Environmental Pollution Analysis

THE DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD) IN WATERS AND EFFLUENTS

The industrial and municipal waste water effluents may contain very high amounts of organic matter and if discharged into natural water bodies, it can cause complete depletion of dissolved oxygen leading to the mortality of aquatic organisms.

Chemical Oxygen Demand (COD) is the amount of oxygen required for the chemical oxidation of the sum of organic compounds that are contained in waters and effluents. It is of great importance in environmental analysis, since it is comprised by all the organic chemical compounds, both those that can be biologically decomposed and those that are toxic and can only be chemically broken down.

Method of determination

The total concentration of organic compounds in water and wastewater can be determined by their oxidation using $K_2Cr_2O_7$ in an acidic environment. The sample is heated using a mixture of $K_2Cr_2O_7$ and sulfuric acid. The excessive amount of $K_2Cr_2O_7$ is back-titrated using a standard Fe^{2+} solution.

The oxidation of organic compounds in general could be described as follows:

$$C_xH_{2y}O_z + [x + (y-z) / 2] O_2 \rightarrow xCO_2 + yH_2O$$

Potassium dichromate is a strong oxidizing agent for organic and inorganic matter in water and wastewater. The reaction can be expressed as follows:

$$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- = 2\ Cr^{3+} + 7\ H_2O$$

Main interferences include the presence of chloride ions, which can be oxidized to chlorine gas. By adding mercuric sulfate $HgSO_4$, a complex of mercuric chloride will be formed and remove the chloride interference. An amount of 1g of Mercury Sulfate is required for 100mg of chlorides to form complex.

Sulfuric acid is added to the mixture so that the mercury is completely dissolved. Besides, it assists in oxidizing the nitrogen compounds in the sample and the increased heat will accelerate the reaction rate.

On the other hand not all the aliphatic chain hydrocarbons can be determined by the method, which could be enhance by adding Silver Sulfate which acts as a catalyst for the oxidation.

Nitrite ions can interfere with the oxidation, since they form nitrates and produce values of 1.4 COD per mg N of nitrite ions. To remove this interference NH_2SO_3H is added (10mg per mg of N-nitrite.

This project has been funded with support from the European Commission. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

Reagents used:

1. Potassium dichromate (Standard solution): $K_2Cr_2O_7$ – 0.25 N
2. Mohr' s Salt: Ferrous ammonium sulfate (Standard solution): $FeSO_4.(NH_4)_2SO_4$ (0.1 N)
3. Mercuric Sulfate: Powdered $HgSO_4$
4. Silver Sulfate: Powdered Ag_2SO_4
5. ferroine (1,10-phenanthroline or $[Fe(o\text{-phen})_3]SO_4$ indicator solution
6. Sulfuric acid: H_2SO_4 1 M

Procedure:

20 mL of sample are added into a refluxing flask along with several boiling stones. Also 0.1 g $HgSO_4$ was added to the solution. 5 mL of concentrated H_2SO_4 were also added to the solution.

To ensure that $HgSO_4$ dissolved completely, the solution is swirled slowly while adding sulfuric acid. 0.1 g of Ag_2SO_4 are also added to this solution. Finally 10 mL of potassium dichromate (0.25N) is added. The flask is then attached to the condenser and further cooling was done. 30 mL of 1M sulfuric acid is finally added to the solution in the flask and the solution is stirred using a magnetic stirrer and refluxed for 1 hour. At the same time a second solution (blank run using 20 mL distilled water instead of sample) is simultaneously conducted.

After cooling, the solution is transferred to an Erlenmeyer flask ensuring that the reflux flask was rinsed thoroughly 3 times, pouring the rinsing water to the Erlenmeyer flask. The solution was diluted to about 150 mL and about 8 drops of indicator is added to the solution, which is titrated against the Mohr's salt until the color of the solution changes from red-green to dark red. The procedure was repeated for the blank run.

The titer volume for the sample titration, is equal to the volume of Ferrous Ammonium Sulfate required to react with the excess potassium dichromate in the solution. Similarly, the titer volume for the blank (distilled water) gives the volume of Ferrous Ammonium Sulfate required to react with the excess potassium dichromate in the blank. The equation for the titration can be expressed as:

$$\mathbf{K_2Cr_2O_7 + 6.FeSO_4.(NH_4)_2SO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + (NH_4)_2SO_4 + 3Fe_2(SO_4)_3 + K_2SO_4 + H_2O}$$

$$\text{COD (mg/L)} = \frac{(V_1 - V_2).N\ .8000}{V_3}$$

V_1 = Original volume of $K_2Cr_2O_7$ for blank (mL)

V_2 = Volume of $K_2Cr_2O_7$ used for oxidation for sample (mL)

V_3 = sample volume (mL)

8000 is the factor of normalization for the O_2 milliequivalents

This project has been funded with support from the European Commission. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.