used in the test should be conditioned by running blank
                       procedures to eliminate traces of organic material.
       4.2   Volatile materials may be lost when the sample temperature rises during the
              sulfuric acid addition step.
       4.3   Chlorides are quantitatively oxidized by dichromate and represent a positive
              interference. A chloride correction is made using theprocedure outlined in 7.7 of
              this method.

5.0   Apparatus

    5.1   Reflux apparatus: Glassware should consist of a 500 mL Erlenmeyer flask or a 300 mL round bottom flask made of heat-resistant glass connected to a 12 inch Allihn condenser by means of a ground glass joint. Any equivalent reflux apparatus may be substituted provided that a ground-glass connection is used between the flask and the condenser.

6.0   Reagents

    6.1   Standard potassium dichromate solution, (0.25 N): Dissolve 12.2588 g of $K_2Cr_2O_7$, primary standard grade, previously dried for 2 hours at 103°C in water and dilute to 1000 mL.
    6.2   Sulfuric acid reagent: Conc. H_2SO_4 containing 23.5 g silver sulfate, Ag_2SO_4, per 4.09 kg. bottle. (With continuous stirring, the silver sulfate may be dissolved in about 30 minutes.)
    6.3   Standard ferrous ammonium sulfate, 0.250 N: Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water. Add 20 mL of conc. H_2SO_4, (6.7), cool and dilute to 1 liter. This solution must be standardized against the standard potassium dichromate solution (6.1) daily.
        6.3.1   Standardization: Dilute 25.0 mL of standard dichromate solution (6.1) to about 250 mL with distilled water. Add 20 mL conc. sulfuric acid (6.7). Cool, then titrate with ferrous ammonium sulfate titrant (6.3), using 10 drops of ferroin indicator (6.5).
                Normality = [(mL $K_2Cr_2O_7$)(0.25)] / [mL $Fe(NH_4)_2(SO_4)_2$]
    6.4   Mercuric sulfate: Powdered $HgSO_4$.
    6.5   Phenanthroline ferrous sulfate (ferroin) indicator solution: Dissolve 1.48 g of 1-10-(ortho) phenanthroline monohydrate, together with 0.70 g of $FeSO_4 \cdot 7H_2O$ in 100 mL of water. This indicator may be purchased already prepared.
    6.6   Silver sulfate: Powdered Ag_2SO_4.
    6.7   Sulfuric acid (sp. gr. 1.84): Concentrated H_2SO_4.

7.0   Procedure

    7.1   Pipet a 50.0 mL aliquot of sample not to exceed 800 mg/L of COD into a 500 ml, flat bottom, Erlenmeyer flask. Add $HgSO_4$ (6.4) in the ratio of 10 mg to 1 mg chloride, based upon the mg of chloride in the sample aliquot and 5 mL of sulfuric acid (6.7). Swirl until all the mercuric sulfate has dissolved. Add 25.0 mL of 0.25N $K_2Cr_2O_7$ (6.1). Carefully add 70 mL of sulfuric acid-silver sulfate solution (6.2) and gently swirl until the solution is thoroughly mixed. Glass beads should be added to the reflux mixture to prevent bumping, which can be severe and dangerous.
            Caution: The reflux mixture must be thoroughly mixed before heat is applied. If this is not done, local heating occurs in the bottom of the flask, and the mixture may be blown out of the condenser.
        7.1.1   If volatile organics are present in the sample, use an Allihn condenser and add the sulfuric acid-silver sulfate solution through the condenser, while cooling the flask, to reduce loss by volatilization.

    7.2   Attach the flask to the condenser and reflux the mixture for two hours.

7.3   Cool, and wash down the interior of the condenser with 25 mL of distilled water. Disconnect the condenser and wash the flask and condenser joint with 25 mL of distilled water so that the total volume is 350 mL. Cool to room temperature.

7.4   Titrate with standard ferrous ammonium sulfate (6.3) using 10 drops of ferroin (6.5) indicator. (This amount must not vary from blank, sample and standardization.) The color change is sharp, going from blue-green to reddish-brown and should be taken as the end point although the blue-green color may reappear within minutes.

7.5   Run a blank, using 50 mL of distilled water in place of the sample together with all reagents and subsequent treatment.

7.6   For COD values greater than 800 mg/L, a smaller aliquot of sample should be taken; however, the volume should be readjusted to 50 mL with distilled water having a chloride concentration equal to the sample.

7.7   Chloride correction(1): Prepare a standard curve of COD versus mg/L of chloride, using sodium chloride solutions of varying concentrations following exactly the procedure outlined. The chloride interval, as a minimum should be 4000 mg/L up to 20,000 mg/L chloride. Lesser intervals of greater concentrations must be run as per the requirements of the data, but in no case must extrapolation be used.

8.0   Calculation

$$\text{mg/L COD} = \frac{[(A - B)C \times 8{,}000] - 50D}{\text{mL of sample}} \times 1.2$$

where:
A =   mL $Fe(NH_4)_2(SO_4)_2$ for blank;
B =   mL $Fe(NH_4)_2(SO_4)_2$ for sample;
C =   normality of $Fe(NH_4)_2(SO_4)_2$;
D =   chloride correction from curve (step 7.7)
1.2 =   compensation factor to account for the extent of chloride oxidation which is dissimilar in systems containing organic and non-organic material.

9.0   Precision and Accuracy

9.1   Precision and accuracy data are not available at this time.

Bibliography

1.   Burns, E. R., Marshall, C., Journal WPCF, Vol. 37, p 1716-1721(1965).