infoPoint

Reagents for COD analysis

The Chemical Oxygen Demand (COD) is a parameter that measures the amount of **substances** dissolved or suspended in a liquid sample **that can be oxidized** by a strong chemical oxidant.
It is used to **measure the degree of contamination** and it is expressed in milligrams per liter of oxygen (mg O_2 /L).
It is an applicable method in inland waters (rivers, lakes or aquifers), sewage, rainwater or water from any other source that may contain an appreciable amount of organic matter. This test is useful for **monitoring and control of wastewater treatment plants.** It does not apply, however, to drinking water, as there is a low content of oxidizable matter and the accuracy of the method would not be appropriate. In this case the method of oxidizability with potassium permanganate is used.

Method of analysis

The most general COD determination uses **potassium dichromate** ($K_2Cr_2O_7$) in excess in an acidic medium with the aid of silver sulfate (Ag_2SO_4) as a **catalyst**, and **mercuric sulfate** ($HgSO_4$) added to remove interference of chlorides. Dichromate oxidizes organic and inorganic matter in the sample, and it is reduced from Cr^{+6} to Cr^{+3}. The test is performed at 150°C under total reflux for 2 hours. After digestion, excess potassium dichromate is **titrated** with the Mohr salt using ferroin as indicator. The solution color changes from green to red.

Calculation

COD as mg O_2/L = (A-B) x M x 8000/mL sample
A: mL Mohr salt used for blank
B: mL Mohr salt used for sample
M: molarity of Mohr salt

- The main reaction involved in the determination of COD is:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{Ag_2SO_4} 2Cr^{3+} + 7H_2O$$

- Chlorides can interfere according to the following reaction:

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{+3} + 7H_2O$$

- To avoid the interference, $HgSO_4$ is added:

$$Hg^{2+} + 2Cl^- \longrightarrow HgCl_2$$

- With insufficient $HgSO_4$:

$$Ag^+ + Cl^- \longrightarrow AgCl$$

The dichromate in excess (not reduced by organic/inorganic matter) is titrated with Mohr salt, Ammonium Iron(II) Sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$:

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

PanReac AppliChem
ITW Reagents

IP-025EN;202101

Product code	Product name	CAS number	Pack size
Oxidizing Agent			
132166	Mercury(II) Sulfate for analysis, ACS	7783-35-9	100 g, 250 g
Catalyst			
282922	Silver Sulfate solution 6.6 g/L in sulfuric acid for volumetric analysis	10294-26-5	1 L
283098	Silver Sulfate solution 10 g/L in sulfuric acid for volumetric analysis	10294-26-5	1 L, 2.5 L
131801	Silver Sulfate for analysis, ACS	10294-26-5	25 g, 100 g, 250 g
Reducing Agent (Mohr's Salt)			
181369	Ammonium Iron(II) Sulfate 0.1 mol/L (0.1N) volumetric solution	7783-85-9	1 L
185227	Ammonium Iron(II) Sulfate 0.12 mol/L (0.12N) volumetric solution	7783-85-9	1 L
131368	Ammonium Iron(II) Sulfate 6-hydrate (Reag. Ph. Eur.) for analysis, ISO	7783-85-9	500 g, 1 kg
Indicator			
283462	Ferroin solution 0.025 mol/L (0.025M) for volumetric analysis	14634-91-4	100 mL
COD Standard			
394546	COD Standard (1000 ppm)		25 mL

References:
Standard Methods 5220, Chemical Oxygen Demand (COD). ASTM D1252, Chemical Oxygen Demand (Dichromate Oxygen Demand) of water. ISO 6060, Determination of the Chemical Oxygen Demand (COD). Dichromate method. DIN 38409, Determination of the Chemical Oxygen Demand (COD). NFT 90-101, Determination of the Chemical Oxygen Demand. UNE 77-004.

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