

1-1 Chromium:

1-1-1: Historical and occurrence of chromium:

A French chemist discovered a new element in 1797 while a mineral found in Siberia.

It was named chromium because formed colored compound

(Greek word, chromium = color)

Chromium doesn't occur free in nature its principal ore is chromite or $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. It's also found as chrome ochre Cr_2O_3 and Crocoisite PbCrO_4 . Chromium is found in large quantities in south Africa, Turkey, Russia and India.

1-1-2: Properties:

Physical Properties

A brilliant silvery metal which is very hard and brittle. It melts at 2173 K, boils at 2963 and has specific gravity 7.2.

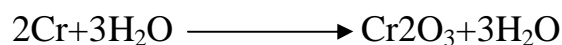
Chemical Properties

Action in Air ?

Does not burn even in moist air but is oxidized to chromic oxide when heated to high temperature in the Oxy-Hydrogen flame.

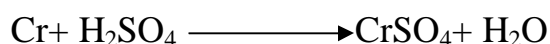
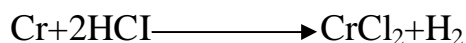
Action of water:

There is not action to ordinary temperatures how, ever it decomposes steam at red heat to give chromic oxide and Hydrogen

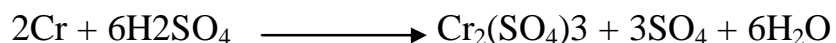


Action of Acids:

Dissolves dilute hydrochloric and sulphuric acid to liberate hydrogen and forming chromous salt.



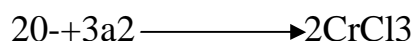
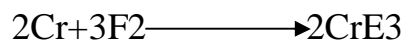
Hot concentrated sulphuric acid gives a chromic sulphate and liberate sulphure dioxide.



Dilute nitric acid doesn't attack the pure metal while concentrated acid render it inactive.

Combination with Halogens:

Chromium combines directly with the flouring and dry chlorine togive chromium III halides.



1-1-3 Uses:

In Chrome Plating:

The articles to be plated with chromium are made the cathode in an electrolytic bath consisting of solution of chromic acid and sulphuric acid, while the anode is made of a plate of lead.

-In Manufacture of alloy steel:

Example chrome steel, chrome vanadium steel and tungsten steel.

1-1-4: Compound of Chromium:

General:

Outer electronic configuration of chromium is $3d^5 4s^1$ and exhibits oxidation state from 0 to 6.

The most important and is table is oxidation state of chromium are +2, +3 and + 6.

Oxides and Hydroxides:

Chromium forms three oxides:

Chromous CrO , chromic oxides Cr_2O_3 , and chromium trioxide CrO_3

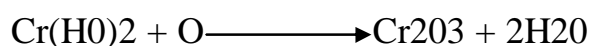
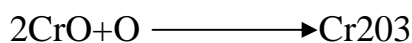
Chromium “II” Oxides:

Or chromous oxide , CrO and chromium “II” hydroxide or chromous hydroxide $Cr(OH)_2$.

Chromous oxides is obtained by gently warming chromium amalgam with dilute nitric acid. . The patten dissolves the mercury leaving behind a black residue of chromium oxide.

Chromous hydroxide $\text{Cr}(\text{OH})_2$ is obtained as brownish yellow precipitate by the action of alkali on chromous solution.

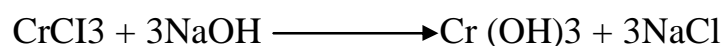
Both of these are very rapidly oxidized to chromic oxide.



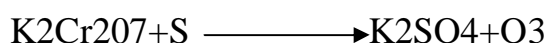
Chromium “III” oxide (Cr_2O_3):-

It may be prepared by either by the following method

1-When alkali is added to solution of chromic salt, Chromic hydroxide is precipitated which on ignition yields chromic oxide.



2- It is also formed when a dichromate is reduced by heating with sulphur.



Properties:

it is a green powder which is not decomposed by heat or reduced by hydrogen.

It can be reduced to metallic chromium by heating it with carbon better still with aluminum powder at high temperature.

Uses:

- It used as a green pigment oil paints under the name of chrome green.

- For coloring glass green.
- It is used as chromium dyes.

Chromium ‘VI’ oxide, chromium trioxide:-

Also named chromic anhydride (CrO₃)

It's obtained as dark red crystals when a well cooled solution of potassium dichromate is treated with concentrated sulphuric acid.

Potassium dichromate K₂Cr₂O₇:

-Properties:

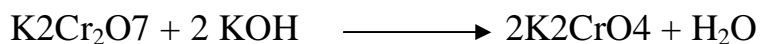
Give orange-red crystals soluble in water.

Action of heat it decomposes on heating to white heat and gives out oxygen.



Action of Alkali:

With the alkali it gives chromate



Oxidizing action: in neutral or in acidic solution, potassium dichromate furnishes nascent and thus act as excellent oxidizing agent.

Uses:-

- as oxidizing agent in organic chemistry.
- in volumetric analysis.
- for the preparation for other chromium compounds.

1-1-5: Chrome Tanning:

Tanning is the art or process of preparing leather from hid skin. Formerly, tanning of leather was done exclusively with various bark extracts. it was a slow process and required many month . The period has been reduced to a few hours when fanning is done with chromium compound (chrome tanning) Sodium dicharomate is used extensively in chrome . Tanning of leather it is reduced with sulphur dioxide when a sluble compound basic chromic sulphate $\text{Cr}(\text{OH})_5\text{O}_4$ is obtained.



1-1-6: Coordination complexes of chromium:

A large number of coordination complexes of Cr^{+3} are known in which the element exhibits a coordination number of “6”.

For example:

$[\text{Cr}(\text{H}_2\text{O})_6]^{+3}$, $[\text{Cr}(\text{NH}_3)_6]^{+3}$, $[\text{Cr} \text{C}_6]^{-3}$, $[\text{Cr}(\text{CN})_6]^{-3}$ Health effect

1-1-7: Health effects of chromium

People can be exposed to chromium through breathmg, eating or drinking and through skin contact with chromium or chromium compounds. The level of chromium in air and water is generally low. In drinking water the level of chromium is usually low as well but contaminated well water may contain the dangerous chromium (IV); hexavalent chromium. For most people eating d that contains chromium(Ii1) is the main route of chromium uptake as chromium(III) occurs naturally in many vegetables, meats, yeasts and grains. Various ways of food lion and storage may alter the chromium contents of I When food in stores in steel tanks or cans chromium concentrations may rise.

Chromium (III) is an essential nutrient for humans and shortages r cause heart conditions, disruptions of metabolisms and diabets. But the uptake of too much chromium (III) can cause effects as well, for instance skin rashes.

Chromium (VI) is a danger to human health, mainly for people work in the steel and textile industry. People who smoke tobacco also have a higher chance of exposure to chromium.

Chromium (VI) is known to cause various health effects. When it is a compound in leather products, it can cause allergic reactions, such as skin rash. After breathing it in chromium (VI) can cause nose irritations and nosebleeds.

Other health problems, that are caused by chromium (VI) are:

- Skin rashes.
- Upset stomachs and ulcers.
- Respiratory problems.
- Weakened immune systems.
- Kidney and liver damage.
- Alteration of genetic material.
- Lung cancer.
- Death.

The health hazards associated with exposure to chromium are dependent on its oxidation state. The metal form (chromium as it exists in this product) is of low toxicity. The hexavalent form is toxic. Adverse effects

of the hexavalent form on the skin may include ulcerations, dermatitis, and allergic skin reactions.

Inhalation of hexavalent chromium compounds can result in ulceration and perforation of the mucous membranes of the nasal septum, irritation of the pharynx and larynx, asthmatic bronchitis, bronchospasms and edema. Respiratory symptoms may include coughing and wheezing, shortness of breath, and nasal itch.

Carcinogenicity Chromium and most trivalent chromium compounds have been listed by the National Toxicology Program (NTP) as having inadequate evidence for carcinogenicity in experimental animals. According to NTP, there is sufficient evidence for carcinogenicity in experimental animals for the following hexavalent chromium compounds; calcium chromate, chromium trioxide, lead chromate, strontium chromate, and zinc chromate. International Agency for Research on Cancer (IARC) has listed chromium metal and its trivalent compounds within Group 3 (The agent is not classifiable as to its carcinogenicity to humans.) Chromium is not regulated as a carcinogen by OSHA (29 CFR 1910 Subpart Z). ACGIH has classified chromium metal and trivalent chromium compounds as A4, not classifiable as a human carcinogen.

1-1-8: Environmental effects of chromium:

There are several different kinds of chromium that differ in their effects upon organisms. Chromium enters the air, water and soil in the chromium(III) and chromium (VI) form through natural processes and human activities.

The main human activities that increase the concentrations of chromium (III) are steel, leather and textile manufacturing. The main human activities that increase chromium (VI) concentrations are chemical, leather and textile manufacturing, electro painting and other chromium (VI) applications in the industry. These applications will mainly increase concentrations of chromium in water. Through coal combustion chromium will also end up in air and through waste disposal chromium will end up in soils.

Most of the chromium in air will eventually settle and end up in waters or soils. Chromium in soils strongly attaches to soil particles and as a result it will not move towards groundwater.

water chromium will absorb on sediment and become immobile.

Only a small part of the chromium that ends up in water will eventually dissolve.

Chromium (III) is an essential element for organisms that can disrupt the sugar metabolism and cause heart conditions, when

the daily dose is too low. Chromium (VI) is mainly toxic to organisms. It can alter genetic materials and cause cancer. Crops contain systems that arrange the chromium-uptake to be low enough not to cause any harm. But when the amount of chromium in the soil rises, this can still lead to higher concentrations in crops. Acidification of soil can also influence chromium uptake by crops. Plants usually absorb only chromium (III). This may be the essential kind of chromium, but when concentrations exceed a certain value, negative effects can still occur.

Chromium is not known to accumulate in the bodies of fish, but high concentrations of chromium, due to the disposal of metal products in

surface waters, can damage the gills of fish that swim near the point of disposal.

In animals chromium can cause respiratory problems, a lower ability to fight disease, birth defects, infertility and tumor formation.^[1]

1-2: Lead

1-2-1: Historical:

Lead was one of the metals known to the ancients. The Romans used lead for marking water pipes and some lead compounds were employed as cosmetics and paints. The modern symbol (Pb) is derived from its Latin name plumbum.

1-2-2: Occurrence:

Although lead occurs in nature as the carbonate cerussite $PbCO_3$, and the sulphate anglesite $PbSO_4$ the principal ore of lead is galena PbS . Which occurs as grayish black cubical crystals. It is often found associated with the sulphides of copper, zinc and antimony.

The chief lead producing countries are the U.S., Spain and Mexico.

1-2-3: Properties of Lead:

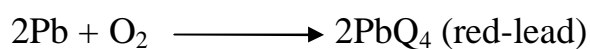
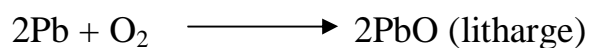
- Physical properties:

Lead is soft, bluish grey metal with low tensile strength, it melts at 600 K

It is a heavy metal that has a specific gravity of 11.34. It is highly malleable and can be rolled into foils but is not ductile. Lead wire may, however, be made by forcing the heated metal through a die but the wire lacks strength. It is a poor conductor of electricity.^[2]

- Chemical properties:

Valence: lead exhibits variable valence positive 1, 2 and 4. Action of air. dry air has no action on lead but in the moist air a protective coating of basic carbonate is formed and protects it from further oxidation. When heated in air forms litharge but at a higher temperature it is oxidized to red lead.



Action of water:

Lead dissolves in water containing dissolved air due to the formation of lead hydroxide.

This solvent action of water on lead is called Plumbo solvency.

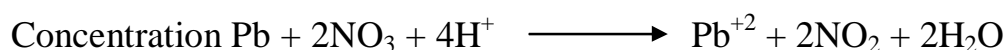
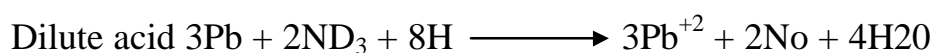
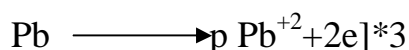
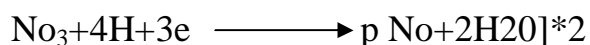
All soluble lead compounds are very poisonous and tend to accumulate in the body.

Thus small doses of lead salts over a long period finally add up and prove fatal.

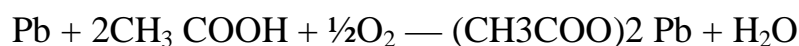
Lead pipes should therefore be used with caution for conveying drinking water.

Action of acid

Hydrochloric acid and sulphuric acid have little effect upon lead but nitric acid reacts with it vigorously. Nitric oxide with the formation of nitrate in each case.

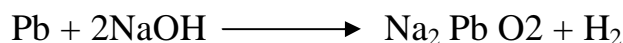


Acetic acid and many other organic acids react with the lead in presence of oxygen.



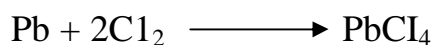
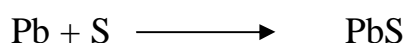
Action of Alkali:

Lead slowly dissolved in caustic alkali with the formation of plumbite and hydrogen.



Action of chlorine and sulphure:

Lead combines with chlorine and sulphure on heating



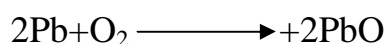
1-2-4 Uses of lead:

- i- Lead is used for making pipes and containers for corrosive.
- ii- Sheet lead is used for making lead chambers of sulphuric acid plant.
- iii- Underground telephone cables and protect by lead covering.
- iv- It's used in strong batteries.
- v- It's used in many alloys for example type metal contains 82 percent lead 15percent antimony, and 3 percent tin. It is used for making types.

1-2-5 Compounds of lead:

- Lead monoxide, PbO

It is obtained as a yellow powder called massicot . When lead is heated in air to about 575k. At higher temperature (1150 k) it fuses to give reddish yellow crystalline mass called litharge.



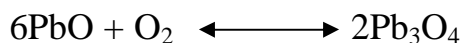
-Uses

Lead monoxide is used in making glass; in the paint and varnish industries; in making lead salts and glazing pottery.

mixed with glycerine is employed as a cement for glass and stone.

- Red lead Pb_3O_4 :-

Red lead is obtained when lead monoxide is heated to about 615k in excess a faire



It's red powder in soluble in water and decomposes on heating giving oxygen

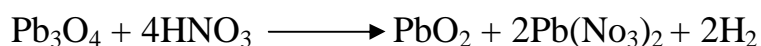
-Uses:

Red lead is used to make protective paint for iron and steel.

It is used as oxidizing agent in the laboratory

- Lead dioxide PbO_2 :-

It's obtained as a chocolate brown powder when red lead is treated with nitric acid

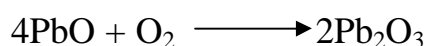


-Uses:

Oxidizing agent

Lead sesquioxide Pb_2O_3 :

It's obtained as a yellowish red powder by heating lead monoxide to 775k in air



-Lead carbonate and white lead:

It occurs native as cerussite in laboratory it may be obtained by adding sodium bicarbonate to the solution of lead



- Properties and uses:

It's a white paint with good covering power which darkens by the action of hydrogen sulphate due to formation of lead sulphide it's used as a white paint.

1-2-6: Paints and Pigments:

A paint may be defined as a fluid of finely divided solute which when applied to surface will dry up to an opaque or transparent film either by oxidation or evaporation it consists of two parts :-

i- A solid which when dispersed in a medium gives a paint this is called pigment.

ii- A liquid known as a vehicle in which the pigment is dissolved to yield a paint.

Paints are used for decoration purposes and also for the protection of the surface against environmental, insect and fungous attacks.

Pigment which yield paints can be classified according to their color:

- White pigment:

Basic lead carbonate (white lead)

- Red pigment:

Red lead

1-2-7: Health effect of lead:

1-2-7 Health Risks of Lead Exposure:

Short-term exposure to high levels of lead can cause vomiting, diarrhea, convulsions, coma or even death. Severe cases of lead poisoning are rare in Canada.

However, ongoing exposure to even very small amounts of lead can be harmful, especially to infants and young children. Lead taken in by pregnant women can also pose a danger to the health of unborn children. You may not notice the symptoms of long-term lead exposure but they are still serious. Anaemia is common and lead can also affect the brain and nervous system. Other signs are:

- Appetite loss
- Abdominal pain.
- Constipation
- Fatigue.
- Sleeplessness.
- Irritability.
- Headache.

If you are continually exposed to lead, as in an industrial setting, it can affect your kidneys.

Lead exposure is most serious for young children because their growing bodies absorb lead more easily than adults and they are more susceptible to its harmful effects. Even low level lead exposure may harm the intellectual development, behaviour, size and hearing of infants. During pregnancy, especially in the last trimester, lead can cross the placenta and affect the unborn child. Female workers exposed to high levels of lead have more miscarriages and stillbirths.

If you are concerned about lead exposure, your doctor can conduct a simple blood test to measure your blood lead level. Your doctor will recommend corrective action if the amount is over 10 micrograms per decilitre.

1-2-8: Sources of Lead Exposure:

Food

Traces of lead are found in almost all food. Airborne lead falls onto crops or soil and is absorbed by plants. Lead solder used in making cans can also contaminate food. However, in Canada food manufacturers have eliminated the use of lead-soldered cans. Infants can also absorb lead from their mothers' bodies through breast milk.

-Air

Lead is released into air through industrial emissions, smelters and refineries. With the introduction of unleaded gasoline in Canada in 1975, lead concentrations in the air have declined significantly, falling 76% between 1973 and 1985. Leaded gasoline in cars was banned in Canada in 1990. Since then levels of lead in the air of most Canadian cities have dropped below detectable limits.

- Dust and Soil

Dust and soil can be significant lead exposure sources, especially for young children. Lead in soil can come from the air or from erosion of lead-bearing rocks, and may be carried indoors as dust. Lead dust can also come from within the home, especially older homes that used lead-based paints or lead solder. Lead dust is especially dangerous for babies and young children, because they tend to put things in their mouths and their breathing zone is closer to floor level where lead dust tends to collect.

-Drinking Water

In most of Canada, the amount of lead in natural water supplies is very low. However, lead can enter the water supply from lead solder in plumbing, lead service connections or lead jps in your home. Homes built before 1950 often have leaded distribution lines and service connections.

In homes, lead may leach from solder for several years until the pipes form a protective oxide layer. Lead is more likely new homes. The National Plumbing Code of Canada does not permit the use of lead solder in new drinking water plumbing or in repairs to existing drinking water systems. Several provinces also limit the amount of lead solder in drinking water supply lines.

Lead levels in tap water increase as water stands in pipes. Drinking fountains may have higher levels of lead than water from nearby taps, because the water usually sits for a longer time. They may also have more soldered joints.

-Paint

In 1976, the amount of lead that could be added to interior paints was limited by law, but exterior paints could still contain higher amounts of lead, provided they carried a warning label. Under the Surface Coating Materials Regulations, which came into effect in 2005, the lead limit was further reduced. Paint manufacturers could no longer add lead to their paint. Canadian manufacturers of interior and exterior consumer paints had already been voluntarily keeping to this limit since 1991. Some specialty coatings, such as artists' paints and metal touch-up coatings, can contain high levels of lead, but if they do, they must be labelled to warn (against applying the paint to surfaces that children and pregnant women might come in contact with).

Most indoor and outdoor paints produced before 1950 contained substantial amounts of lead. If you spray or sand old paint that contains lead, you could breathe in lead particles.^[3]

1-3: Cobalt

1-3-1: Historical:

Cobalt was discovered in 1735 by Brandt who isolated the metal in 1742. It is named after the German word for cobalt meaning goblin or evil spirit.

1-3-2: Occurrence:

Cobalt doesn't occur free in nature in the combined state, it occurs mainly as an arsenide in association with several other metals such as iron, nickel and silver in smaltite, speiss, COASS, and cobaltite or cobalt glance COASS.

Many cobalt ores contain varying amounts of silver. Small amounts of cobalt are present in the ores of some other metals and are obtained as a by-product during the refining of zinc, copper and manganese. The presence of cobalt in vitamin B12 is of considerable biochemical interest.

13-3: Properties:

- Physical properties:

It's a bright silvery metal with slight reddish tinge:

It's slightly harder than iron and takes good polish.

The metal is very tenacious, malleable and ductile.

Its various physical constants are:

Melting point = 1768 K.

Boiling point = 3373 K.

Atomic mass = 58.93.

Atomic number = 27.

Density = 8.9

It is more magnetic than any other metal except iron and retains its magnetic properties up to about 1.370 k.

The metal exists in at least two allotropic forms with transition temperature of about 760 k. The allotrope stable below this temperature is in hexagonal close packing while the one stable at about this temperature is in cubical close packing.

-Chemical properties:-

-Action of air:

Cobalt is not affected by air at room temperature. If heated in air the metal is slowly oxidized to Co_3O_4 .

Action of alkali:

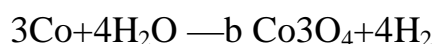
It is little attacked by even concentrated caustic soda solution. It is however attacked by melted caustic potash at 820 k.

-With carbon monoxide:

Finely divided cobalt combines with carbon monoxide at 420 k and under 30 atmospheres pressure to form carbonyl $\text{Co}_2(\text{CO})_2$ an orange colored powder.

-Action of Steam:

It decomposes steam when passed over heated metal



1-3-4: Uses:

I- In Electroplating

ii- For the manufacture of special steel for example Satellite contains 55% Co, 15% Cr, 22% W and 5% Mo.

1-3-5: Compound of cobalt:

Cobalt give to series of salts , cobalt “II” or cobaltous .and cobalt “III” or cobaltic.

- Cobalt “II” oxide or cobaltous oxide CoO :

It is obtained as a dark brown or olive-green powder by heating

cobaltous hydroxide nitrate or carbonic to 1270 k in the absence of air.

- **Uses:**

It's employed for preparing cobalts salt

Blue glass pigment

- Cobalt i/f/I) chloride or cobaltous chloride CoCl_2

Ruby-red monoclinic crystals of the hydrate salt — $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ are obtained by crystallizing a solution of cobaltous oxide in hydrochloric acid.

It's property of changing colors on heating.

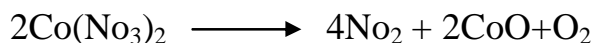
- **Uses:**

I Its used in synthetics inks anything written with cobalt chloride solution when becomes visible on heating

-Cobalt to nitrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$:

It is prepared by dissolving cobalt carbonate in dilute nitric acid and evaporating the solution.

The salt decomposes in heating giving nitrogen dioxide.



- Uses:

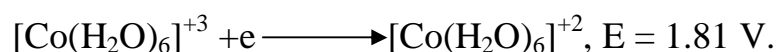
It's used in the detection of aluminum, Zinc and magnesium by Charcoal test.

-Cobalt "II" sulphide:

It is obtained as black precipitate when a solution cobalt (II) salt is treated with ammonium sulphide.

1-3-6 complex of cobalt:

Cobalt "III" is unstable in water and only a few simple salts can be isolated. The aqua complex $[\text{Co}(\text{H}_2\text{O})_6]^{+3}$ is strong oxidant.



$[\text{CoF}_6]^{3-}$ is only halogen complex of cobalt "III" and also is only one which is high spin and hence paramagnetic.^[4]

1-4 Nickel:

1-4-1 Historical:

Nickel was discovered by Cronstedt in 1751. It was isolated from an Ore which was called Kupfer Nickel, German term meaning false copper, and was called nickel.

1-4-2: Occurrence

Nickel is present in meteoric iron * chief ore of nickel are:

i- Smaltite (Fe, Co, Ni) as.

ii- Kupfer nickel or nickoflite Ni As.

jj- Pentlandite (Ni, Cu, Fe) S.

iv- Garnierite (Ni, Mg) H_2SiC_4 .

In these metal is associated with copper, iron , cobalt and small amounts of silver, gold and the platinum metals .The ore are usually very lean and as obtained from the mine contain only about 2 percent of Nickel and about double this amount of copper.

1-4-3 Properties:

- Physical properties:

Nickel is a silver white fairly soft metal both malleable and ductile and can be highly polished:

- It's a heavy metal with density 8.9:

- Melting point 1725 k.

-Boiling point 3193 k.

- It can easily forged and welded and rolled into sheets. It can be magnetized though not so intensely as iron.
- Divided nickel can adsorb large quantities of hydrogen

Molten nickel occludes 17 times its volume of hydrogen which is given out energetically on solidification of the metal. The phenomenon is called or known as spitting.

- Chemical properties:

With air or oxygen:

Nickel is resistant to oxygen at room temperature but reacts slowly when heated to yield the oxide (NiO).

In air containing oxide of sulphur nickel becomes covered with a green film of basic sulphate.

-With water

It doesn't react with water but decomposes steam very slowly at red heat



-With acid:-

Nickel is little attacked by dilute hydrochloric acid or dilute acid.

It's more rapidly attacked by dilute nitric, especially if heated to yield a green solution from which crystals of $(\text{Ni NO}_3)_2 \cdot 6\text{H}_2\text{O}$ are deposited on evaporation. Concentrated nitric acid renders nickel passive.

It dissolves in aqua regia and the solution obtained when evaporated deposits deliquescent green crystals $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$.

With Alkali:

Nickel is not attacked by alkalis even when these are fused. Nickel crucibles can therefore be used safely for alkali fusion.

14-4-Experiments:

-With chlorine:

It's forms chloride NiCl_2 , when heated in a current of dry chlorine.

- With carbon monoxide:

At about 330k nickel is attacked by carbon monoxide with the formation of volatile nickel carbonyl $\text{Ni}(\text{Co})_4$ which plays an part in the metallurgy of nickel

1-4-5 Uses:

- For nickel plating.
- As metal assistant to alkaline corrosion.
- In the manufacture of important alloys D As a hydrogenation catalyst.
- Some compound of nickel it is employed as a mordent in dyeing and printing.

1-4-6 Alloys of nickel:

Invar steel it contains 35% Ni and 3% carbon.

Monel metal 70%Ni,30%Cu.

It's resistant to correction and it's used in chemical plant

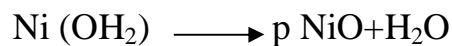
Ni chrome (80%Ni, 20%Cr)

It's used very resistant to oxidation and is therefore, used in making heating elements in electric heater.

1-4-7 Compound of nickel:

- Nickel "II" oxide: NiO

This oxide is produced when nickel "II" hydroxide or carbonate is heated.



- Nickel "II" chloride (Ni Cl₂ . 6H₂O):

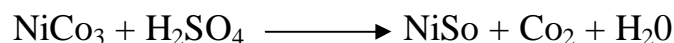
It's prepared by dissolving nickel in aqua regia the crystals are soluble in water and slightly effloresce on standing in air on heating the crystals lose water leaving behind the anhydrous salt yellow in color.

-Uses:

- El As catalyst.
- LI In nickel plating.
- LI It is used in synthetic inks.

-Nickel "II" sulphate (Ni So₄. 7H₂O):

Nickel sulphate is prepared by dissolving the nickel "H" carbonate in dilute sulphuric acid and crystallizing the product



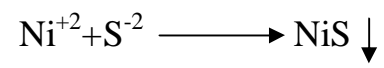
It's formed bright green crystals of the hydrated NiSo₄. 7H₂O

- Uses:-

- In nickel plating.
- In paints.
- It is employed as mordant in dyeing and printing.

- Nickel ‘H’ sulphide NIS:

Nickel sulphide is a black compound in soluble water and precipitated by the action of ammonium sulphide solution on solution of nickel salt.^[4]



2-1 Hena Powder:

Henna or hina (*Lawsonia inermis*, family Lythraceae) is a flowering plant or shrub native to tropical and subtropical regions of Africa, and Southern Asia. Henna is commercially cultivated in Morocco, Sudan, India, Pakistan, Yemen, and other countries. Henna contains a burgundy dye molecule, lawsone (2-hydroxy-1,4-naphthoquinone). This dye molecule has the ability to bond with proteins, and consequently has been widely used in body art to dye skin, hair and fingernails, and to dye silk, leather, and wool. Henna body art is made by applying henna paste to the skin. Henna paste is prepared by drying the henna leaves and grinding them to powder, and then this powder is mixed with oil or water to form the paste. When this henna paste is applied to the skin the dye (lawsone) migrates from the paste to the outermost layer of the skin; more lawsone will migrate if the paste is left on the skin for a longer time, thus creating a red-brown stain.

Henna has been used to adorn women's bodies during marriage ceremonies and other social celebrations since the Bronze Age. In the Arab world and Indian subcontinent henna is used for skin decoration and hair dying during social celebrations, and during marriage ceremonies people celebrate by adorning the bride, and sometimes the groom, with henna.

Despite the wide spread use of natural henna, specially, in countries where henna art is traditionally practiced, reports of allergic contact dermatitis to natural henna are very rare in the literature. It can therefore be assumed that natural henna is a very weak skin allergen.

Individuals may be occupationally exposed to PPD during its manufacture or use, and the exposure may occur through inhalation, skin and/or eye contact, and ingestion.

2-2 Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied.

The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments.

Dyed flax fibers have been found in the Republic of Georgia dated back in a prehistoric cave to 36,000 BP.¹²¹ Archaeological evidence shows that, particularly in India and Phoenicia, dyeing has been extensively carried out for over 5000 years. The dyes were obtained from animal, vegetable or mineral origin, with no or very little processing. By far the greatest source of dyes has been from the plant kingdom, notably roots, berries, bark, leaves and wood, but only a few have ever been used on a commercial scale.

2-2-1 Organic dyes:

The first human-made (synthetic) organic dye, mauveine, was discovered by William Henry Perkin in 1856. Many thousands of synthetic dyes have since been prepared.

Synthetic dyes quickly replaced the traditional natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties to the dyed materials. Dyes are now classified according to how they are used in the dyeing process.

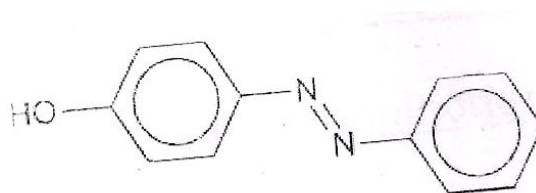
- Acid dyes are water-soluble anionic dyes that are applied to fibers such as silk, wool, poly and modified acrylic fibers using neutral to acid dye baths. Attachment to the fiber is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fiber. Acid dyes are not substantive to cellulose fibers.
- Basic dyes are water-soluble cationic dyes that are mainly applied to acrylic fibers, but find some use for wool and silk. Usually acetic acid is added to the dye bath to help the uptake of the dye onto the fiber. Basic dyes are also used in the coloration of paper.
- Mordant dyes require a mordant, which improves the fastness of the dye against water, light and perspiration. The choice of mordant is very important as different mordants can change the final color significantly. Most natural dyes are mordant dyes and there is therefore a large literature base describing dyeing techniques. The most important mordant dyes are the synthetic mordant dyes, or chrome dyes, used for wool; these comprise some 30% of dyes used for wool, and are especially useful for black and navy shades. The mordant, potassium dichromate, is applied as an after-

treatment. it is important to note that many mordants, particularly those in the heavy metal category, can be hazardous to health and extreme care must be taken in using them.

- Vat dyes are essentially insoluble in water and incapable of dyeing fibres directly. However, reduction in alkaline liquor produces the water soluble alkali metal salt of the dye, which, in this leuco form, has an affinity for the textile fibre. Subsequent oxidation reforms the original insoluble dye. The color of denim is due to indigo, the original vat dye.
- Reactive utilize a chromophore attached to a substituent that is capable of directly reacting with the fibre substrate. The covalent bonds that attach reactive dye to natural fibers make them among the most permanent of dyes. ‘Cold’ reactive dyes, such as Procion

MX, Cibacron F, and Drimarene K, are very easy to use the dye can be applied at room temperature. Reactive dyes are by far the best choice for dyeing cotton other cellulose fibers at home or in the art studio.

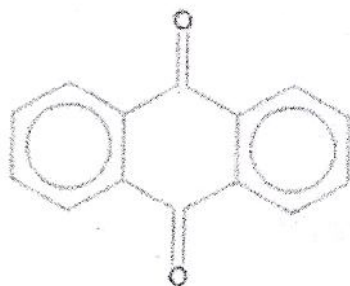
- Azoic dyeing is a technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with both diazoic and coupling components. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique, in that the final color is controlled by the choice of the diazoic and coupling components.



- Sulfur dyes are two part “developed” dyes used to dye cotton with dark colors. The initial bath imparts a yellow or pale chartreuse color, This is aftertreated with a sulfur compound in place to produce the dark black we are familiar with in socks for instance. Sulfur Black 1 is the largest selling dye by volume.

- Food dyes

One other class which describes the role of dyes, rather than their mode of use, is the food dye. Because food dyes are classed as food additives, they are manufactured to a higher standard than sonic industrial dyes. Food dyes can be direct, mordant and vat dyes, and their use is strictly controlled by legislation. Many are azoic dyes, although anthraquinone and triphenylmethane compounds are used for colors such as green and blue. Some naturally-occurring dyes are also used.



Anthraquinone

2-3- Chemical classification:

By the nature of their chromophore, dyes are divided into:

Category: Acridine dyes, derivates of acridine.

Category: Anthraquinone dyes, derivates of anthraquinone Arylmethane dyes.

Category: Diarylmethane dyes, based on diphenyl methane.

Category: Triarylmethane dyes, derivatives of triphenyl methane.

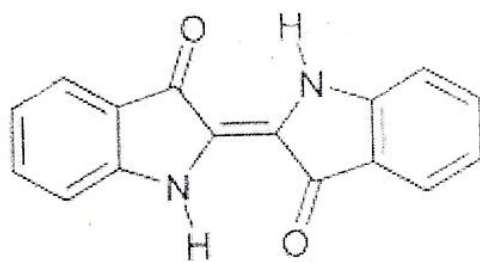
Category: Azo dyes based on $-N=N-$ azo structure. Cyanine dyes, derivatives of phthalocyanine. Diazonium dyes, based on diazonium salts. Nitro dyes, based on a $-NO_2$ nitro functional group. Nitroso dyes, based on a $-N=O$ nitroso functional group

Phthalocyanine dyes, derivatives of phthalocyanine Quinone-imine dyes, derivatives of quinone.

Halochromic dyes and Indicators:

A halochromic material is a material which changes colour when pH changes occur. The term 'chromic' is defined as materials that can change colour reversibly with the presence of a factor. In this case, the factor is pH. pH indicators have this property.

Halochromic substances are suited for use in environments where pH changes occur frequently, or places where changes in pH are extreme. Halochromic substances detect alterations in the pH of substances, such as detection of corrosion in metals. Curcumin is a halochromic dye at high pH its $-OH$ groups become ionised to $-O^-$ and its colour changes from red to yellow. Redox indicators are not halochromic. These compounds change colour according to whether they are oxidised or reduced. Indigo (left) is blue and insoluble when oxidised, but is colourless and soluble when reduced (right). In the reduced state it is known as leucoindigo.



Indigo Leucoindigo

Disperse dye:

Disperse dyes were originally developed (1923) for the dyeing of cellulose acetate, but can also be used to dye nylon, triacetate and polyester fibres. They are fast if the correct dye is selected for the fibre, but can be used to dye wool, but are only moderately fast and will not take intense dyeing.

Chemically, disperse dyes are water-insoluble azo and anthraquinone dyes. The dyes are finely ground in the presence of a dispersing agent and then sold as a paste, or spray-dried and sold as a powder.

The dyes are applied as dispersions (emulsions). In some cases, a dyeing temperature of 130 °C is required, and a pressurised dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.

Disperse Yellow 7 is a diazo disperse dye. Note the lack of -NH (basic) or -SO₃ (acidic) groups.

3-1 Para-Phenylenediamine (PPD):

Para-Phenylenediamine (PPD) is an aromatic amine compound; its chemical formula is C₆H₈N₂ and its molecular weight is 108.15 g/mol. It is white to light purple powder that darkens on exposure to air (it oxidizes, turning first red, then brown then finally black); it is slightly soluble in water. It is primarily used as an ingredient of oxidative hair coloring products at a maximal concentration of 4.0%, however, after mixing in a 1:1 ratio with hydrogen peroxide prior to use this concentration will be 2% at the time of application to the hair. In addition to hair dyes; PPD may also be found in fur or textile dyes . para-Phenylenediamine is also used as a photographic developing agent as well as an antioxidant in rubber compounds.

3-2- Chemical/Physical Properties:

Molecular Formula:

C₆-H₈-N₂

Molecular Weight:

108.14

Color/Form:

WHITE TO SLIGHTLY RED CRYSTALS

WHITE PLATES FROM BENZENE, ETHER

Boiling Point:

267 DEG C

Melting Point:

145-147 DEG C

Density/Specific Gravity:

Greater than 1 (water = 1)

Dissociation Constants:

The pKa value of the conjugate acid is 6.2.

Octanol/ Water Partition Coefficient:

log Kow = -0.25

Solubilities:

SOL IN 100 PARTS COLD WATER; SOL IN ALCOHOL,
CHLOROFORM, ETHER SQL IN HOT BENZENE

Water solubility= 38,000 ppm

Spectral Properties:

MAX ABSORPTION (CYCLOHEXANE): 246 NM (LOG E= 3.93), 315

NM (LOG E= 3.30); SADTLER REFERENCE NUMBER: 4111 (IR,
PRISM); 1187 (UV)

IR: 8322

UV: 6-80

MASS: 45 (Aldermaston, Eight Peak Index of Mass Spectra, UK)

Vapor Density:

3.72 (AIR= 1)

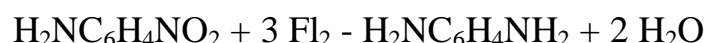
Vapor Pressure:

<1 mm Hg at 21 deg C (technical product) Other Chemical/Physical Properties:

BLACK COLOR DEVELOPED WITH 3% HYDROGEN PEROXIDE, BROWN WITH 5% IRON CHLORIDE SOLN, DARKENS ON EXPOSURE TO AIR.

3-3- Production:

PPD is produced via three routes. Most commonly 4-nitrochlorobenzene is treated with ammonia and the resulting 4-aminonitrobenzene is then hydrogenated:



In the DuPont route, aniline is converted to diphenyltriazine, which is converted by acid-catalysis to 4-aminoazobenzene. Hydrogenation of the latter affords PPD.

3-4 Uses:**Precursor to polymers:**

PPD is a precursor to aramid plastics and fibers such as Kevlar. This polymer arises from the reaction of PPD and terephthaloyl chloride. The reaction of PPD with phosgene gives the diisocyanate, a precursor to urethane polymers.

Other uses:

PPD is easily oxidized, and for this reason PPD is used as antioxidants in production of rubber products. PPD is also used as a developing agent in the C-41 color photographic film development process, reacting with the silver grains in the film and creating the colored dyes that form the image.

Dyeing:

This compound is used in almost every dye on the market, regardless of brand. The darker the colour, usually, the higher the concentrations. Some of the so-called "natural" and herbal hair colours, while ammonia-free, contain PPD. Some products sold as henna also contain PPD added, particularly black henna. Using body art-quality (BAQ) pure henna, or indigo, is the only way to avoid PPD in hair dye. Although a niche application, PPD is added to henna to create so called Black Henna. In many cases, PPD causes allergic reaction, and can cause scarring in some people. PPD should never be applied directly to the skin in its pure form or mixed with anything else).

3-5- Safety:

The aquatic LD50 of PPD is 0.028 mg/L.- The U.S. Environmental Protection Agency reported that in rats and mice chronically exposed to PPD in their diet, it simply depressed body weights, but there were no other clinical signs of toxicity, as were observed in several studies. Between 1992 and 2005, thirty-one articles were published a causal association between PPD and cancer. Associations between personal hair dye use and non-Hodgkin's lymphoma, multiple myeloma, acute leukemia, and bladder cancer were observed in at least one well-designed study with detailed exposure assessment, but were not consistently observed across studies. However, the EPA has not classified PPD as a

carcinogen. Therefore, no warnings of toxicity have been printed on boxes of hair dye.

The CDC lists PPD as being a contact allergen. Exposure routes are through inhalation, skin absorption, ingestion, and skin and/or, eye contact; symptoms of exposure include throat irritation (pharynx and larynx), bronchial asthma, and sensitization dermatitis.¹ Sensitization is a lifelong issue, which may lead to active sensitization to products including, but not limited to black clothing, various inks, hair dye, dyed fur, dyed leather, and certain photographic products.^[5,6,7]

4-1 Materials and Method:

Identification and quantification of heavy metals in henna tt mixtures by Atomic Absorption Spectroscopy (AAS).

4-2 -Procedure:

Analysis of heavy metal

A 0.4g sample was added to a 15 ml falcon tube with pure water to make 10 ml solution.

The solution was heated in an 80-90c° water bath for 30 min After cooling it was sonicated for 15 min and filtered to make the test solution.

Stock solution of Co, Ni, Cr and Pd were made by diluting standard solution of 1000mg/l.

Result of A.A.S:

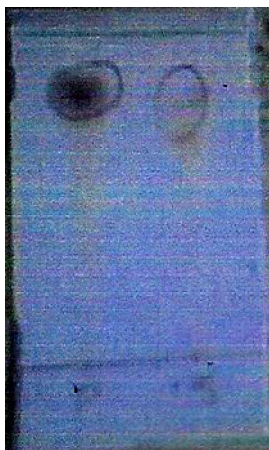
Sample	Nicke (Mg/ml)	Cobalt (Mg/ml)	Lead (Mg/ml)	Chromium (mg/ml)
Henna	0.083	0.242	0.201	0.196
Soft	N.D	0.194	0.038	0.133
Tancho	N.D	0.157	0.009	0.146
Radico	N.D	0.265	0.196	0.091
PPD	N.D	0.394	0.299	0.054

N.D Not detected

4-5- Qualitative analysis of PPD by using TIC:



Chromatogram explain separations dyes (tanchO radico) component by using aluminum plate plating by silica gel and standard PPD and solvent formed from acitic acid, methanol and water by ratio 2 : 3 : 95 and the volume of plate 5x10



Chromatogram explain separations of dyes (Soft) component (PPD) by using aluminum plate plating by silica gel and uses standard PPD and solvent formed from acetic acid , Methanol and water by ratio 2: 3: 95 and volume of plate 4x7.



Chromatogram explain separation of dyes (Henna) component (PPD) by using aluminum plate plating by silica gel and uses standard PPD and solvent formed from acetic acid, Methanol and water by ratio 2: 3 : 95 and volume of plate 4x7.

4-6-Discussion:

According to a above result of qualitative analysis all sample contain Para phenylene diamine except henna and from quantitative analysis all sample contain chromium ,cobalt lead on deffrent concentration but there are only sample containing nickel called henna hennahas been used to make temporary tattoo in the middle east and south Asia and Africa especially in sudan since medieval time henna leaves contain active substance naphthoquinone it is used extensively for treatment and as a substitute for chemical hair dye but the addition of PPD increases the risk of Allergic contact dermatitis. According to the food and drug administration the only legal use of PPD in cosmetic in hair dye .it,s not approved for direct application to skin , further more the scientific committee for cosmetic products and Non food products intended for consumer use has also stated in their laws that lawsone is not suitable for use as Non oxidizing colouring reagent for dyeing and by extension is not suitable for any other cosmeUc use this led s postule that heavy metal suth as nickel ,cobait ,lead and chromium play a role in the occurrence of allergic contact dermatitis caused henna tattoo mixtures.

Lastly we “want to say to all sudanes peope move away from utilization that cosmetic contain PPD and tattoo, hair dye. Prevention is better than cure.

5-4 Reference:

1. F. Albert cotton, Geofferey wilkinon, corlos A.Marillo, Manfred Bochmann, Advanced Inorganic Chemistry, uses and reactions and properties of chromium, (1988, page: 736-756).
2. S.C BHATIA, environmental chemistry, toxic elements and elemental forms, (2002, page: 441- 465).
3. Catherine, E.House croft and alan G. Sharpe, inorganic chemistry (uses and reaction of lead (2001, page: 873 – 876).
4. F. Albert cotton, Geofferey wilkinon, corlos A.Marillo, Manfred Bochmann, Advanced Inorganic Chemistry, uses and reactions and properties of cobalt and Nickel, (1988, page: 814 – 835).
5. www.organicdyes.com.
6. wwwen.wikipedia.org/wiki/ppd.
7. www.nedragondye.com.