

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956) Coimbatore – 641 021.

LECTURE PLAN DEPARTMENT OF CHEMISTRY B.Sc CHEMISTRY

Name of the Staff	:	Dr. M. Makeswari and Mrs.H.Revathi
Department	:	Chemistry
Title of the Paper	:	Industrial chemicals and Environment Practical
Paper Code	:	16CHU512A
Class	:	III-B.Sc-Chemistry A and B section
Year and Semester	:	III Year and VI-Semester
Total Hours	:	40 Hours

S. No.	Duration Hours	Name of the Experiment	Support Material
1.	4	Procedure Writing	
2.	4	Percentage of available chlorine in bleaching powder.	R1, R2
3.	4	Measurement of chloride	R1, R2
4.	4	Determination of dissolved oxygen in water.	R1, R2
5.	4	Estimation of total alkalinity of water	R1, R2
6.	4	Measurement of dissolved CO ₂ .	R1, R2
7.	4	Estimation of salinity of water	R1, R2
8.	4	Determination of Chemical Oxygen Demand (COD)	R1, R2
9.	4	Revision and Viva	
10.	4	Model practical examination	

SUGGESTED READINGS:

REFERENCE BOOKS

R1: A. K. De. *Environmental Chemistry*. New Delhi: New Age International Pvt. Ltd. **R2:** Venkateswaran.N., Veerasamy.R., and Kulandaivelu. A.R., (2004), Basic principles

of Physical Chemistry, III Edition, S.Chand publications. New Delhi.



KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956) Coimbatore – 641 021.

SYLLABUS DEPARTMENT OF CHEMISTRY B.Sc CHEMISTRY

Class	:	B.Sc Chemistry
Subject	:	Industrial Chemicals and Environment practical
Subject Code	:	16CHU612B
Semester / Year	:	VI / III

Semester-VI

16CHU612BCHEMISTRY-DSE LAB: INDUSTRIAL CHEMICALS AND
ENVIRONMENT PRACTICAL4H 2C

Instruction Hours/week: L:0 T:0 P:4 Marks: Internal: 40 External: 60 Total:100

Scope

The course deals with practical aspects of industrial chemicals and their impact on environment

Objectives

The course will enable the student to

- 1. Determine the dissolved oxygen, CO₂, COD and BOD in water
- 2. Determine the chloride, sulphate content and alkalinity of water

Methodology

Titrations

- 1. Determination of dissolved oxygen in water.
- 2. Determination of Chemical Oxygen Demand (COD)
- 3. Determination of Biological Oxygen Demand (BOD)
- 4. Percentage of available chlorine in bleaching powder.
- 5. Measurement of chloride, sulphate and salinity of water samples by simple titration method (AgNO3 and potassium chromate).
- 6. Estimation of total alkalinity of water samples (CO₃²⁻, HCO₃⁻) using double titration method.
- 7. Measurement of dissolved CO₂.
- 8. Study of some of the common bio-indicators of pollution.
- 9. Preparation of borax/ boric acid.

Suggested Readings

Text Books:

- 1. Stocchi, E. Industrial Chemistry, Vol-I. UK: Ellis Horwood Ltd.
- 2. Felder, R.M. & Rousseau, R.W. *Elementary Principles of Chemical Processes*. New Delhi: Wiley Publishers.
- 3. Kent, J. A. Riegel's *Handbook of Industrial Chemistry*. New Delhi: CBS Publishers.

Reference Books:

- 1. A. K. De. Environmental Chemistry. New Delhi: New Age International Pvt. Ltd.
- 2. Khopkar, S. M. Environmental Pollution Analysis. New Delhi: Wiley Eastern Ltd.
- 3. Venkateswaran.N., Veerasamy.R., and Kulandaivelu. A.R., (2004), Basic principles of Physical Chemistry, III Edition, S.Chand publications. New Delhi.

CIA Marks Allocation

Category	Marks
Attendance	5
Observation	5
Record	5
Model Exam	20
Viva-Voce	5
Total	40

ESE Marks Allocation

Category	Marks
Experiment	40
Viva-Voce	10
Record	10
Total	60

INDUSTRIAL CHEMICALS AND ENVIRONMENT PRACTICAL

LAB MANUAL

FOR

III B.Sc., CHEMISTRY STUDENTS



DEPARTMENT OF CHEMISTRY

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University established Under section 3 of UGC Act, 1956)

Eachanari Post, Pollachi main road,

Coimbatore-641021

Tamilnadu, India

EXPERIMENTS

- 1.Determination of percentage of available chlorine in bleaching powder
- 2. Measurement of chloride ion in water sample
- 3.Determination of dissolved oxygen in water
- 4.Estimation of alkalinity of water
- 5. Measurement of dissolved CO_2 in water
- 6.Estimation of salinity of water
- 7. Determination of COD in water

Experiment No 1

Determination of percentage of available chlorine in bleaching powder

CALCULATION:

Weight of the K₂Cr₂O₇ present in the whole of the given solution = W g Normality of standard K₂Cr₂O₇ = $\frac{W \times 4}{Equivalent \ mass \ of \ K_2Cr_2O_7}$ = $\frac{W \times 4}{49}$ N₁ = ------ N

TITRATION-I: Standardization of Sodium thiosulphate

(Standard K₂Cr₂O₇ solution Vs Sodium thio solution)

S.No.	Volume of	Burette Read	ling (ml)	Volume of	Concordant
	Pipette Solution	Initial	Final	Burette	Value (ml)
	(ml)			Solution (ml)	
1.					
2.					X
3.					

$$N_2 = \frac{V_1 N_1}{V_2}$$

Normality of Sodium this solution $N_2 = y N$

ESTIMATION OF AVAILABLE CHLORINE IN THE BLEACHING POWDER

AIM

To estimate the amount of available chlorine present in the given sample of bleaching powder being supplied with $K_2Cr_2O_7$ crystals of AR quantity and an approximately decinormal solution of sodium thiosulphate are provided.

PRINCIPLE

By available chlorine means that a sample of bleaching powder liberates chlorine by the action of dilute acids on it. Its amount is expressed as percentage of chlorine available in the sample. Commercially, obtainable bleaching powder contains 36% - 38% of available chlorine.

Bleaching powder essentially consists of Calcium hypochloride Ca(OCl₂). When a solution of bleaching powder is treated with an excess of a solution of potassium iodide and strongly acidified with acetic acid, the following reaction takes place,

 $OCl^{-} + 2l^{-} + 2H^{+} \leftarrow Cl^{-} + I_2 \uparrow + H_2O$

The liberated iodine is treated with standard sodium thiosulphate solution using starch solution as the indicator. From the amount of liberated I_2 , the equivalent of Cl_2 and hence the available chlorine in the sample of bleaching powder is calculated.

PROCEDURE

Preparation of standard N/10 K₂Cr₂O₇ Solution

Accurately about 0.49 g of $K_2Cr_2O_7$ of AR quality is weighed in a chemical balance. It is transferred into 100 ml flask and the solution is made up to the mark. The solution is shaken well to get a homogenous solution. Solution of this known strength is taken in the burette after thoroughly rinsing with it.

Titration-I

Standardization of Sodium Thio Sulphate solution

(Standard K₂Cr₂O₇ solution Vs Sodium thiosulphate solution)

The burette is filled with the given sodium thiosulphate solution. Exactly 20 ml of standard $K_2Cr_2O_7$ solution is pipetted out into a clean conical flask. About 20 ml of 2N dil. HCl (5 ml of Con. HCl) is added followed by 10 ml of 10% KI solution. The dark brown coloured solution liberates iodine which is titrated against thiosulphate taken in the burette. When the colour of the solution becomes pale yellow, about 1 ml of freshly prepared starch solution is added and the titration is continued till the end point is reached.

TITRATION-II: Estimation of Available Chlorine

(Standardized Sodium thio sulphate solution Vs Unknown Bleaching Powder solution)

S.No.	Volume of	Burette Reading (ml)		Volume of	Concordant
	Pipette Solution	Initial Final		Burette Solution	Value (ml)
	(ml)			(ml)	
1.					
2.					Z
3.					

 N_1

 N_2

Volume of Sodium thio sulphate solution Normality of Sodium thio sulphate solution Volume of Bleaching powder solution Normality of Bleaching powder solution $V_1 = z \quad V$ $= y \quad N$ $V_2 = 20ml$ = ? $V_1N_1 = V_2N_2$

$$N_2 = \frac{V_1 N_1}{V_2}$$

Normality of Bleaching powder Solution $N_2 = a N$

The amount of Cl present in the whole of the given solution = Strength of solution x Equivalent mass of Cl

 $= \frac{10}{N(a) \times 35.46}$ $= \frac{10}{10}$ $= \frac{10}{10}$

= $\frac{1}{5} \times 100$

The end point is the disappearance of starch blue colour leaving behind bright green colour. The titration is repeated for concordant values. From the titre values the strength of thiosulphate is calculated.

<u> Titration – II</u>

Estimation of Available Chlorine

(Standardized Sodium thio sulphate Vs Unknown Solution)

The given K₂Cr₂O₇ solution is made up to 100 ml in a standard flask. Exactly 20 ml of the made up solution is pipette out into a clean conical flask. 5 ml of 5 ml of Con. HCl is added (20 ml of dil. HCl) followed by 10 ml of 10% KI solution. The brown coloured solution liberates iodine which is titrated against thiosulphate taken in the burette. When colour of the solution becomes pale yellow, about 2 ml of freshly prepared starch solution is added and the titration is continued till the end point is reached. The end point is the disappearance of blue colour and appearance of green colour. The titration is repeated for concordant values. From the titre values the strength and amount of available Chlorine in the given sample solution is calculated. From that, the percentage of available chlorine in the sample bleaching powder solution is calculated.

Result:

The % of Chlorine present in the whole of the given solution $= \dots \%$

2. Experiment No 2

Measurement of chloride in water sample by Argentometric method

AIM

To estimate the amount of chloride ion present in the water sample by Argentometric method (Mohr's method). You are provided with standard NaCl solution of strength 0.01 N and a link solution of AgNO₃ (approximately 0.01N).

CHEMICALS REQUIRED

Standard NaCl solution, AgNO3 solution, Potassium chromate indicator

PRINCIPLE

Natural water contains chloride ions in the form of NaCl, KCl, CaCl₂, MgCl₂. The concentration of chloride ions more than 250 ppm is not desirable for drinking purposes.

This determination is based on precipitation titration. When AgNO₃ solution is added to the water sample, in presence of K_2Cr O₄, the chlorides present in it are precipitated first as AgCl.

AgNO₃ NaCl AgCl NaNO₃ In water White ppt.

When all the Cl \square ions is removed, AgNO3 added from the burette will react with K₂CrO₄ to give a reddish brown colour due to silver chromate (Ag₂CrO₄). This is the end point.

 $2 \text{ AgNO}_3 \square \text{ K}_2\text{Cr O}_4 \square \text{ Ag}_2\text{CrO}_4 \square \square 2\text{KNO}_3$

Yellow colour reddish brown

PROCEDURE

Titration 1: Standardisation of AgNO3

The burette is washed well with distilled water and rinsed with small amount of AgNO₃ solution. The pipette is washed with distilled water and rinsed with small amount of standard NaCl solution. 20ml of this solution is pipetted out into a clean conical flask. 1ml of 2% K₂CrO₄ indicator solution is added and titrated against AgNO₃ solution taken in the burette. The end point is the change of colour from yellow to reddish brown. The titration is repeated for concordant values.

Titration 2 : Estimation of Chloride

Water sample vs Standard AgNO3

Sl.	Volume of	Burette reading (ml)		Volume of	Concordant	Indicator
N O	water sample (ml)	Initial	Final	AgNO3 (ml)	value (ml)	
1.	20	0				K ₂ CrO ₄
2.	20	0				

Calculation of the normality of water sample (Chloride ion)

Volume of water sample	$\Box V_1 \Box \Box 20 ml$
Strength of water sample	$\square \mathbf{N}_1 \square \square ?$
Volume of AgNO ₃	$V_2 \square \square_m l$
Strength of AgNO3	$\square N_2 \square$
□ <u>□</u> NAccording to volumetric	formula
$v_1 N_1 \ \square \ v_2 N_2$	
$\mathbf{N}_1 \ \square \ \mathbf{V}_2 \ \square$	
N ₂ /20	
Strength of water sample Calculation of amount of chloride	
Amount of chloride present in 1 litre the given water sample	e of Eq.wt of chloride ion □ Normality of chloride ion
Amount of chloride ion present in ml of the given water sample	100 □ 35.46 □ Normality of chloride ion □ 100/1000g
	m

Titration 2: Estimaton of Chloride ion

The given water sample is made up into 100 ml in a standard flask using distilled water. 20ml of this solution is pipetted out into a clean conical flask and 1ml of 2% K₂Cr O₄ indicator solution is added. It is then titrated against standard AgNO₃ solution taken in the burette. The end point is the change of colour from yellow to reddish brown. The titration is repeated for concordant values.

RESULT

The amount of chloride ion present in 100 ml of the given water sample $\Box \Box \Box gms$.

3. Experiment No 3

Estimation of dissolved oxygen in water

AIM

To determine the dissolved oxygen in the boiler feed water.

CHEMICALS REQUIRED

Na₂S₂O₃ (N/40), MnSO₄ solution, KI, starch, conc. H₂SO₄

PRINCIPLE

Oxygen dissolves in water to the extent of 7 - 9 mgs/lit at a temperature range of 25 - $35\Box$ C. The estimation of dissolved oxygen in water is useful in studying water pollution. Water sample is collected carefully avoiding aeration/deaeration in ground stoppered flask. Initially manganous sulphate and alkali-iodide reagents are added and the reaction occur as follows

 Mn^{2} 2OH $Mn OH_{2}$ White

 $Mn \bigcirc OH \bigcirc 2 \bigcirc 1 \bigcirc 2 \bigcirc 2 \bigcirc \bigcirc Mn \bigcirc OH \bigcirc 2 \bigcirc \bigcirc Yellow brown \bigcirc$

Potassium iodide and the precipitate react with concentrated sulphuric acid liberating iodine and the liberated iodine is titrated against Na₂S₂O₃

 \Box I₂ \Box \Box \Box Na₂S₄O₆ \Box 2NaI

PROCEDURE

Titration I

Standardisation of sodium thiosulphate

The burette is washed and rinsed with sodium thiosulphate solution. Then the burette is filled with the given sodium thiosulphate solution. 20 ml of 0.0125N potassium dichromate solution is pipetted out into a clean conical flask. To this, 5 ml of sulphuric acid and 50 ml of 5% potassium iodide are added. This is titrated against sodium thiosulphate solution. When the solution becomes straw yellow colour, starch indicator is added and then titration is continued.

The end point is disappearance of blue colour and appearance of light green colour. The titration is repeated to get concordant values.

Step II : Estimation of dissolved oxygen

Titration II (Water sample vs Sodium thiosulphate)

SLNo	Volume of	Burett reading e (ml)		Volume of Sodium	Indicator	
51.110	Potassium dichromate (ml)	Initial	Final	thiosulphate (ml) V ₂	Indicator	
1	20	0			Starc h	
2	20	0				
3	20	0				

Volume of Sodium thiosulphate (V_1) \Box

Strength of Sodium thiosulphate (N_1) \Box

Volume of water sample (V₂) \Box 100

ml

Strength of water sample $\Box N_2 \Box$ \Box

□□□ N According to volumetric formula

$$V_1 N_1 \square V_2 N_2$$
$$N_2 \square \frac{V_1 N_1}{V_2}$$

Amount of dissolved oxygen in one litre of tap water

= Normality \Box Eq.wt.of O₂ \Box 1000 mg.

 $\Box \quad \Box \Box \Box \Box \quad N \ \Box \ 8 \ \Box \ 1000$

 \Box \Box \Box \Box \Box \Box mg \Box lit

Titration II

Estimation of dissolved oxygen

100-150ml of the water sample is taken in the iodine flask, 2ml of manganese sulphate and 2 ml of alkali-iodide are added. The stopper is replaced and the flask is inverted and shaken several times for thorough mixing of the reagents. The flask is left aside for sometime. When half of the precipitate settles down, the stopper is removed and 2 ml of concentrated sulphuric acid is added.

The stopper is replaced and the flask is inverted several times for complete dissolution of the precipitate. 100 ml of the brown coloured solution is pipetted out and titrated against standardized sodium thiosulphate solution. Starch indicator is added when the solution becomes light yellow. The titration is continued until the blue colour disappears. From the titre value, the strength of dissolved oxygen and hence the amount of dissolved oxygen in the water sample is calculated.

RESULT

Amount of dissolved oxygen in water sample = mg/lit

4. Experiment No 4

Estimation of alkalinity of water

AIM

To determine the typeand amount of alkalinity present in the given water sample. A standard solution of sodium hydroxide of strengthN and a link solution of hydrochloric acid are provided.

PRINCIPLE

Alkalinity is caused by the presence of hydroxide, carbonate and bicarbonate. There are five alkalinity conditions possible in a given sample of water, hydroxide only, carbonate only, bicarbonate only, combination of carbonate and hydroxide or carbonate and bicarbonate. The various alkalinities can be determined by titrating with a standard acid using phenolphthalein and methyl orange indicators successively.

1. Phenolphthalein end point

When alkaline water is titrated with acid using phenolphthalein indicator, hydroxide alkalinity is completely neutralized and carbonate alkalinity is partially neutralized.

 $OH^+ H^+ \longrightarrow H_2O$

 $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$

2. Methyl orange end point

After thephenolphthalein end point, methyl orange indicator is added and titrated with acid. Bicarbonate neutralization occurs.

 $HCO_3 + H^+ \longrightarrow CO_2 + H_2O$

From the two titre values the different alkalinities are calculated.

When,

P = M, hydroxide alkalinity

2P = M, carbonate alkalinity

P = 0, bicarbonate alkalinity

 $P \Box M$, carbonate and bicarbonate alkalinity

$$CO_{\frac{1}{2}}^{\frac{3}{2}} = 2P,HCO = M - 2P$$

PROCEDURE

<u>TITRATION – I</u>

Standardisation of HCl

The burette is washed well with water and rinsed with the given hydrochloric acid solution. It is then filled with the same upto zero mark. 20 ml of the standard sodium hydroxide solution is pipetted out in a clean conical flask. 2 - 3 drops of phenolphthalein indicator is added, the colour turn to pink colour. It is then titrated against the hydrochloric acid taken in the burette. The end point is disappearance of pink colour. The titration is repeated to get concordant values. From the titre values, the normality of HCl is calculated.

TITRATION – II

With Phenolphthalein Indicator

20 ml of the water sample is pipetted out in a clean conical flask. A drop of phenolphthalein indicator is added. Pink colour is observed. This solution is titrated against the standard HCl, already taken in the burette, until pink colour is disappeared. The end point is noted. This titre value correspondstophenolphthalein end point (P).

<u>TITRATION – III</u>

With Methyl orange Indicator

Few drops of methyl orange indicator is added to the same solution after the phenolphthalein end point. The titration is continued until the solution becomes red orange. The total titre value is noted. This titre value corresponds to methyl orange end point (M). The titration is repeated for concordant values.

From the titre values the amount of each alkalinity present in given water sample is calculated.

TABLE – I

Titre values and different alkalinities

S. No	Result of titration of [P] and [M]	Hardness causing ions			
		OH -	CO3 ² -	HCO ₃ -	
1.	$[\mathbf{P}] = 0$	0	0	[M]	
2.	[P] = [M]	[P] or [M]	0	0	
3.	$\mathbf{P} = -\frac{\overline{1}}{2}\mathbf{M}$	0	2[P] or [M]	0	
4.	$P \Box \frac{\overline{1}}{2}M$	2[P] – [M]	2[M] – [P]	0	
5.	$\begin{array}{c} P \Box \overline{\frac{1}{2}}M \\ 2 \end{array}$	0	2[P]	[M] – 2[P]	

<u>TITRATION – I</u>

HCl Vs Std. NaOH

Sl.	Volume of NaOH	Burette Readings		Concordant Volume of HCl	Indicator
INO	ml	Initial ml	Final ml	ml	
1.	20	0			Phenolphthalein
2.	20	0			

Volume of NaOH	$V_1 = 20 ml$		
Normality of NaOH	N ₁ =N		
Volume of HCl	$V_2 = \dots ml$		
Normality of NaOH	$N_2 = ?$		

According to the law of volumetric analysis

$$V_1 N_1 = V_2 N_2$$
$$N_2 = \frac{V1 \times N1}{V2}$$

$$\mathbf{N}_{2}=\frac{20\ \mathbf{X}....\mathbf{N}}{\mathbf{N}_{2}}$$

.....

TITRATION IL & III

Water Sample Vs. Std. HCl

CI.	Volume of water sample ml	Burette Readings		Concordant Volume of HCl	
51. No		Phenolphthalein end point [P] Ml	Methyl Orange end point [M] ml	P	M ml
1.	20	0			
2.	20	0			

CALCULATIONS:

If the data satisfies the condition P

i.) Volume of HClrequired for $[OH^{-}]$ alkalinity = 2 * P – M

= 2 x

=.....ml

ii.) Volume of HClrequired for [CO $\frac{2}{31}$ -]alkalinity = 2 * M - 2 * P = 2 x $\frac{2}{31}$ -]alkalinity = 2 * M - 2 * P

1. <u>Calculation of OH-alkalinity</u>

Volume of $HCl V_1 = \dots ml$

Strength of $HCl N_1 = \dots N$

Strength of water sample $N_2=$?

According to the law of volumetric analysis

$$V_1 N_1 = V_2 N_2$$
$$N_2 = \frac{V1 \times N1}{V2}$$

$$N_2 = \underbrace{= \dots N_1 \times \dots N_2}_{20}$$

Amount of **OH**⁻content present in 1 litre of water sample, in terms of **CaCO**₃equivalent =

Strength of water sample x eqv.Wt.ofCaCO₃

ie.,OH ⁻alkalinity interms of CaCO₃equivalent =N x 50 x 1000ppm

Alkalinity due to OH⁻ions =.....ppm

P $\frac{1}{2}$ \Box M, carbonate and hydroxide alkalinity

$$CO_3^2 = 2(M-P), OH = 2P - M$$

Alkalinity values are expressed in terms of milligrams per litre as calcium carbonate.

	Calculation of CO ₃ ² – alkalinity
Volume of HCl	$\mathbf{V}_1 = \dots \dots \mathbf{ml}$
Strength of HCl	$\mathbf{N_1} = \dots \mathbf{N}$

Volume of water sample $V_2 = 20 \text{ ml}$

Strength of water sample $N_2 = ?$

According to the law of volumetric analysis

$$V_1 N_1 = V_2 N_2$$
$$N_2 = \frac{V1 \times N1}{V2}$$

Amount of CQ_{m1X}^{2-} content present in 1 litre of water sample, in terms of CaCO equivalent = Strength of water sample x eqv. Wt.of CaCO₃

ie., CO_3^{2-} alkalinity in terms of CaCO equivalent = N x 50 x 1000ppm

Alkalinity due to CO₃²⁻ions = ppm

<u>RESULT</u>

Water sample contains the following alkalinity

i.) Hydroxide alkalinity (OH ⁻)	=	ppm
(ii)Carbonate alkalinity (CO_3^{2-})	=	ppm

5. Experiment No 5

Determination of COD in water

AIM

To measure Chemical Oxygen Demand.

BACKGROUND AND PRINCIPLE:

The chemical oxygen demand (COD) determines the amount of oxygen required for chemical oxidation of organic matter using a strong chemical oxidant, such as, potassium dichromate under reflux conditions. This test is widely used to determine:

a) Degree of pollution in water bodies and their self-purification capacity,

b) Efficiency of treatment plants,

c) Pollution loads, and

d) Provides rough idea of Biochemical oxygen demand (BOD) which can be used to determine sample volume for BOD estimation.

The limitation of the test lies in its inability to differentiate between the biologically oxidizable and biologically inert material and to find out the system rate constant of aerobic biological stabilization.

Most of the organic matters are-destroyed when boiled with a mixture of potassium dichromate and sulphuric acid producing carbon dioxide and water. A sample is refluxed with a known amount of potassium dichromate in sulphuric acid medium and the excess of dichromate is titrated against ferrous ammonium sulphate. The amount of dichromate consumed is proportional to the oxygen required to oxidize the oxidizable organic matter.

SELECTION OF METHODS

There are two methods available for COD determination namely open reflux and closed reflux.

Open Reflux Principle:

- Suitable for a wide range of wastes with a large sample size.
- Due to it higher oxidizing ability dichromate reflux method is preferred over other procedures using other oxidants (e.g. potassium permanganate).
- Oxidation of most organic compounds is up to 95-100% of the theoretical value.

Closed Reflux Principle:

- This method is conducted with ampules and culture tubes with pre-measured reagents.
- Measurement of sample volume and reagent volume are critical.

- This method is economical in the use of metallic salt reagents and generate smaller quantity of hazardous wastes.
- Volatile organic compounds (VOC) gets completely oxidized in a closed system than the open because of longer contact time with oxidants.

Chemical Reactions:

 $C_nH_aO_bN_c+d Cr_2O_7^{2-} + (8d+c) H^+ => nCO_2 + [(a+8d-3c)/2]H_2O+c NH_4^+ + 2dCr^{3+} (1)$

Here d = (2n/3) + (a/6) - (b/3) - (c/2)

During experiment, excess dichromate concentration is determined by titrating it with ferrous ammonium sulfate (FAS). The reaction is given by:

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

Here d = (2n/3) + (a/6) - (b/3) - (c/2)

SAMPLING AND HANDLING REOUIREMENTS

S	Determinatio	Container	Preservatio	Min	Maximum	Regulator
	n		n	Vol	storage	У
Ν			Technique	, ml	Recommende	
0					d	
1.	COD	Plastic,	Analyze as soon as	100	7 days	28 d
		Glass	possible, or add		-	
			H_2SO_4 to $pH < 2$;			
			refrigerate			

REAGENTS:

> <u>Standard Potassium dichromate ($K_2Cr_2O_7$) digestion solution, 0.01667M:</u>

Add to about 500 mL distilled water 4.903 g $K_2Cr_2O_7$, primary standard grade, previously dried at 150°C for 2 h, 167 mL conc. H_2SO_4 , and 33.3 g HgSO₄. Dissolve, cool to room temperature, and dilute to 1000 mL.

➤ Sulfuric acid reagent:

Add H_2SO_4 at the rate of 5.5 g Ag2SO4/kg H_2SO_4 or 10.12 g silver sulphate/L H_2SO_4 . Let stand 1 to 2 d to dissolve and mix. This accelerates the oxidation of straight- chain aliphatic and aromatic compounds.

(1 Kg = 543.47826 mL of H₂ SO₄ and take 20.24 g of Ag₂SO₄ to 2 L of H₂ SO₄ or 22.264 g of Ag₂SO₄ to 2.2 L of H₂ SO₄)

Ferroin Indicator solution

This indicator is used to indicate change in oxidation-reduction potential of the solution and indicates the condition when all dichromate has been reduced by ferrous ion. It gives a very sharp brown color change which can be seen in spite of blue color generated by the Cr^{3+} ions formed on reduction of the dichromate.

> <u>Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10M:</u>

Dissolve 39.2 g Fe $(NH_4)_2(SO_4)_2.6H_2O$ in distilled water. Add 20 mL conc. H_2SO_4 , cool, and dilute to 1000 mL. Standardize solution daily against standard $K_2Cr_2O_7$ digestion solution as follows: Pipet 5.00 mL digestion solution into a small beaker. Add 10 mL reagent water to substitute for sample. Cool to room temperature. Add 1 to 2 drops diluted Ferroin indicator and titrate with FAS titrant.

Molarity of FAS solution = $[V_{K2Cr2O7} \times 0.1] / (V_{FAS})$

Where: $V_{K2Cr2O7}$ = volume of K₂Cr₂O₇ (mL); V_{FAS} = volume of FAS (mL)

PROCEDURE:

- 1. Wash culture tubes and caps with 20% H₂SO₄ before using to prevent contamination.
- 2. Place sample (2.5 mL) in culture tube and Add K₂Cr₂O₇ digestion solution (1.5 mL).
- 3. Carefully run sulphuric acid reagent (3.5 mL) down inside of vessel so an acid layer is formed under the sample-digestion solution layer and tightly cap tubes or seal ampules, and invert each several times to mix completely.
- 4. Place tubes in block digester preheated to 150°C and reflux for 2 h behind a protective shield.
- 5. Cool to room temperature and place vessels in test tube rack. Some mercuric sulfate may precipitate out but this will not affect the analysis.
- 6. Add 1 to 2 drops of Ferroin indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10 M FAS.
- 7. The end point is a sharp color change from blue-green to reddish brown, although the blue green may reappear within minutes.
- 8. In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.
- 9. COD is given by

 $COD (mg O_2 / L) = [(A-B) \times M \times 8000) / (V_{sample})$

Where:	А	=	volume of FAS used for blank (mL)
	В	=	volume of FAS used for sample
	Μ	=	(mL)
			molarity of FAS
	8000 =	milli e	equivalent weight of oxygen (8) $\times 1000$ mL/L.

<u>RESULT</u>

Amount of COD in water sample=