



## *Chemical Oxygen Demand of Water*

### **Introduction**

Chemical Oxygen Demand (COD) is an important parameter for wastewater or surface water testing and plants. This determination gives information about the degree of water pollution by organic material. This application note concerns COD determination by potassium dichromate. Another method using potassium permanganate is used for low COD determinations.

### **Principle**

Organic matter contained in a water sample is oxidised in 50% sulphuric acid, by a known excess of potassium dichromate. After digestion, remaining unreduced dichromate is determined by potentiometric titration using a Fe(II) solution according to the following reaction:



A blank titration with distilled water as sample is run for every cycle.

The result is expressed as oxygen equivalent.

### **Electrode and reagents**

For titration in a beaker

M231Pt Metal Electrode, platinum (part no. E31M002) with CL114 cable (part no. A94L114)

REF601 Reference Electrode, mercurous sulphate (part no. E21M012)

For titration directly in digestion flask

MC602Pt Metal Electrode, combined platinum/mercurous sulphate (part no. 945-360)

Titrant (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O (Mohr's salt) 0.15 eq/l (MW = 392.14 g/mol)

Weigh and dissolve 58.82 g of Mohr's salt in 500 ml of distilled water

Add 100 ml of sulphuric acid approximately 1N

Using a volumetric flask, dilute to 1000 ml with distilled water. Calibrate as indicated in separate application note

Potassium dichromate 0.25 eq/l solution or 0.0417M (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)

(A 0.1 eq/l K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution contains 1/60 mole of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> that has a molecular weight of 294.19 g/mol)

Dry the potassium dichromate (analytical grade) for 2 hours at 120°C and let it cool to room temperature

Weigh exactly 12.258 g and dissolve exactly with freshly distilled water to 1000 ml using a volumetric flask

Sulphuric acid reagent

Add 5.5 g of Ag<sub>2</sub>SO<sub>4</sub> to 1 kg of concentrated H<sub>2</sub>SO<sub>4</sub> and leave to stand for 2 days to dissolve the Ag<sub>2</sub>SO<sub>4</sub>

Solid mercuric sulphate HgSO<sub>4</sub>

### **End Point titration settings**

#### **Back titration with blank**

Burette volume:	25 ml
Stirring speed:	400 rpm
Working mode:	mV (with i=0)
Back titration:	Manual
Number of end points:	1
End point:	300 mV
Stirring delay:	30 seconds
Minimum speed:	0.1 ml/min
Maximum speed:	2.5 ml/min
Proportional band:	350 mV
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	20
Blank volume:	determined by blank titration
Excess:	0.0 ml
Titration:	Decreasing potential
Results	
Results number:	1
Result unit:	mg/l

### **Procedure**

#### **Blank preparation and titration**

Using distilled water as sample, prepare and titrate a blank with the same procedure and reagents (see below)

Accept the obtained titrant volume as blank volume

The theoretical blank volume can be calculated according to the following formula:

$$\text{Vol. of blank} = 10 * 0.25 / 0.15 = 16.67 \text{ ml}$$

10 = volume of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution in ml

0.25 = Concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in eq/l

0.15 = concentration of Mohr's salt solution in eq/l

### Sample preparation

Place 20 ml of water in a 250 ml refluxing flask or in a special COD tube. Add 0.4 g of  $\text{HgSO}_4$  and glass beads and very slowly 2 ml of sulphuric reagent while mixing. Then add 10.00 ml of dichromate solution and 28 ml of sulphuric acid reagent and connect to condenser. Mix thoroughly and boil under reflux during 2 hours.

After rinsing condenser with 5/10 ml of distilled water, transfer to titration beaker using 25/30 ml of distilled water to rinse. Total volume does not exceed 100 ml.

### Sample titration

Prepare the titration manager with 25 ml burette and 0.15 eq/l ferrous solution as titrant.

Connect M231Pt electrode via the CL114 cable and the REF601 reference electrode or, if necessary, the MC602Pt combined electrode.

Dip electrodes and delivery tip in the sample beaker.

Start method by pressing the RUN key.

### Results

#### Expressed as mg/l of oxygen equivalent according to

$$\text{COD (in mg/l of oxygen)} = (\text{Vbl} - \text{Vtit}) \cdot C \cdot 8 \cdot 1000 / \text{Vsample}$$

Vbl = titrant volume consumed during blank titration (close to 16.67 ml for application note conditions)

Vtit = titrant volume consumed during sample titration

(Vbl - Vtit) = directly calculated by TIM8xx

C = titrant concentration in mol/l or equivalent/l

8 = equivalent weight for oxygen (16/2)

Vsample = sample volume in ml

#### For a result in mg/l of oxygen

Enter

The sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen

1 Titrant and 1 Sample in the COEFFICIENTS display

8 as equivalent weight for oxygen

The Titration Manager gives a result according to the above formula, as (Vbl - Vtit) is directly calculated by the Titration Manager.

#### For 5 determinations

Mean: 450 mg/l oxygen

Standard deviation: 15 mg/l

Rel. standard deviation: 3%

### Working range

With application note conditions, titrant concentration of 0.15 eq/l and sample volume of 20 ml

(Vbl - Vtit) = 1 ml corresponds to a COD of 60 mg/l

(Vbl - Vtit) = 15 ml corresponds to a COD of 900 mg/l

### Notes

The Titration Manager uses the same electrodes for titration and reagent calibration. For titrant calibration with the electrodes in this note, you can use the application note TTEP01.03MIN with a change in the end point potential.

The latest standard NFT 90.101(2001) uses the same procedure but uses as reagents

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (Mohr's salt) 0.12 mol/l

Potassium dichromate solution or 0.040 mol/l ( $\text{K}_2\text{Cr}_2\text{O}_7$ )

Works with 10 ml of sample

### Bibliography

EPA method number 410.1

Standard methods for water and wastewater 18th edition (1992) 5-6 part 5220

ISO 6060 (1989)

NFT90-101 (2001)