Section 2: Water Analysis

Water Analysis:

Process by which we identify and quantify the chemical components and the properties of water.

Analysis is carried out **on**

- **water** used in industrial processes
- waste-**water** stream
- rivers and stream
- Rainfall
- on the sea.

Constituents of Water and Wastewater

PHYSICAL CHARACTERISTICS

- Turbidity
- Color
- Taste
- Odor
- Temperature

CHEMICAL CHARACTERISTICS

1. Nitrogenous compounds
2. Chlorides
3. Sulphides
4. Chemical Oxygen Demand
5. Dissolved Oxygen
6. Metals and cations

(Manganese, Aluminium, Iron, Zinc, Copper, Lead…)

7. Water hardness (Ca^{2+} and Mg^{2+}).
8. pH, Acidity and Alkalinity.
9. Biochemical Oxygen Demand ` (BOD)
10. Solids
11. Organic Carbon and Volatile Organic Compounds
12. Phosphorus
13. Fats, Oils, Waxes, and Grease
14. Surfactants

[1] Nitrogen in Water

[1] Nitrogen in water

- Nitrogen is a major component of wastewater
- Protein contains about 16% nitrogen (organic nitrogen)
- Hydrolysis of organic nitrogen by microorganisms produces ***Ammonia*** (free ammonia)
- ***Nitrites*** and ***Nitrates*** are the result of the oxidation of ammonia. The nitrite form of nitrogen is very unstable and is easily oxidized to the nitrate .
- The sum of the free ammonia, nitrite, and nitrate is called ***total nitrogen***.
- The free ammonia may hydrolyze in water to produce ammonium ion NH_4^+ according to the following equation:

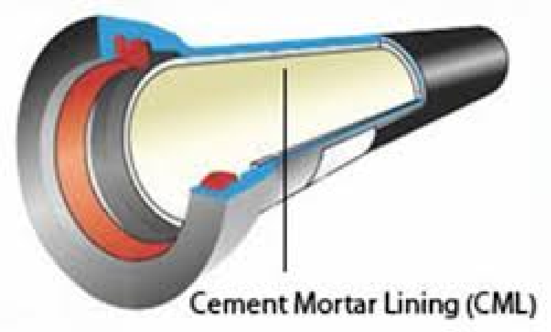
$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Q. What are the different forms of nitrogen in water?

[1.a.] Ammonia in water

Sources of Ammonia in water

- From industrial effluents
- Disinfection with chloramines : monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3).
- Protein decomposition in soil.
- Fertilizers after rainfall.
- Cement mortar used for coating the insides of water pipes may release considerable amounts of ammonia into drinking-water



- WHO standards, 0.05 mg/l.

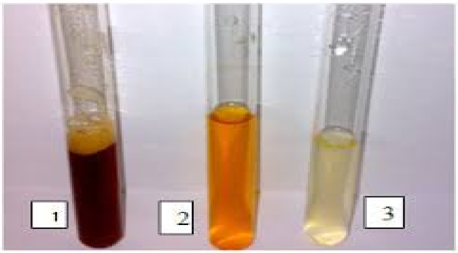
[1.a.] Ammonia in water

Effect of pH on Ammonia in water

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

- At pH levels below 7, the above equilibrium is shifted to the right and the predominant nitrogen species is , the ionized form.
- At pH is above 7, the equilibrium is shifted to the left and the predominant nitrogen species is ammonia.

- The unionized form is most lethal to aquatic life.



- Useful for low range ammonia nitrogen determinations.

Nessler's reagent method

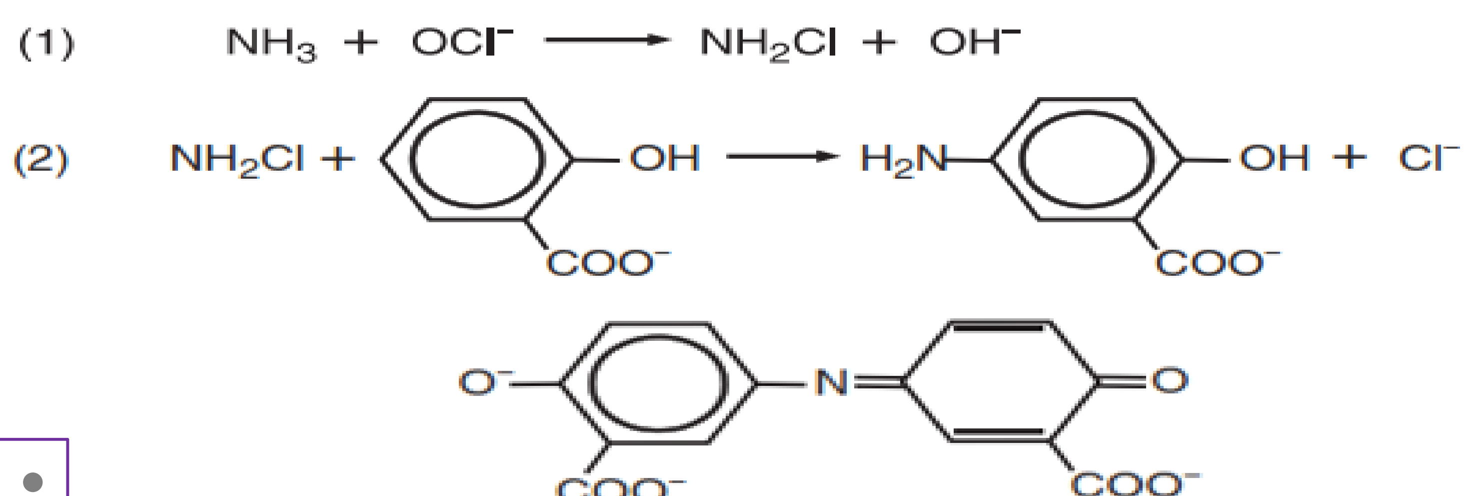
- Ammonium ions react with Nessler's reagent (Potassium tetraiodomercurate(II)), $K_2[HgI_4]$
- It forms yellow salt of the ammonobasic mercuric iodide. At higher concentration of ammonia, it tends to form brown precipitate.
- The color obtained is measured either photometrically at λ_{max} or by Nesslerization technique (A method for measuring NH_3 colorimetrically).

$$2[HgI_4]^{2-} + NH_4^+ + 4OH^- \rightarrow HgO\cdot Hg(NH_2)I \downarrow + 3H_2O + 7I^-$$

Yellow to brown ppt

Salicylate method

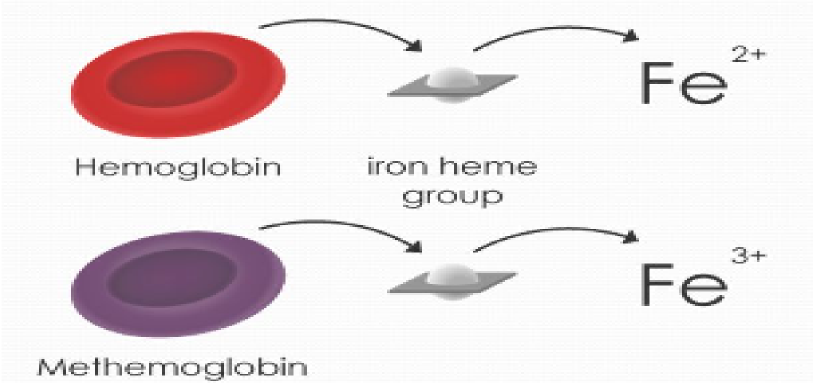
- (1) Ammonia combined with hypochlorite to form monochloramine
- (2) then reacts with salicylate to form 5-aminosalicylate.
- (3) Oxidation of 5-aminosalicylate is carried out in the presence of a catalyst, nitroprusside or $[Fe(CN)_5NO]^{2-}$ (also called nitroferricyanide), results in the formation of indosalicylate, a blue-colored compound. The blue color is masked by the yellow color (from excess nitroprusside) causing a green-colored solution. The intensity of the color which is directly proportional to the ammonia concentration in the sample.



Indosalicylate

[1.b.] Nitrites and Nitrates in water

- Nitrates in water can cause *methemoglobinemia*, (infant cyanosis or blue babies). the iron in the heme group is in the Fe^{3+} state, not the Fe^{2+} of normal hemoglobin. Methemoglobin cannot bind oxygen.



- Therefore, Nitrates is a very important parameter in drinking water standards. The maximum contaminant level (MCL) for nitrates is 10 mg/L as *N*.
- The Nitrate concentration is usually determined by colorimetric methods.

Q. Explain the toxicity of Nitrates in drinking water?

Methods of Determination of Nitrites in water

Diazotizaiton & Coupling
[Griess-ILosvay method]

Griess test is an analytical chemistry test which detects the presence of nitrite ion in drinking water.

1- Nitrite is converted to nitrous acid (HNO_2)

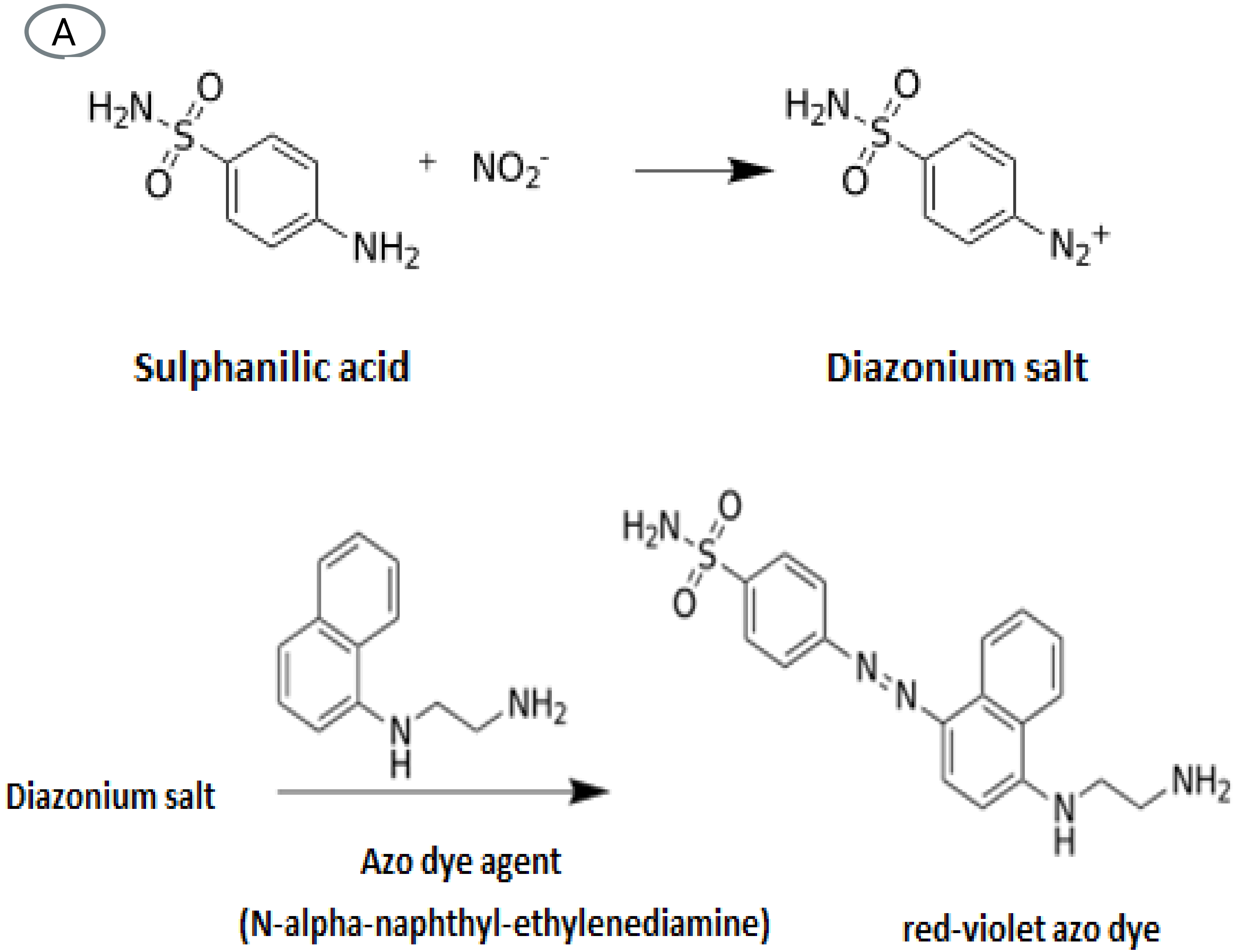
2- the acid is then diazotized with aromatic amine (sulphanilic acid) to yield a diazonium salt.

3- the salt is coupled with either :

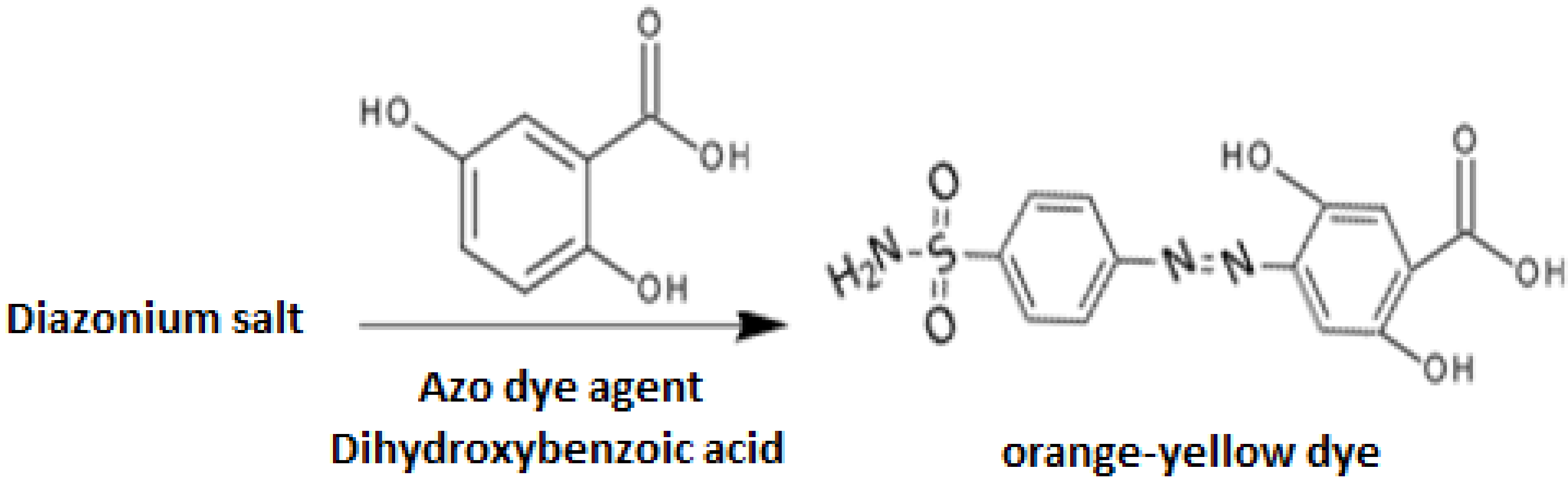
a) N-naphthyl-(1)-ethylenediamine to produce a red-violet azo dye.

b)Dihydroxybenzoic acid to produce an orange- yellow azo dye.

4- The colored products are measured at the corresponding λ_{max} or by colorimetric comparison technique.


A
H_2N
NO_2^-
NH_2
N_2^+
Sulphanilic acid
Diazonium salt
Diazonium salt
Azo dye agent
(N-alpha-naphthyl-ethylenediamine)
red-violet azo dye

B



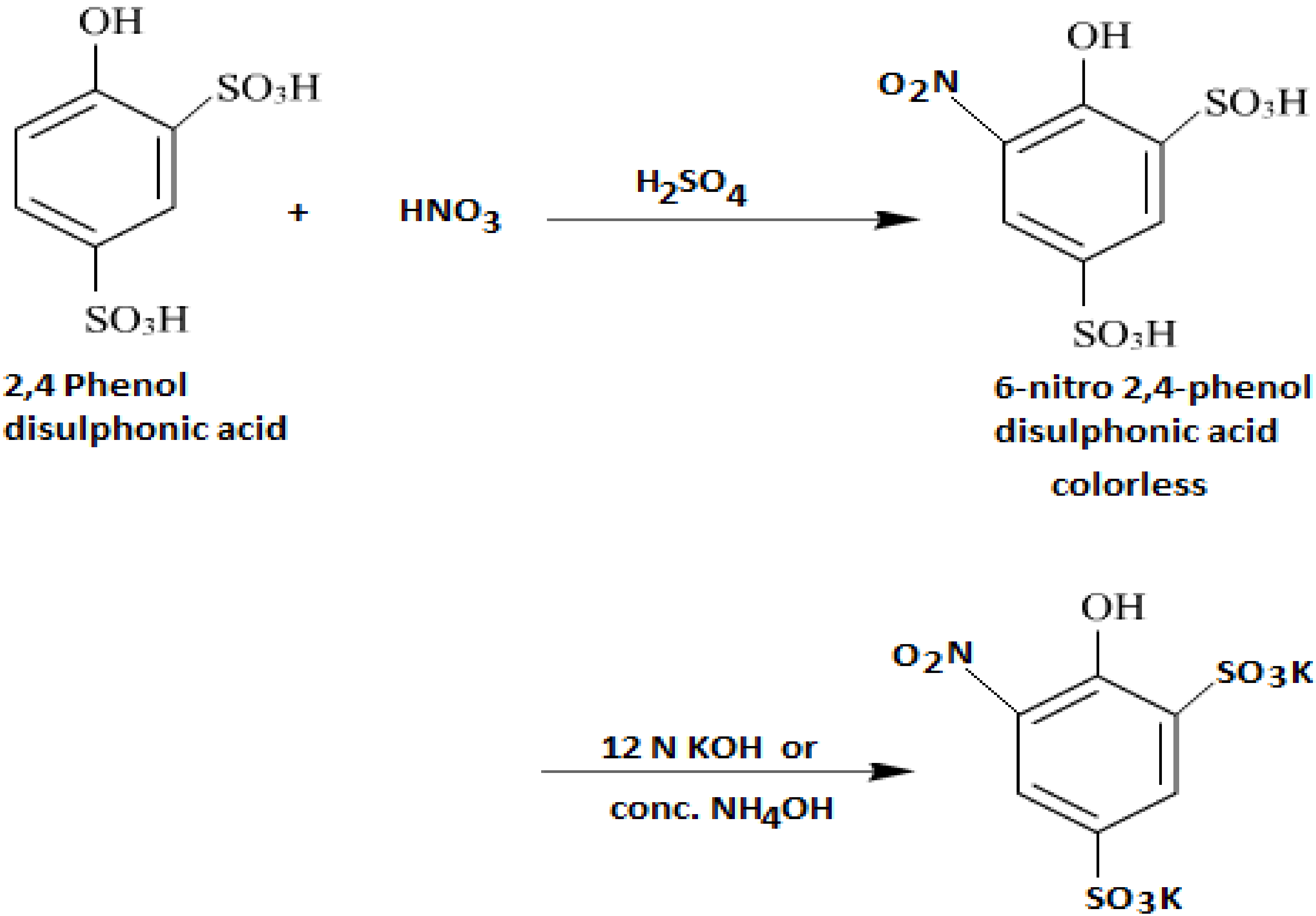
Q. What are the oxidized forms of nitrogen in water? Which of them is the most abundant form?

Q. Write the method of analysis of Nitrites in water?

Methods of Determination of Nitrates in water

Phenol disulphonic acid method

Nitrate reacts with phenoldisulphonic acid (PDA) to produce a nitro derivative, which in alkaline solution develops a yellow colour. The colour produced follows Beer's law and is proportional to the concentration of NO_3^- present in the sample. The concentration of NO_3^- is determined using a colorimeter or spectrophotometer.



2,4 Phenol disulphonic acid

6-nitro 2,4-phenol disulphonic acid colorless

Yellow salt

[2] Chlorides in Water

[2] Chlorine in water

- Chloride concentrations of up to 400 mg/l is safe
- water can taste salty if it contains more than about 100 mg/l Cl^-

Forms of chlorine

Free chlorine

As elemental chlorine (Cl_2), hypochlorous acid (HOCl) or hypochlorite ion (OCl^-).

Combined chlorine

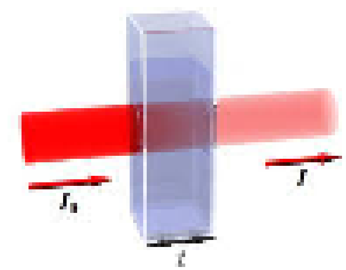
Chloramines or other chloro derivatives.

Q. What are the different forms of chlorine in water?

The photometric method is more sensitive, more precise and more accurate than the titrimetric method.

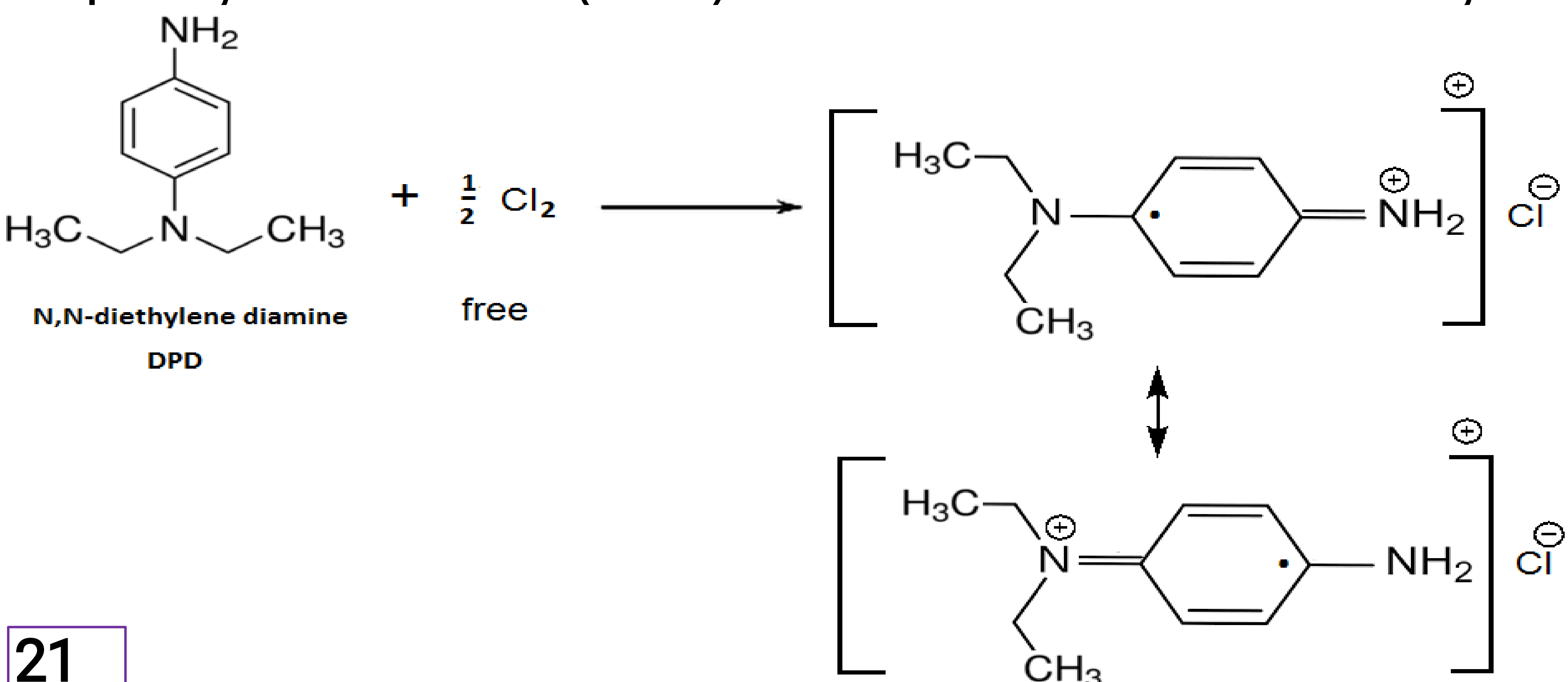
Examples on titrimetric methods:
Mohr, volhard, mercurimetric

Photometric method



A DPD reagent:

- Elemental chlorine Cl_2, hypochlorous acid HOCl and hypochlorite OCl^- ion react with N,N-diethyl-1,4-phenylenediamine (DPD) to form a red colored azo dye

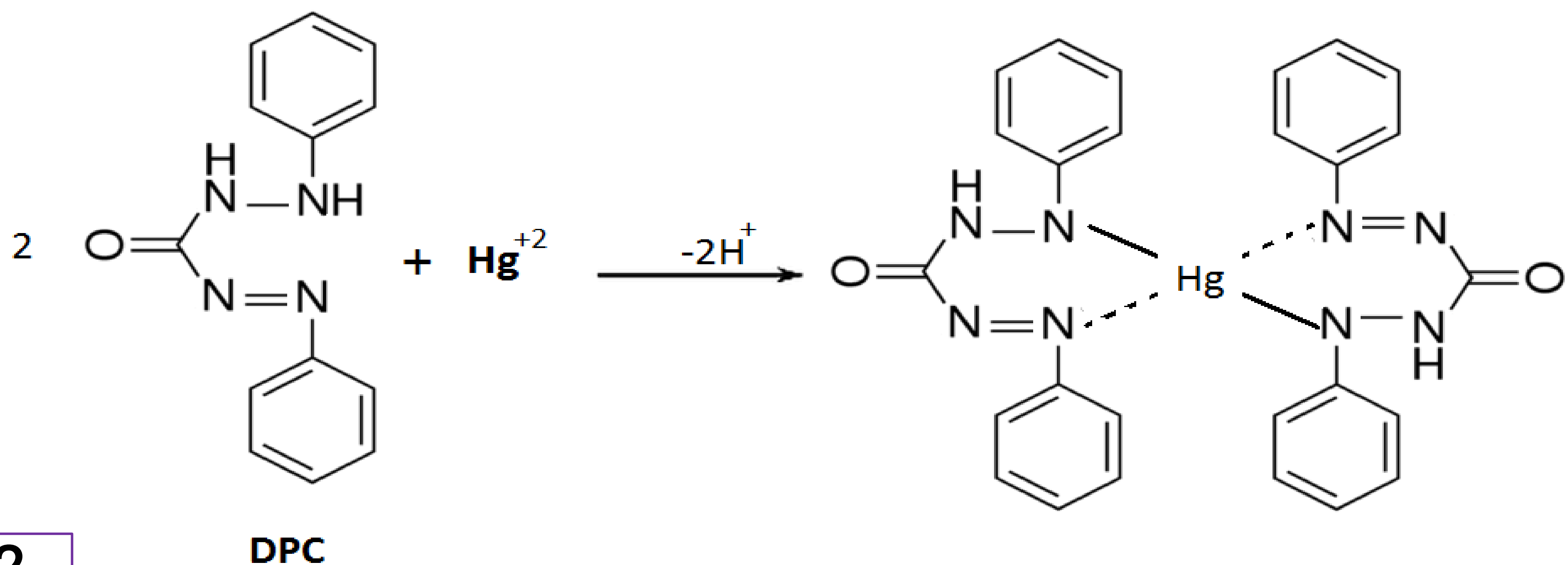


Photometric method

B DPC reagent:

- Mercury Hg(II) ions react with chloride ions to form mercury (II) chloride.

-Excess mercury (II) ions react with diphenyl carbazone to form a blue violet complex in a solution acidified with nitric acid.



Photometric method

C

- Chloride reacts with mercury (II) thiocyanate to form mercury (II) chloride and chloromercurate (II) inions.

$$Hg(SCN)_2 + 2\,Cl^- \rightarrow HgCl_2 + 2\,SCN^-$$

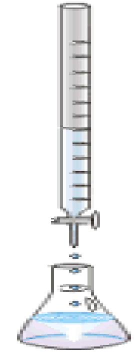
$$Hg(SCN)_2 + 4\,Cl^- \rightarrow (HgCl_4)^{2-} + 2SCN^-$$

The thiocyanate released reacts with iron (III) nitrate in nitric acid solution to yield blood-red iron thiocyanate.

$$SCN^- + Fe^{3+} \rightarrow Fe(SCN)^{2+}$$

blood-red color

Titrimetric method (Iodometric titration)



- To the acidified water sample, add KI solution. Titrate the liberated iodine against st. $Na_2S_2O_3$ using starch as indicator.

$$Cl_2 + 2KI \rightarrow I_2 + 2KCl$$

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

[3] Sulphides in Water

[3] Sulphides in water

- Most of Sulphides in water exist in the form of Hydrogen sulphide, H_2S

Sources:

- **Sulfur-reducing bacteria**, which use sulfur as an energy source, are the primary producers of large quantities of H_2S. These bacteria chemically change natural sulfates in water to hydrogen sulfide. Sulfur-reducing bacteria live in oxygen-deficient environments such as deep wells, plumbing systems, water softeners, and water heaters.

The microbial breakdown of organic matter in the absence of oxygen gas is called **Anaerobic Digestion**.

- Other sources of sulphides are sewage and leather industries.

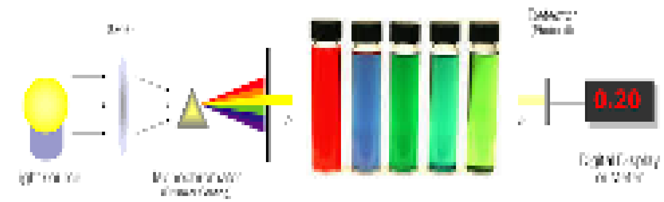
Potential health effects of hydrogen sulfide in drinking water

- It has odor of rotten eggs.
- It is very poisonous and corrosive.

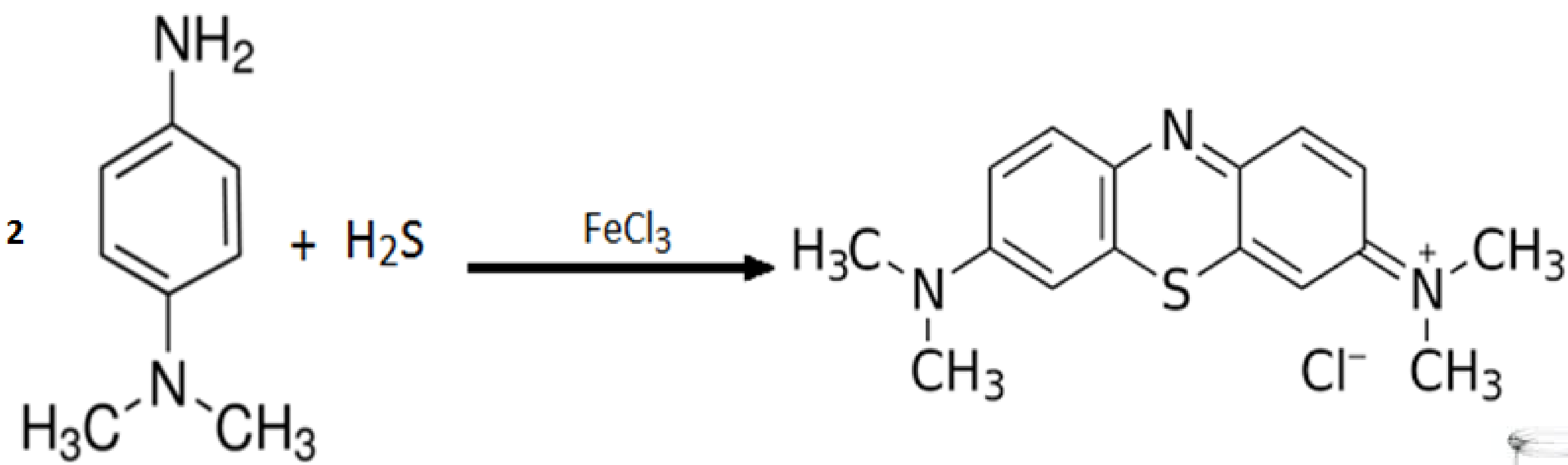
$$H_2S + 2O_2 \rightarrow H_2SO_4$$

- Drinking water is not allowed to contain any hydrogen sulfide due to its toxicity (does not have a **drinking water** standard).
- The presence of this compound is an indicator of bacterial water pollution.
- Hydrogen sulfide gas is flammable and at high concentrations.

Photometric method



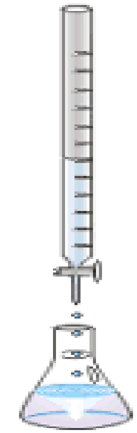
❑ Addition of *p*-aminodimethyl aniline to the sample



***p*-amino dimethyl aniline**

Methylene Blue

Titrimetric method (Iodometry)



- Water sample is acidified with HCl. Then, known excess standard iodine (I_2) solution is added.

$$H_2S + I_2 = 2H+ + 2I^- + S\downarrow$$

Back titrate the excess unused I_2 against standard sod. thiosulphate ($Na_2S_2O_3$) using starch.

<u>Titration reaction</u>

$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2NaI + Na_2S_4O_6$$

Treatment

Continuous chlorination

For levels up to 75 mg/L chlorine is used in the purification process as an oxidizing chemical to react with hydrogen sulfide. This reaction yields insoluble solid **sulfur**. Usually the chlorine used is in the form of sodium hypochlorite.

Aeration

For concentrations of hydrogen sulfide less than 2 mg/L aeration is an ideal treatment process. Oxygen is added to water and a reaction between oxygen and hydrogen sulfide react to produce odorless **sulfate**

Nitrate addition

Calcium nitrate is used to prevent hydrogen sulfide formation in wastewater streams.

[4] Chemical Oxygen Demand (COD)

[4] Chemical Oxygen Demand ,COD.

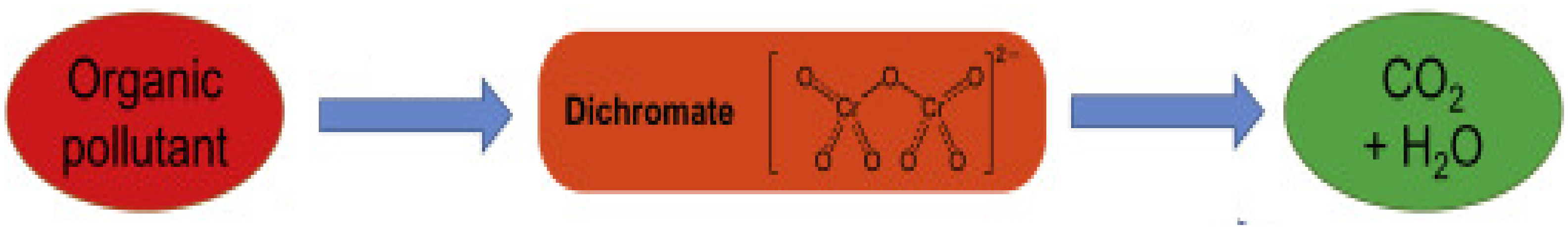
It is the amount of oxygen required for the oxidation of the reducing matter that is present in water. (organic and inorganic matter)

Significance of COD values:

- COD often is used as a measurement of pollution in water.

COD = 1 ppm → sample of good purity.
= 3 ppm → sample of medium purity
= 4 ppm → sample of doubtful purity.
> 4 ppm → polluted sample.

Determination of COD



- Organic pollutants in water are determined by oxidation with amount of O_2 that is chemically equivalent to the dichromate consumed

- The sample is heated with $K_2Cr_2O_7$
- The organic matter is converted to CO_2 and H_2O
- The dichromate is converted/reduced to Cr^{+3}
- The excess dichromate is determined by titration with ferrous ammonium sulphate

- The main redox reactions:

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

$$Fe^{2+} \longleftrightarrow Fe^{3+} + e^-$$

Interferences

- Any substance in water that reduces $Cr_2O_7^{2-}$ will interfere with the COD experiment.
- One of the common interferences is Cl^- which is oxidized by the dichromate to Cl_2
- If Chloride is known to be present in the sample, $HgSO_4$ is added to the reaction mixture to **tie up** Cl^- as soluble Hg(II) chloride .

[5] Dissolved Oxygen (DO)

[5] Dissolved Oxygen, DO.

It is the oxygen already dissolved or present in water during its aeration. It is a measure of water aeration.

Significance of DO:

- It is very important to detect the amount of DO.

- DO-data determine conditions for aquatic life.

- DO-data determine conditions affecting corrosion of iron and steel in water pipes and boilers. (↑ O_2 corrosion↑).

$$\text{organic + inorganic matter} \xrightarrow[\text{High DO}]{\text{Aerobic bacteria}} \text{harmless effect}$$

$$\text{organic + inorganic matter} \xrightarrow[\text{Low DO}]{\text{Anaerobic bacteria}} \text{harmful effect}$$

Winkler's method

1 $Mn^{2+} + 2OH^- \rightarrow Mn(OH)_2\downarrow$ white ppt.

2 $2Mn(OH)_2 + \frac{1}{2}\ O_2 + H_2O \rightarrow 2Mn(OH)_3\downarrow$ brown ppt.

3 $2Mn(OH)_3\downarrow + 6HCl \rightarrow 2MnCl_3 + 6H_2O$

4 $2MnCl_3 + 2KI \rightarrow I_2 + 2KCl + 2MnCl_2$

The liberated iodine is equivalent to DO

$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$

Interferences

A) Oxidizing agents

Give more liberated I_2 than the actual amount

Example: Fe^{3+} , NO_2^-,….

Ox. Agent + KI $\rightarrow$ I_2

- Removal of Fe^{3+} by adding phosphoric acid. By forming colorless complex bis(phosphato) ferrate(III) $[Fe(PO_4)_2]^{3-}$

B) Reducing agents

Give less liberated I_2 than the actual amount

Example: Fe^{2+} , S^{2-}, SO_3^{2-} ….

- Removal is by adding dilute MnO_4^- drop wise to the sample, till the persistence of very faint color. Excess MnO_4^- may be removed by adding one drop of dilute Na-oxalate solution.

- Removal of NO_2^- : by addition of Hydrazoic acid

$$HN_3 + NO_2^- + H^+ \rightarrow N_2\uparrow + N_2O\uparrow + H_2O$$

Interferences

B) Reducing agents

Give less liberated I_2 than the actual amount

Example: Fe^{2+} , S^{2-}, SO_3^{2-} ....

 Removal is by adding dilute MnO_4^- drop wise to the sample, till the persistence of very faint color. Excess MnO_4^- may be removed by adding one drop of dilute Na-oxalate solution.

$$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

[6] Cations in Water

[6.a.] Manganese (Mn^{2+})

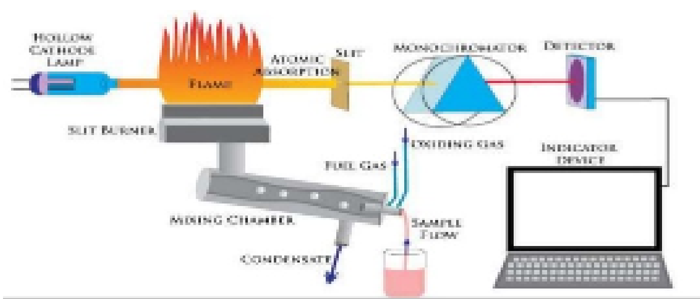
Significance

- **Manganese** is a mineral that naturally occurs in rocks and soil.
- Although it is an essential, non-toxic trace element, the maximum limits in drinking water is 0.05 mg/l, because of the staining which may be caused.

- In Ground water Manganese present as divalent ion due to the absence of oxygen
- In the surface water it present in the trivalent and quadrivalent states

Methods of Determination of Manganese

Atomic absorption spectrophotometric method



Chemical reactions

Photometric methods

Persulphate Reaction

Persulphate oxidation method

$$2\,Mn^{2+} + 5\,S_2O_8^{2-} + 8\,H_2O + 8H^+ \xrightarrow{AgNO_3} 2\,MnO_4^- + 10\,SO_4^{2-} + 16\,H^+$$

colourless Purple

- Persulphate $S_2O_8^{2-}$ oxidize manganese ion to permanganate

Interferences

- One of the common interferences is Cl^- (………. Agent) which is oxidized to Cl_2
- Cl^- may reduce MnO_4^- back to Mn^{2+}, or reduce $S_2O_8^{2-}$ to SO_4^{2-}
- This can be eliminated by adding mercuric nitrate $Hg(NO_3)_2$ solution which forms stable tetrahedral coordination **complex** $[HgCl_4]^{2-}$.

[6.b.] Aluminium ion (Al^{3+})

Sources

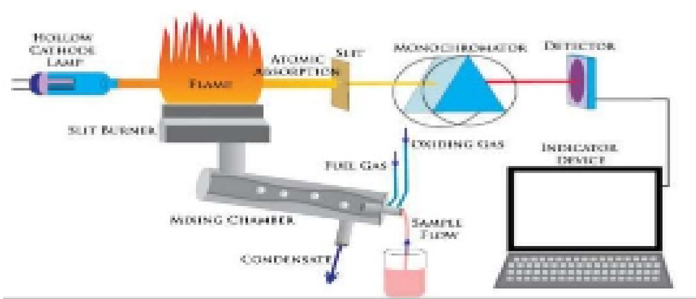
- ❑ Aluminium salts are added during the purification of drinking and swimming pool water to flocculate the suspended substances and contaminants.

Significance

- ❑ The maximum aluminium limit allowed is 0.2 mg/l in drinking water.

Methods of Determination of Al^{3+}

Atomic absorption spectrophotometric method

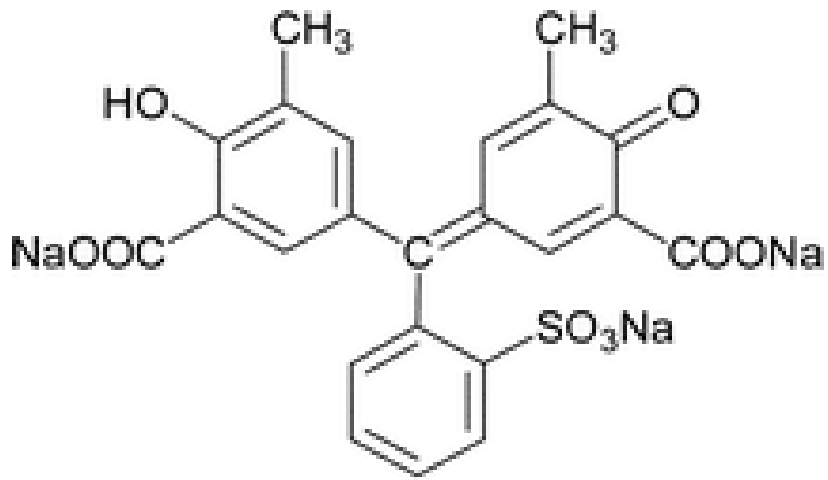


Chemical reactions

Photometric method

Eriochrome Cyanine-R Reaction

Eriochrome Cyanine-R Reaction



Eriochrome Cyanine R.

- Aluminum solution is buffered to a pH 6
- Eriochrome Cyanine R is added
- A red to pink complex is formed which has λ_{max} = 535 nm
- The intensity of the color is proportional to the Al^{3+} concentration.

[6.c.] Iron in water (Fe^{3+} or Fe^{2+})

- Hydrated ferric oxide $Fe_2O_3 \cdot H_2O$ is the predominant form of iron in water. But under reducing conditions, iron exists in Fe^{2+} state.

Sources

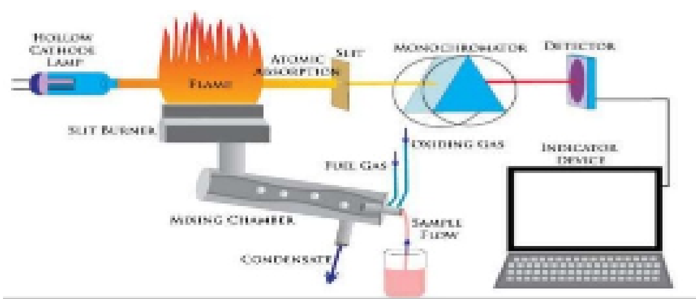
- It may originate from **water pipes**.
- Iron salts are added to water samples as flocculating agents to remove suspended matters from water during purification processes.

significance

- The maximum conc. in public waters is 0.2 mg/l.
- Higher conc. must be removed as it may cause unaccepted taste and staining problems.

Methods of Determination of iron

Atomic absorption spectrophotometric method



Chemical reactions

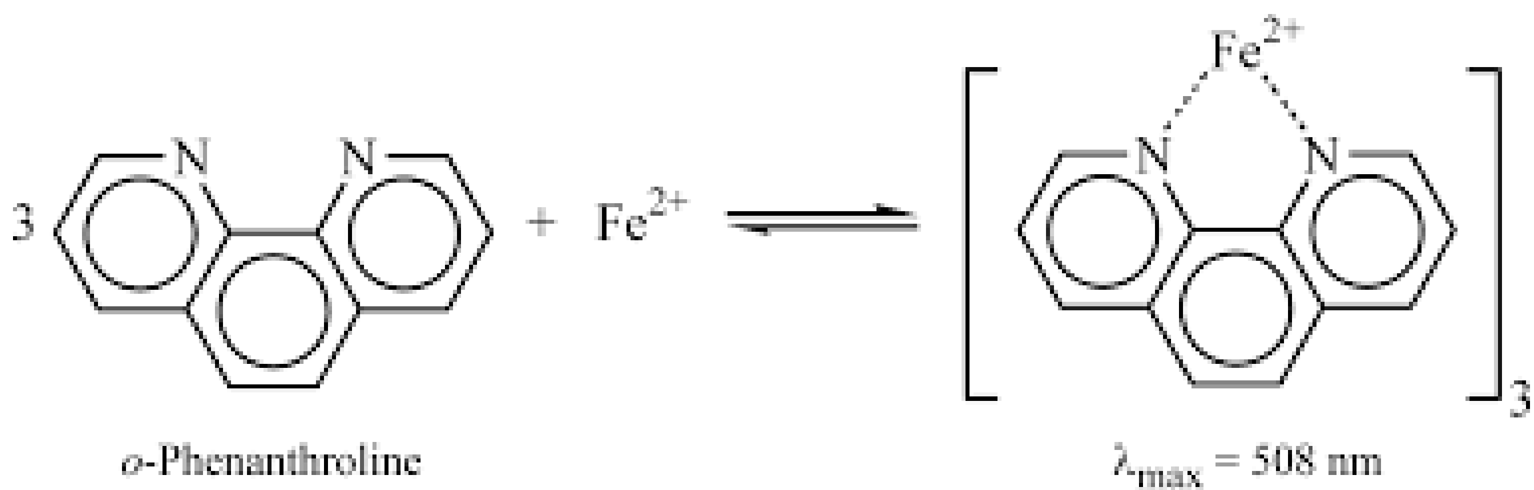
- All Fe^{3+} should be Reduced to Fe^{2+} by boiling with hydroxyl amine or adding Ascorbic acid

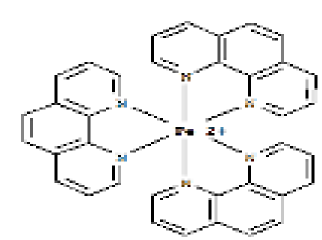
Phenanthroline Reaction

Bipyridine method

Phenanthroline Reaction

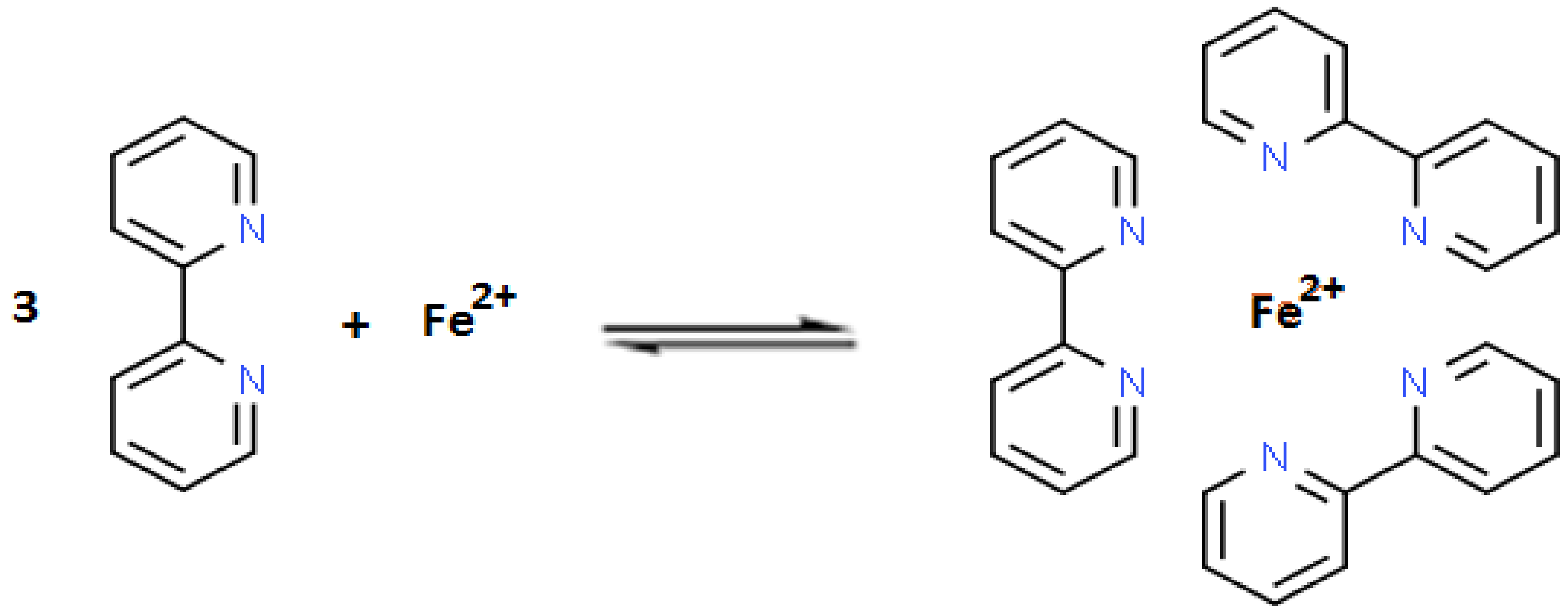
- Reduce the Fe^{3+} to Fe^{2+} by boiling with hydroxyl amine or adding Ascorbic acid
- The pH is adjusted between 3 to 3.5
- Three molecules of 1,10-phenanthroline chelate an atom of Fe^{2+} to form an orange-red complex.





Bipyridine Reaction

- Reduce the Fe^{3+} to Fe^{2+} by boiling with hydroxyl amine or adding Ascorbic acid
- The pH is adjusted between 1 to 7
- Three molecules of Bipyridine chelate an atom of Fe^{2+} to form an pink-deep red complex.



[6.d.] Zinc ion in water (Zn^{2+})

Sources

- Zinc most commonly enters the domestic water supply from the deterioration of **galvanized water pipes** made of brass (brass = mixture of Zn & Cu)

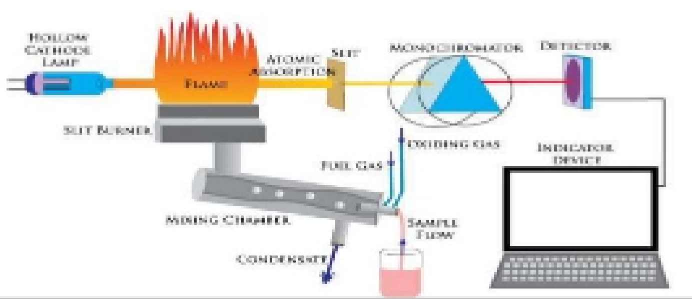
- From industrial waste
- Pb^{2+} and Cd^{2+} are the impurities of Zinc in galvanization process
- When water is left to stand in pipe work, zinc metal, as a reducing agent, reduces nitrate to nitrite.

significance

- Zinc is essential in body growth. The activity of more than 80 enzymes is zinc-dependent. The daily requirement for humans is 2 → 10 mg Zn.
- However, > 5mg/l Zinc in water causes bitter taste.

Methods of Determination of Zinc

Atomic absorption spectrophotometric method



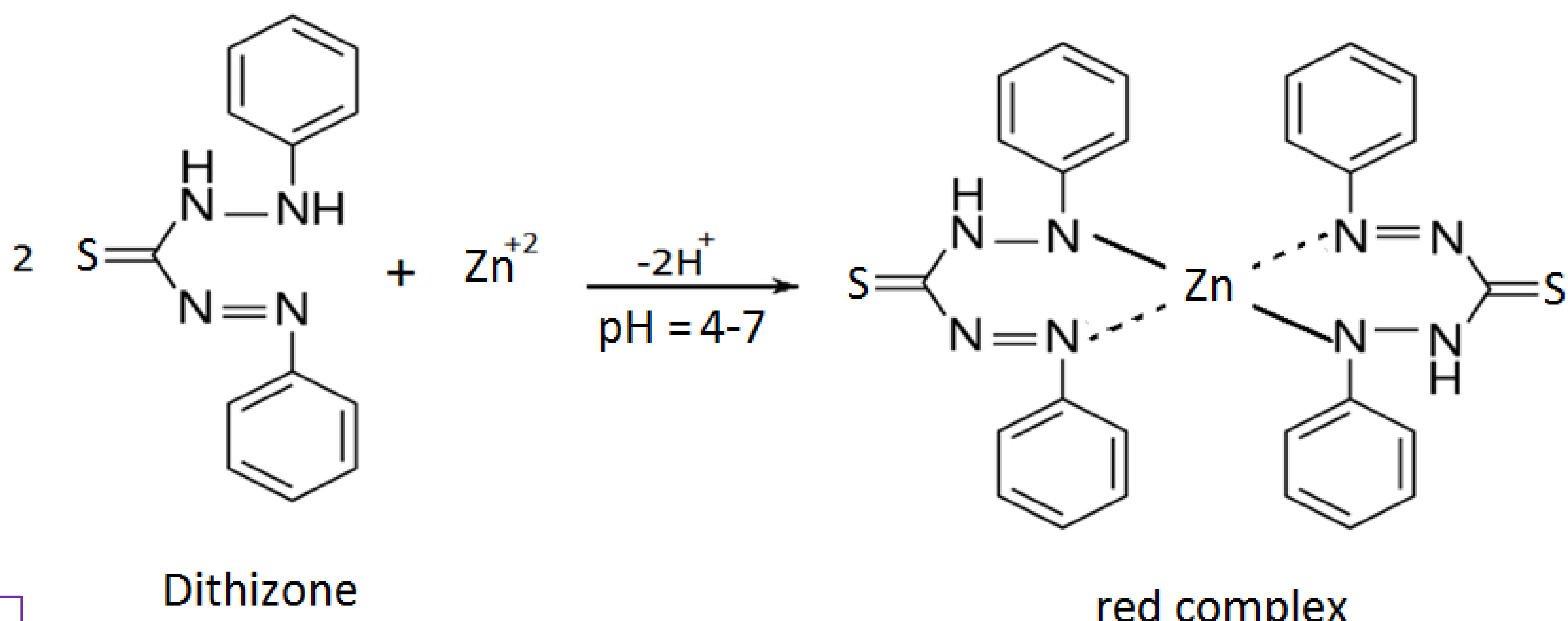
Chemical reactions

- Dithizone method
- Ferrocyanide method

Give reason: contamination of water sample by Zinc ions points to the presence of Pb^{2+} and Cd^{2+}

Dithizone method

- Zinc reacts with dithizone (diphenyl thiocarbazone) reagent in weakly acidic medium to form a red compound (zinc dithizonate) which is extractable with CCl_4 and measured photometrically.



Interferences

- Dithizone is not a specific reagent for zinc.
- In the pH range 4 → 7 Cu^{2+}, Bi^{3+}, Ni^{2+}, Pb^{2+}, and other elements can be complexed by the reagent.
- These elements can be masked by the addition of **~~KCN~~** and sodium thiosulfate, by forming stable complexes.

Ferrocyanide method (Turbidimetric ↓)

$$2\,ZnSO_4 + K_4[Fe(CN)_6] \xrightarrow{Na_2SO_3} Zn_2[Fe(CN)_6]\downarrow + 2\,K_2SO_4$$

Potassium Ferrocyanide

Zinc ferrocyanide
white ppt.

Interferences

- Fe^{3+} interferes with the determination of zinc, it gives blue colored complex of $Fe_3\,[Fe(CN)_6]_2$ (Ferrous Ferri cyanide).
- Sodium sulphite Na_2SO_3 reduces Fe^{3+} to Fe^{2+}.

Lab Case Study:

Given a sample of drinking water contaminated with Zinc ions, illustrate how to analyze the sample after the removal of all expected interferences .

Keys to answer:

1- check whether Zn ion is oxidizing or reducing agent…..

2- write all the oxidizing contaminants that could be present in your sample……..

3- solve the problem of each of the oxidizing interferences…….

4- write the method of determination of the required component…..

[6.e.] Copper ions (Cu^{2+}, Cu^{+})

Sources

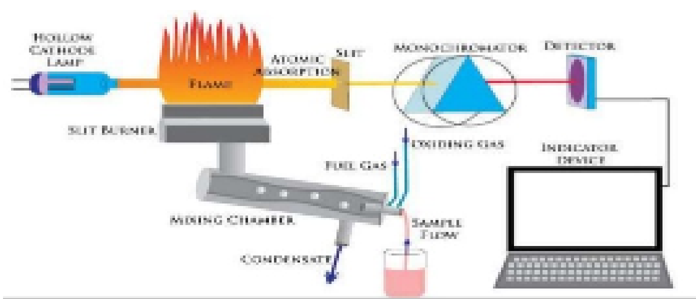
- $CuSO_4$ is added to water tanks to control algae growth.

Significances

- Traces of copper is **essential** for normal body metabolism, its absence may cause anaemia in children.
- Permissible conc. limit in drinking water according to WHO is **1 mg/l**

Methods of Determination of Cu^{2+}, Cu^{+}

Atomic absorption spectrophotometric method

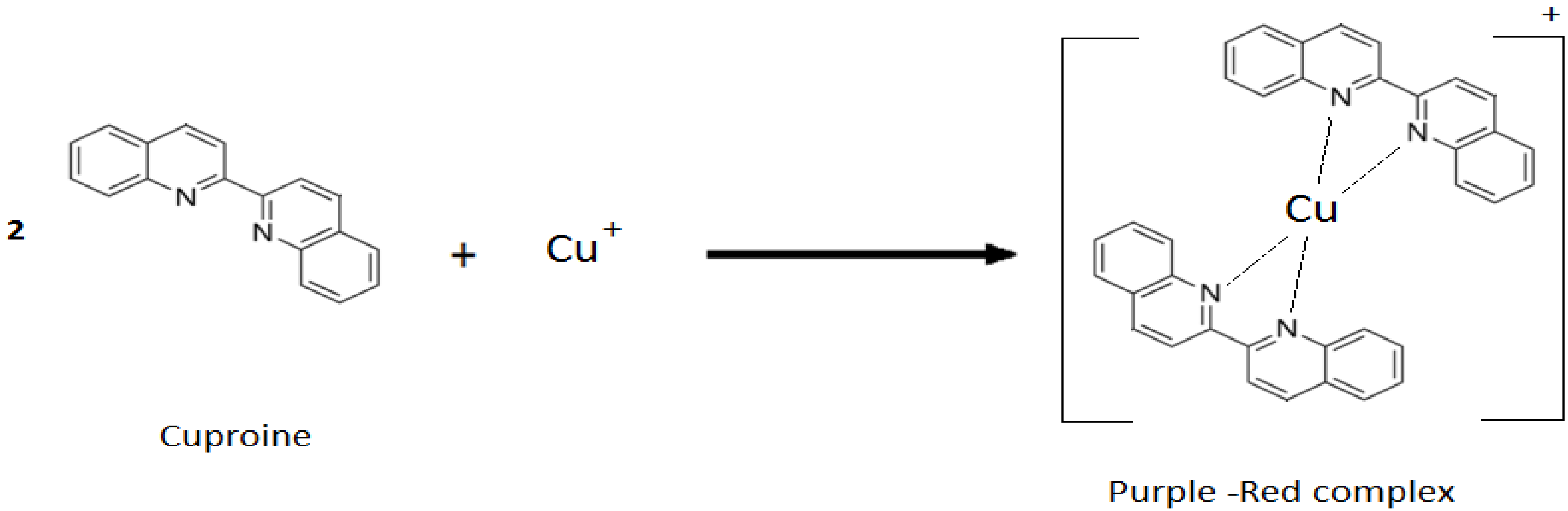


Chemical reactions

- Cuproine method
- Diethyl dithiocarbamate method
- Turbidimetric method ↓

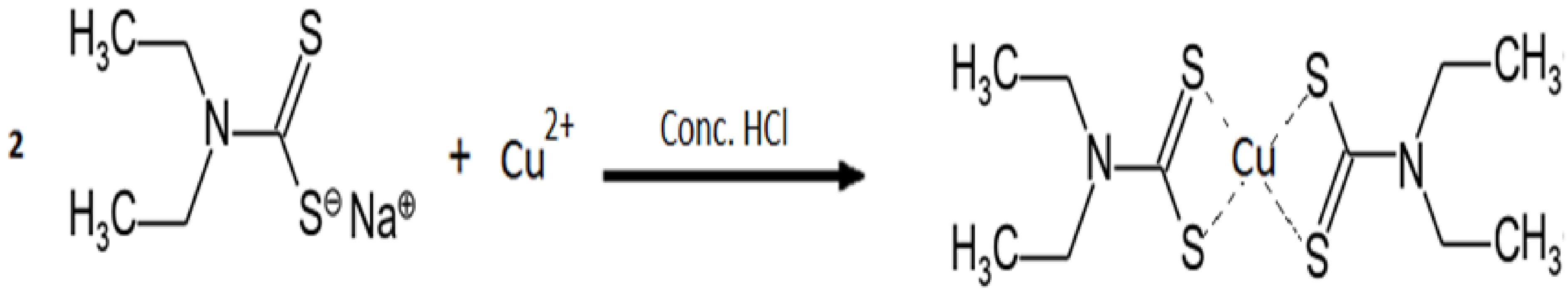
Cuproine method

- Copper (I) ions combine with 2,2-biquinoline (cuproine) in alcoholic-aqueous solution to form a purple red complex.
- copper (II) ions must be reduced prior to the reaction.



Diethyl dithiocarbamate method

- Copper (II) ions combine with diethyl dithiocarbamate to form Golden yellow complex.
- Absorbance is measured at λ_{max} = 435 nm



Golden yellow
complex

Turbidimetric method ↓ (Ferrocyanide)

$$2\ Cu^{2+} + K_4[Fe(CN)_6] \xrightarrow{Na_2SO_3} Cu_2[Fe(CN)_6]$$

Potassium Ferrocyanide

Brown ppt.

Interferences

- Fe^{3+} interferes with the determination of zinc, it gives blue colored complex of $Fe_3\,[Fe(CN)_6]_2$ (Ferrous Ferri cyanide).
- Sodium sulphite Na_2SO_3 reduces Fe^{3+} to Fe^{2+}.

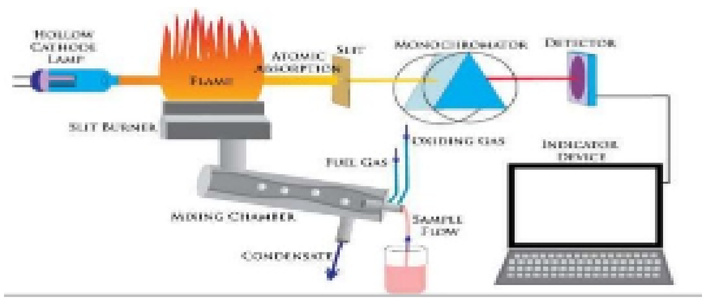
[6.f.] Lead ion (Pb^{2+})

Sources

- ❑ Water stored in tanks and pipes painted with lead.

Significances

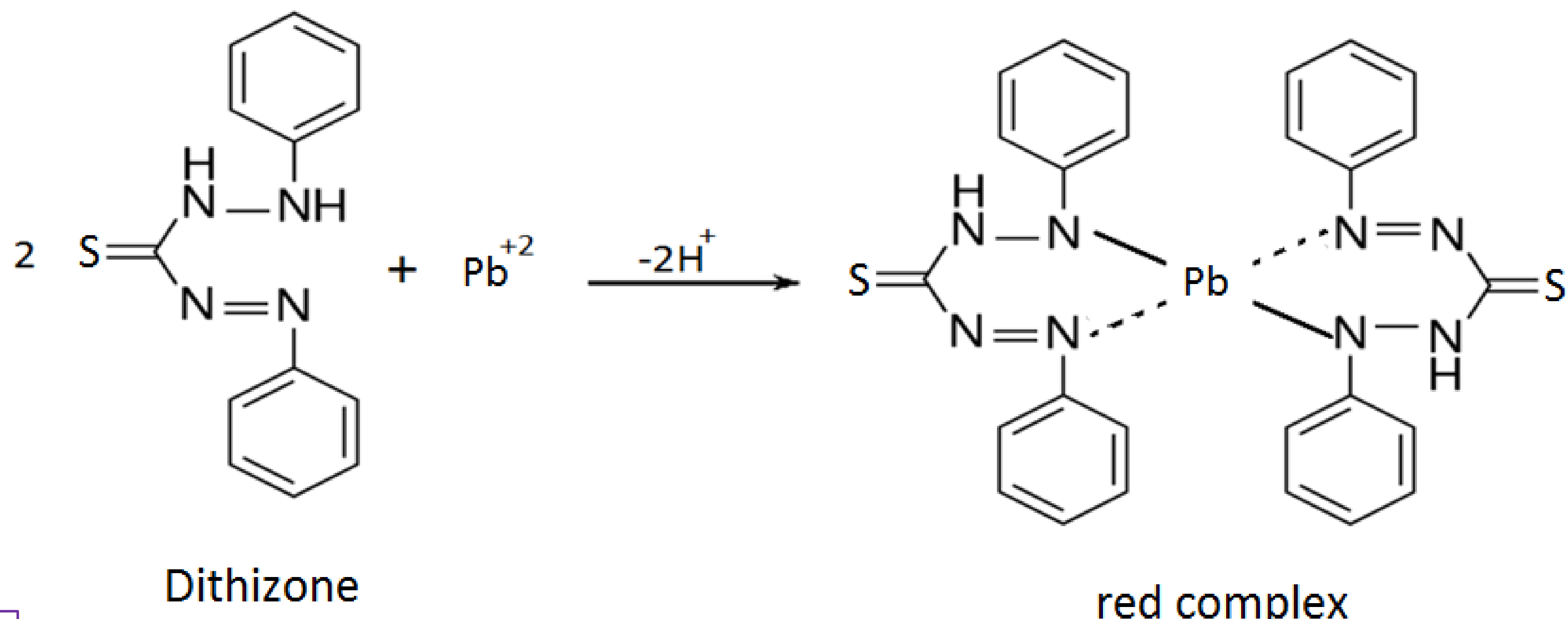
- ❑ Lead is a serious poison; it accumulates in the bone structure and may cause brain damage and death.
- ❑ Maximum allowed limit in drinking water **0.1 mg/l**.



Dithizone method
(Photometric)

Dithizone method

- Dithizone (diphenylthiocarbazone) reagent reacts with lead in basic solution containing citrate buffer to give red color of lead dithizonate complex which is extracted in $CHCl_3$ and measured photometrically.



Interferences

- Interfering elements are Bi^{3+}, Cu^{2+}, Hg^{2+}, Ag^{+}, Zn^{2+}, Sn^{2+}.
- Reduction with hydrazine acetate to lower the oxidation state of elements that capable of oxidizing the dithiazone.
- The interfering ions are then removed by complexation with dithiazone at pH 2-3
- Pb^{2+} is extracted at pH 8-9 (by addition of citrate buffer).

Q: pH meter is an essential apparatus in the experiment of determination of Pb^{2+}????

ANALYSIS OF BASIC RADICALS OR CATIONS

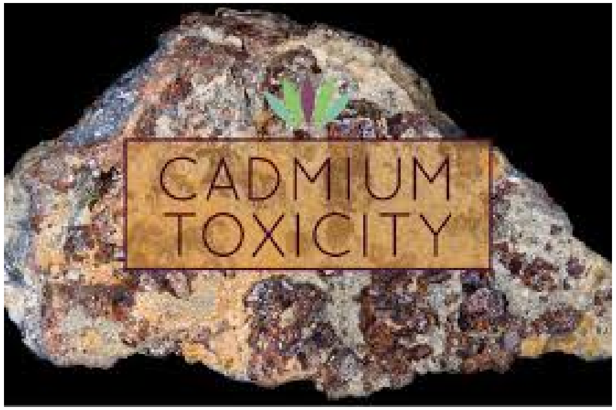
This is classified into 6 groups. They are mentioned as below:

GROUP	RADICALS	GROUP REAGENTS
I	Pb^{2+} , Ag^{+}	Dilute Hydrochloric acid(HCl)
II	Pb^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+}	Dilute HCl + H_2S gas.
III	Al^{3+} , Fe^{2+} , Fe^{3+}	NH_4Cl(s) + NH_4OH
IV	Zn^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+}	NH_4Cl(s) + NH_4OH + H_2S gas
V	Ca^{2+} , Sr^{2+} , Ba^{2+}	NH_4Cl(s) + NH_4OH + $(NH_4)_2CO_3$
VI	Mg^{2+} , NH_4^{+}	-Nil-

[6.g.] Cadmium(Cd^{2+})

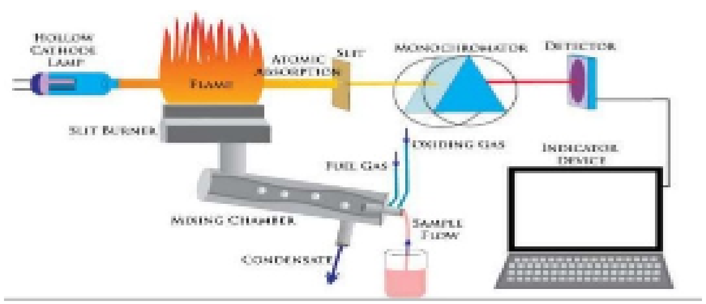
Sources

- ❑ Cadmium may enter water from deterioration of Galvanized pipes.
- ❑ From Industrial effluents.



Significances

- ❑ Cadmium is highly toxic
- ❑ Maximum allowed limit in drinking water **0.4 µg/l.**



Concentrations of metal ions found in water sample do not interfere with the Cd^{2+} measurements?

Dithizone method (Photometric)

1. Adjust the pH for the complexation
2. Cd^{2+} form red complex with the dithizone
3. The complex is extracted with chloroform
4. The extract is measured photometrically at certain wavelength.
5. Cd^{2+} conc. Is obtained by standard calibration curve (standard solution of Cd^{2+})

[6.h.] Mercury (Hg^{2+})

Sources

- Levels of mercury in the environment are increasing due to discharge from **hydroelectric**, mining, and **paper industries**.

Significances

- Mercury is highly toxic
- No standards for mercury or its salts (not allowed to present in the potable water).

  Minimum detectable quantity is **1µg/l**

Cold Vapor Atomic Absorption (CVAA) Spectroscopy for Hg

- Free Hg atoms exist at room temperature, no requirement for heating
- Sample may contain Hg^0, Hg_2^{2+} or Hg^{2+}
- Reduction with a strong reducing agent (e.g. $SnCl_2$ or $NaBH_4$)

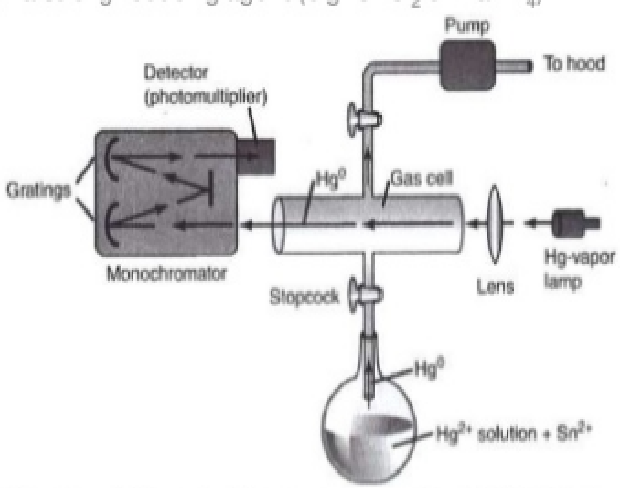
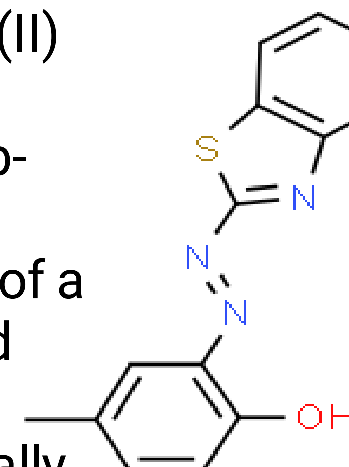


Figure 9.5 Schematic diagram of cold vapor mercury analyzer (Girard, JE, Principles of Environmental chemistry, 2005, Jones and Bartlett publishers, Sudbury, MA. WWW.jbpub.com. Reprinted with permission.)

(Photometric)

1. A colored complex is formed between Hg(II) and 2-(2-benzothiazolylazo)-p-cresol.
2. mercury in the form of a complex is extracted and determined spectrophotometrically at 650 nm



[7] Water hardness

Ca^{2+} & Mg^{2+}

Types of hardness

- Generally hardness is due to Ca^{2+}, Mg^{2+} (mainly) and Fe^{3+} ions.

Temporary hardness

- Due to the presence of calcium and magnesium as **bicarbonate**.
- Temporary hardness is destroyed and removed by boiling.

Permanent hardness

- Due to the presence of **sulphates, chlorides** and **nitrates** of calcium and magnesium.

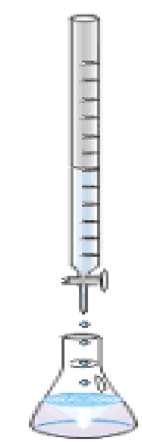
Classification of water

Waters are commonly classified in terms of the degree of hardness.

Type water sample	Hardness in terms of mg $CaCO_3$/L
Soft water	0-75 ppm
Moderately Hard water	75-150 ppm
Hard water	150-300 ppm
very Hard water	300ppm or more

Palmitate method for (Total hardness)

❖ The hard water sample is titrated with standard solution of potassium palmitate. Palmitate anion precipitates Ca^{2+}/ Mg^{2+} cation producing insoluble Ca & Mg palmitates. Any excess amount of the palmitate solution will be hydrolysed rendering the solution alkaline to ph.ph.



❑ <u>During titration :</u>

K-palmitate + $CaCl_2 \rightarrow$ Ca-palmitate + 2KCl

$MgCl_2 \rightarrow$ Mg - palmitate

(white precipitates)

❑ <u>At the end point:</u>

Hydrolysis

K palmitate $\rightarrow$ KOH + palmitic acid (salt of weak acid)

(pink colour with ph.ph.)

Palmitate method

- For magnesium hardness alone, the calcium should be first precipitated as Ca-oxalate.
- For the determination of permanent hardness only, the temporary hardness is first removed by boiling.

ETDA method

*(For total Ca^{2+} and Mg^{2+} contents)

- water sample + buffer **pH= 10** using NH_4Cl/NH_4OH
- titrate with st. EDTA using **Erio-T indicator**.

* For calcium hardness alone :

- water sample **+ NaOH to pH=12**
- titrate against st. EDTA using **Murexide indicator**.
- Mg hardness is measured by difference.

[8] Water alkalinity, Basicity and pH

It is caused by dissolved carbon dioxide "free carbonic acid", mineral acids and salts of **strong acids** and weak bases.

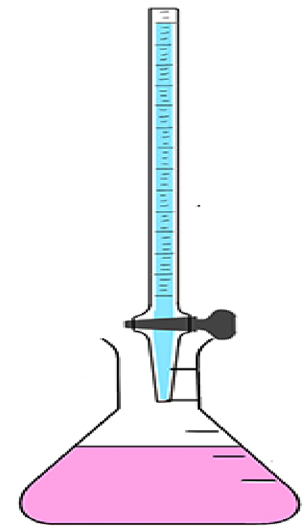
It is usually caused by the presence of strong or weak bases dissolved in water (e.g. carbonate, bicarbonate, phosphate, silicate and borate ...).

It is determined potentiometrically, using pH-meter.

The determination of water acidity, alkalinity and pH gives an indication of the degree of the corrosivity of water.

Water acidity (Base capacity)

This determination is important in water analysis as a basis for calculating the **dissolved carbon dioxide content**.



Determination : (Titrimetry)

- (a) Total acidity:

  water sample is titrated ≠ st. alkali (NaOH) using p ph. indicator.

- (b) Mineral acids acidity:

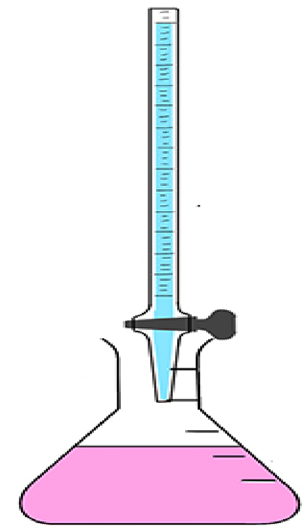
  water sample is titrated ≠ st. alkali (NaOH) using M. O. indicator.

* The acidity is calculated as ppm $CaCO_3$.

Eq.wt. of $CaCO_3$ x 1000

$$\text{Acidity as mg/l } CaCO_3 = \frac{(N \times V)_{NaOH} \times 50000}{\text{ml sample}}$$

Water Basicity (Acid capacity)



Determination: (Titrimetry)

- (a) *Phenophthalein alkalinity* :
  Titrate water sample against st. acid using ph.ph. indicator.
- (b) *Methyl orange alkalinity* :
  Titrate ≠ st. acid using M.O. indicator.
- The alkalinity is calculated as ppm $CaCO_3$.

$$\text{Alkalinity or } [\text{Alk}]_T \text{ as mg/l } CaCO_3 = \frac{(N \times V)_{HCl} \times 50000}{\text{ml sample}}$$

Reference:

Standard Methods for the Examination of Water and Wastewater

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