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Chemistry

Determination of the Chemical Oxygen Demand in water

Titrimetric method

Introduction

The chemical oxygen demand (COD) is an analytical parameter that allows to indirectly measure the concentration of the polluting compounds present in surface water, both natural and industrial. This parameter is determined by a titration after having treated a water sample with a strong oxidizing agent in hot acid environment.

Principle of the method

This method is based on the complete oxidation of organic and inorganic compounds, present in a water sample, by using a potassium dichromate solution, concentrated sulfuric acid and silver sulfate as a catalyst. The amount of dichromate in excess is titred with a ammonium and iron (II) sulphate solution. The concentration of organic and inorganic compounds (pollutants), in these conditions, is directly proportional to the amount of consumed potassium dichromate.
Chloride ion is considered an interference because its oxidation can occur only in the conditions used in this method for COD determination and not in those present in natural water, then we use mercuric sulfate to avoid this problem.

Apparatus

Reflux flask
Heating plate
Bubble cooler
Boiling stones
Graduated cylinder
500 mL conical flask
50 mL burette with 0,1 mL divisions

Reagents

Deionized water
Standard potassium dichromate solution (0,25 N)
Diluted potassium dichromate solution (0,025 N)
Concetrated sulfuric acid, H_2SO_4 (d=1,84)
Mercuric sulfate, $HgSO_4$

Silver sulfate, Ag_2SO_4
Phenantroline ferrous sulfate (ferroin) indicator solution
Standard ferrous ammonium sulfate (0,125N)
Diluted ferrous ammonium sulfate (0,0125 N)

Procedure

For water with COD>50 mg/L

1. Chemical digestion with potassium dichromate

- Place 400 mL of sample and 8 g of $HgSO_4$ in the reflux flask, followed by several boiling stones.
- Add 5,0 mL of concentrated H_2SO_4 (stir until the mercuric sulfate has dissolved).
- Place reflux flask in an ice bath and slowly add, with stirring, 200 mL of 0.25 N $K_2Cr_2O_7$, followed by 0,4 g of silver sulfate.
- Insert a bobble cooler and start with water circulation. Now add 600 mL of concentrated sulfuric acid to the cooled reflux flask.
- Apply heat to the flask and reflux at the temperature of 150 °C for 2 hours.
- After this time, allow the flask to cool and wash down the bobble cooler with about 25 mL of distilled water.

2. Titration

- Take a part (100 mL) of the sample, previously treated with $K_2Cr_2O_7$, and dilute it to about 200 mL with distilled water inside a 500 mL conical flask and control that solution is to about room temperature.
- Add 2 to 3 drops of ferroin indicator and titrate the excess dichromate with 0.125 N ferrous ammonium sulfate solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.
- Repeat the titration to obtain two concordant volume values.

For water with COD between 20 and 50 mg/L

1. Chemical digestion with potassium dichromate

- Place 400 mL of sample and 8 g of $HgSO_4$ in the reflux flask, followed by several boiling stones.
- Add 5,0 mL of concentrated H_2SO_4 (stir until the mercuric sulfate has dissolved).
- Place reflux flask in an ice bath and slowly add, with stirring, 200 mL of 0.025 N $K_2Cr_2O_7$, followed by 0,4 g of silver sulfate.
- Insert a bobble cooler and start with water circulation. Now add 600 mL of concentrated sulfuric acid to the cooled reflux flask.
- Apply heat to the flask and reflux at the temperature of 150 °C for 2 hours.
- After this time, allow the flask to cool and wash down the bobble cooler with about 25 mL of distilled water.

2. Titration

- Take a part (100 mL) of the sample, previously treated with $K_2Cr_2O_7$, and dilute it to about 200 mL with distilled water inside a 500 mL conical flask and control that solution is to about room temperature.
- Add 2 to 3 drops of ferroin indicator and titrate the excess dichromate with 0.0125 N ferrous ammonium sulfate solution to the end point. The color change will be sharp, changing from a blue-green to a reddish hue.
- Repeat the titration to obtain two concordant volume values.

Calculation

The chemical oxygen demand (COD) is determined by using the following equation

$COD = [V_T \cdot N_T \cdot 8000]/V_A$

in which: COD = chemical oxygen demand (in mg/L); V_T = volume (in mL) of the ammonium and iron (II) solution consumed for sample; N_T = normality of the ammonium and iron (II) solution used; 8000 = equivalent weight of the oxygen multiplied by 1000, to refer the value to the volume of one liter; V = volume (in mL) of the sample used for analysis.