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:

\[
\text{Cr}_2\text{O}_7^{2-} + 2\text{Fe}^{++} + 14\text{H}^+ \rightarrow 2\text{Cr}^{+++} + 6\text{Fe}^{+++} + 7\text{H}_2\text{O}
\]

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 (NH₄)₂Fe(SO₄)₂, 6H₂O (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 (K₂Cr₂O₇)

(A 0.1 eq/l K₂Cr₂O₇ solution contains 1/60 mole of K₂Cr₂O₇ 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 Ag₂SO₄ to 1 kg of concentrated H₂SO₄ and leave to stand for 2 days to dissolve the Ag₂SO₄

Solid mercuric sulphate HgSO₄

Electrode and reagents
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
Titrination: 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:

\[ \text{Vol. of blank} = \frac{10 \times 0.25}{0.15} = 16.67 \text{ ml} \]

10 = volume of K$_2$Cr$_2$O$_7$ solution in ml
0.25 = Concentration of K$_2$Cr$_2$O$_7$ 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 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

\[ \text{COD (in mg/l of oxygen)} = \frac{(\text{Vbl} - \text{Vtit}) \times C \times 8 \times 1000}{\text{Vsample}} \]

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 Titrator
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 Titrator gives a result according to the above formula, as (Vbl - Vtit) is directly calculated by the Titrator 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 Titrator 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 NF T 90.101(2001) uses the same procedure but uses as reagents
(NH$_4$)$_2$Fe(SO$_4$)$_2$, 6H$_2$O (Mohr’s salt) 0.12 mol/l
Potassium dichromate solution or 0.040 mol/l (K$_2$Cr$_2$O$_7$)
And works with 10 ml of sample

**Bibliography**
EPA method number 410.1
5-6 part 5220
ISO 6060 (1989)
NF T90-101 (2001)