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UNIT –I A-Forensic Chemistry

1.0 Introduction

The following categories are examined to identify the nature, source, chemical constituents and Forensic significance:

- Analysis of Alcohol in Liquors/drinks
- Adulteration of Petroleum products
- Cement, mortar & concrete
- Fire investigation

Alcohol:
1.1 Analysis of Alcohol in Liquors/Drinks:

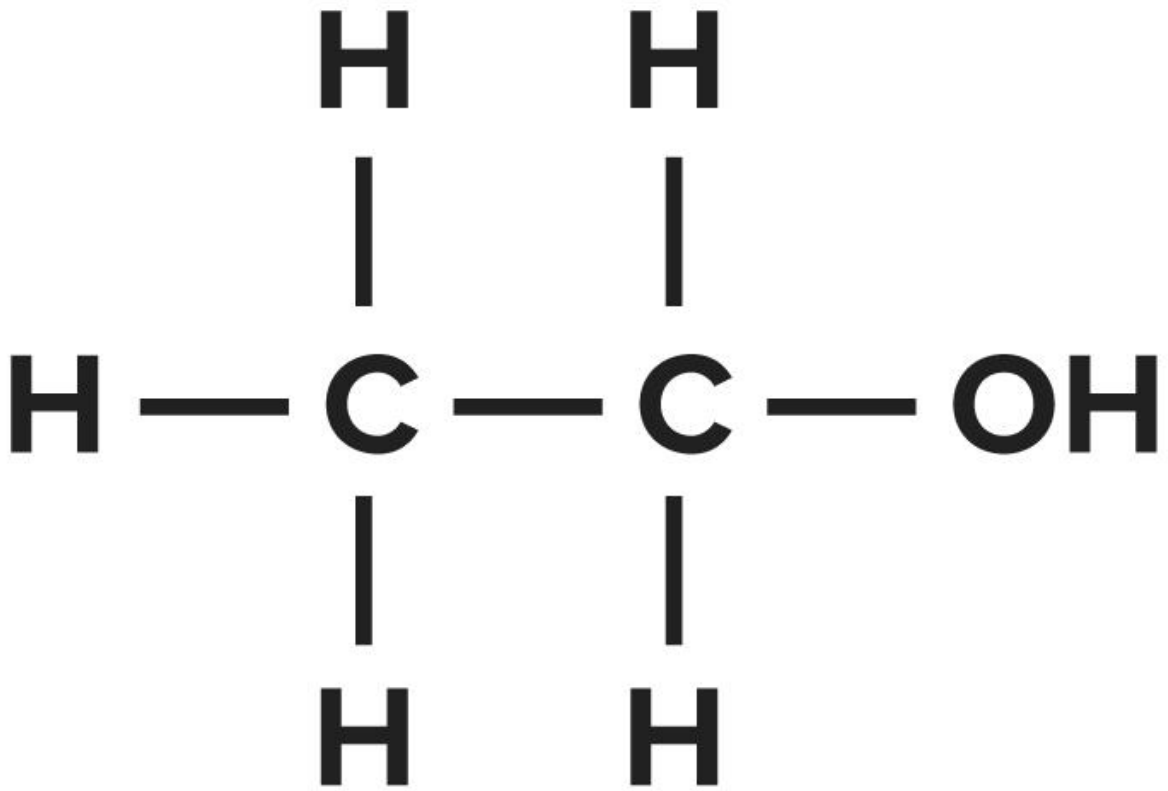
1.1.1 Introduction:

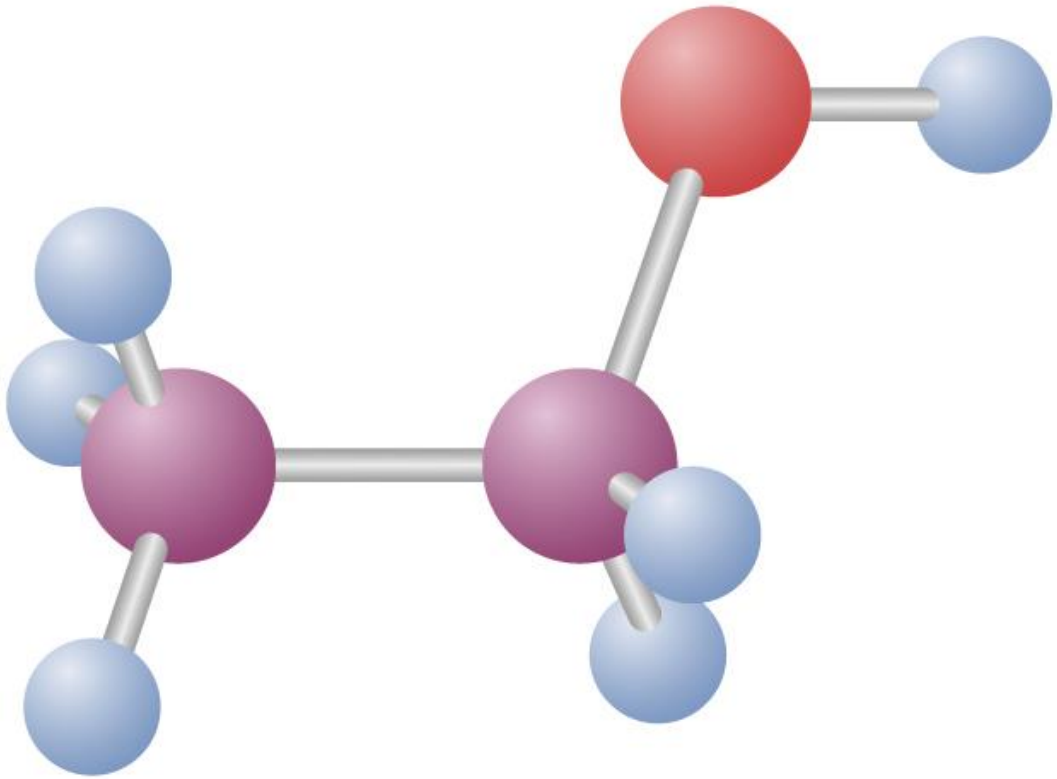
Almost 1.4 lakh people die of Cirrhosis of liver every year.

One Indian dies every 96 minutes due to Alcohol consumption.

- Liquors are covered by Excise Act
- Liquors are manufactured as per the specifications given in Bureau of Indian Standards (BIS).
- Liquors are mixture of Alcohol and Water .
- Liquors are manufactured by fermentation process in which carbohydrates are fermented by enzymes.
- Liquor is examined for 2 purposes:
- 1)Excise purpose for qualitative and quantitative analysis of ethyl alcohol in various liquor samples.
- 2)Liquor is examined for quality control/duplicate samples.

Ethanol





- Liquor is usually a mixture of Alcohol and Water.The term alcohol is often used for Ethyl Alcohol.Liquor is manufactured by fermentation process in which carbohydrates are fermented in the presence of enzymes as per specification given in Bureau of Indian Standard(BIS)

- Country made liquor is a alcoholic product usually prepared from fermentation of carbohydrates present in cereals,jaggery,fruits,mahua,palm,molasses etc.The liquors sold in the market are covered under Excise Act.Possession,sale,transportation is allowed as per Rules and Regulatios of Excise and Prohibition.

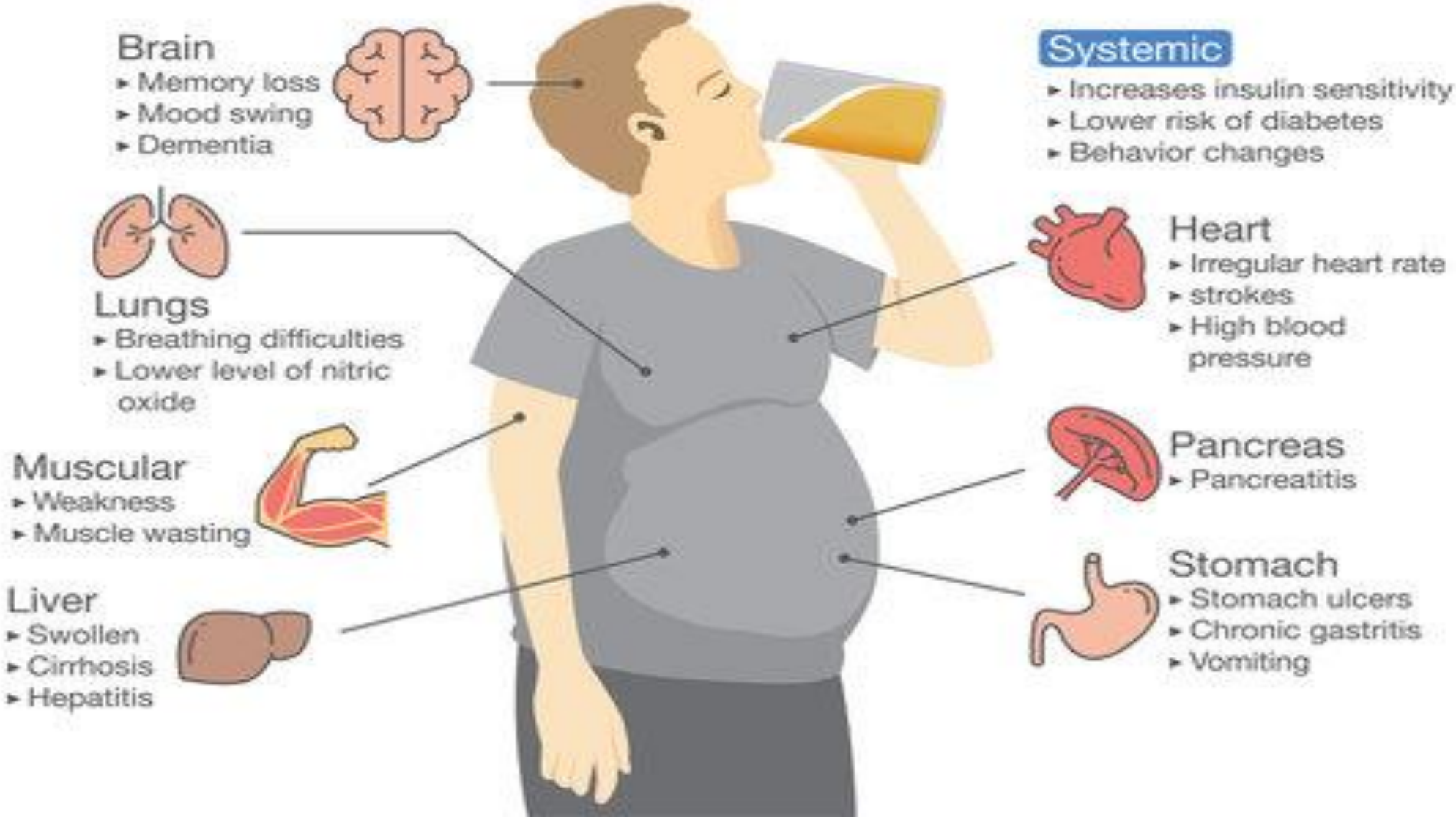
- Many times these liquors are being smuggled from one state to the other,illegally possessed and transported without valid documents.These samples are seized by the police and submitted to the Forensic Sciences Department through courts for examination.
- Department analyses Rectified Spirit,Neutral Spirit,Arrack,Illicit arrack,Toddy,Sondi Soru,Brandy,Whisky,Rum,Gin,Beer,Wines,Chloral Hydrate,IMFL mixed with Atropine, Ayurvedic Preparations,Coloured Flavoured Alcohol,Molasses,Flavouring Agents,Caramel,kadukkai(Terminalia Chebula),Urea,Ammonium Sulphate,Iodine Tincture,Cough Syrup etc.

- The approximate percentage of Alcohol by Volume is:
- Whisky,Brandy,Gin:40 to 45%
- Rum&Other Liquors:50 to 60%
- Vodka:60 to 65%
- Port,Sherry:20%
- Wine,Champagne:10 to 15%
- Beer :4 to 8%
- Inebriant Poisons produce intoxication,i.e. light headedness,confusion,disorientation and drowsiness.

Symptoms:

- Stage of excitement, Stage of in-coordination, Stage of coma.
- Prolonged coma may cause irreversible hypoxic brain damage and death.
- Fatal Dose:150 to 250 ml of Absolute Alcohol consumed in 1 hour.
- Fatal Period:12 to 24 hours.
- Treatment: One litre of Normal Saline in 10% Glucose,100 mg Thiamine and 15 units of Insulin are useful. If coma deepens, nerve stimulants should be used.
- Artificial respiration
- Haemodialysis or Peritoneal dialysis.
- Treat symptomatically.

Symptoms of Alcoholism



Common Symptoms of Alcohol Withdrawal
Headache
Clammy skin
Shakiness
Fatigue
Appetite loss
Difficulty thinking clearly
verywell

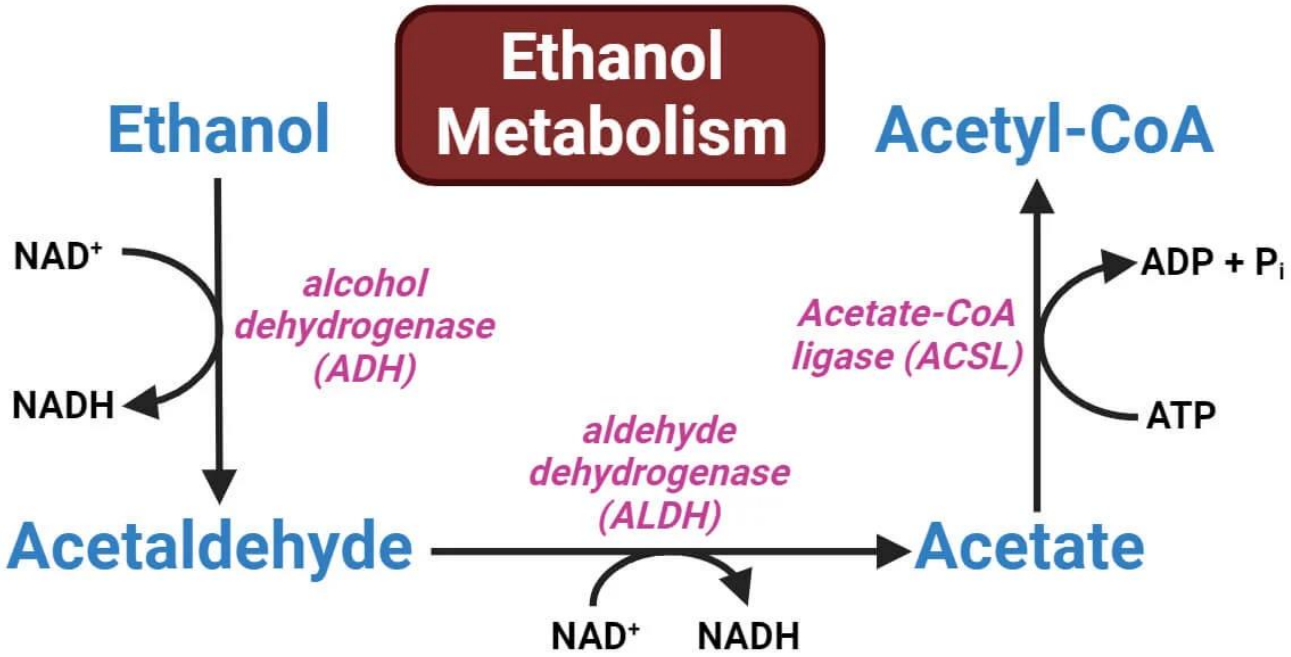
Alcohol Elimination

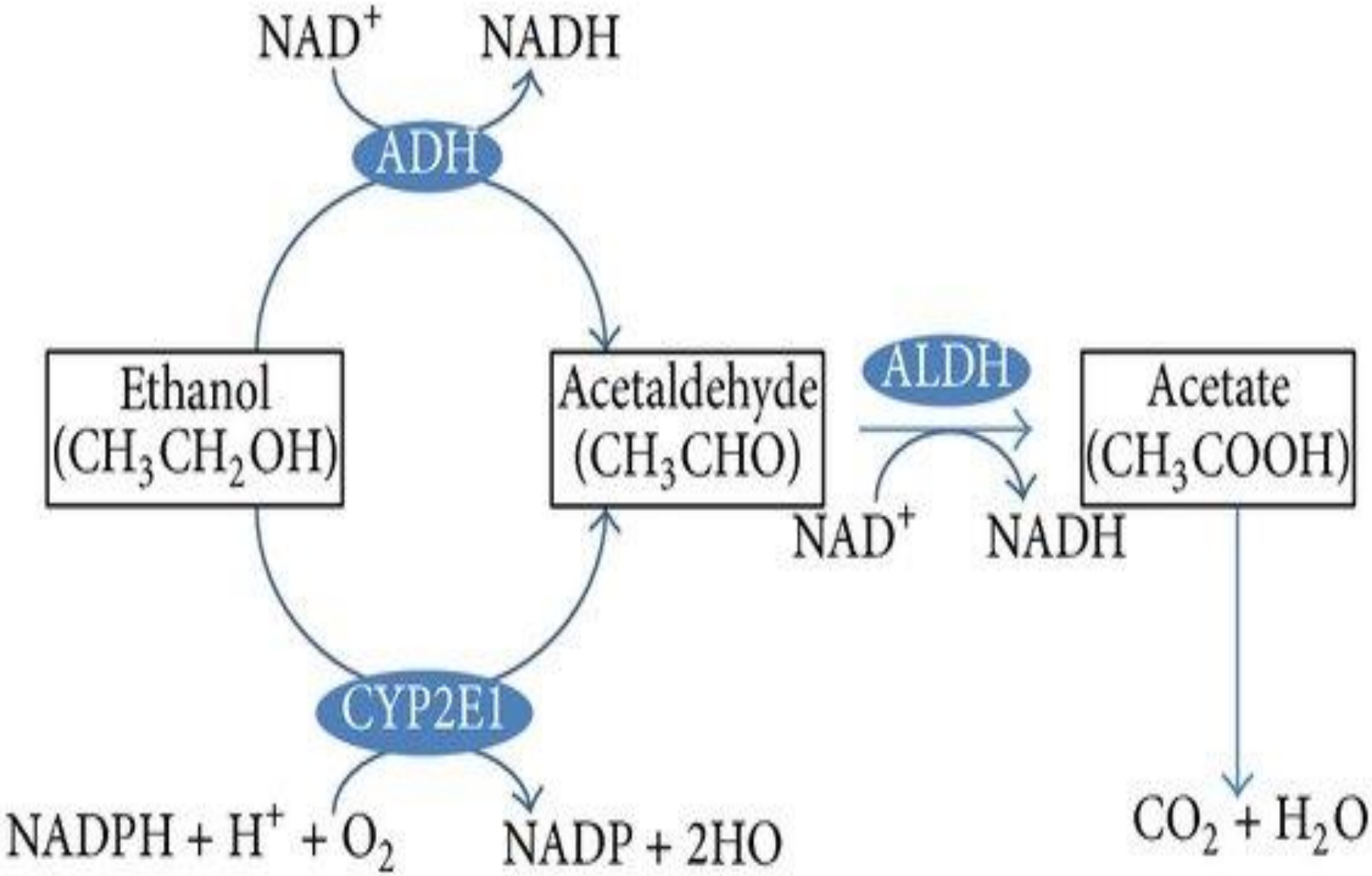
2 mechanisms for elimination:

- Oxidation takes place in the liver

Ethanol oxidised to:

- Acetaldehyde further oxidized to
- Acetic acid and then to
- CO 2 + H 2 O


Ethanol Metabolism
Ethanol
Acetyl-CoA
NAD+
NADH
alcohol dehydrogenase (ADH)
Acetate-CoA ligase (ACSL)
ADP + Pi
ATP
aldehyde dehydrogenase (ALDH)
Acetaldehyde
Acetate
NAD+
NADH


NAD+
NADH
ADH
Ethanol
(CH3CH2OH)
Acetaldehyde
(CH3CHO)
ALDH
Acetate
(CH3COOH)
NAD+
NADH
CYP2E1
NADPH + H+ + O2
NADP + 2HO
CO2 + H2O

Elimination through :

- Breath
- Perspiration
- Urine

1.1.2 Methods:Qualitative Analysis of Liquor:

- Test for Ethanol:
- Iodoform Test: 1ml sample + 1ml of 5% of Sodium Hydroxide followed by dropwise solution of Iodine in Potassium Iodide (10gmsof Iodine+ 20 gms of KI in 100 ml Water)Dark brown color obtained. Add dilute Sodium Hydroxide to remove excess Iodine. Add equal volume of water. Keep it for 10 minutes. Yellow crystalline precipitate indicate the presence of Ethanol.
- Dichromate Test:1 ml of the sample+0.2 ml of 2% Potassium Dichromate followed by 1 ml of con.H_2SO_4.Yellow color of the dichromate changes to green or blue indicate the presence of Ethanol.

Test for Copper & Iron

- 5ml of sample+ 1 drop of Nitric acid + 1ml of .25M Ferro cyanide- Prussian blue indicates the presence of iron.
- Chocolate color indicates the presence of copper.

Test for Furfural&Aldehyde:

- 5ml sample+ 1ml aniline+ 0.5ml HCL, allow it to stand for 15mins – Appearance of red color indicates the presence of furfural.
- Test For Aldehyde:
- To 5 ml of sample,add Schiff"s Reagent.Pink color appears if Aldehyde is present.

Quantitative analysis

- Using Hydrometer – Determine the density at room temperature .From reference chart, specific gravity obtained.
- Distillation: Distil the sample. weigh 25ml of the distillate in the specific gravity bottle, apply bottle correction & temperature correction. Calculate the alcohol content.
- Excise samples are analyzed are per IS 3752:1988.
- Determination of Ash
- Total Acidity
- Volatile Acidity
- Fixed Acidity
- Residue on evaporation

- Esters
- Higher Alcohols
- Aldehydes
- Copper
- Furfural

1.1.3 Illicit Liquor

- 1.1.3.1 Definition
- Mixture of alcohol and water is known as Liquor.Alcohol is produced by the fermentation of sugar or starch by enzymes.
- Country liquor is a distilled alcoholic beverage made from locally available cheap raw material such as sugarcane,rice,palm,coconut etc.Common variety of country liquor is Arrack.
- Produced clandestinely in small production units, carried out as cottage industries.
- Alcohol concentration varies upto 56% . Adulterated with Methyl alcohol, Varnish etc. Mass poisoning & death occurs due to this. Many lose their eyesight& become blind due to Methanol poisoning.
- 1.1.3.2 Toddy:
- Obtained as juice / sap of palmyra.
- Toddy is adulterated with Chloral hydrate, Varnish, diazepam, citric acid, foaming agents, starch etc.

- 1.1.3.3 IMFL: Indian made foreign liquor includes brandy, whiskey, rum, gin etc.

- Brandy gives fruity odor
- Whisky smoky odor
- Rum Sweety odor
- Gin flavor: Due to Juniper berries
- Beer:Bitter taste due to Hops resin.

1.1.4 Laboratory Analysis

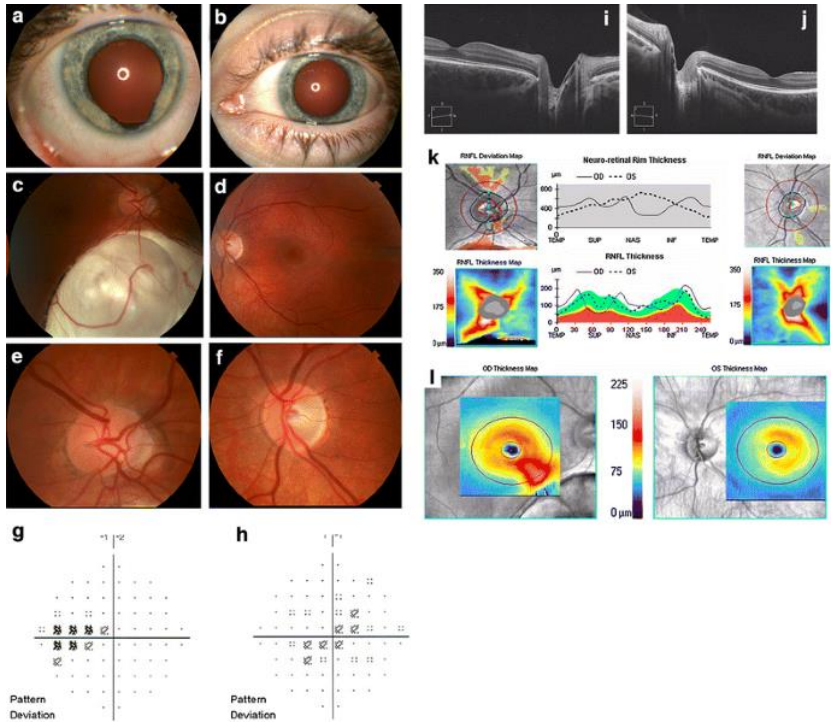
Conducted for 2 main purposes:

- Excise purpose – Qualitative and Quantitative analysis
- Quality control.
- Methods and Procedures:
- 1)Physical Examination
- 2)Chemical Examination
- 3)Instrumentation Methods:Gas Chromatography,Headspace GC with Flame Ionisation Detection(FID).

Methanol Poisoning:

- Wood Alcohol: It is a colourless volatile liquid with a burning taste.
- Symptoms: Nausea, vomiting, abdominal cramps, head ache, neck stiffness, depressed cardiac action, photophobia
- Blurred or misty vision, complete blindness due to Optic Neuritis.
- Methanol is oxidized to Formaldehyde in the Liver which is 33 times more toxic than Methanol.
- Formaldehyde is further oxidized to Formic Acid which is responsible for metabolic Acidosis.
- Test for Methanol:
- Chromotropic Acid Test:

Drug Expert
@drugexpert_drx
Methanol poisoning & Antidote
Methanol
" Antidote "
alcohol dehydrogenase
Inhibit
fomepizole
Formaldehyde " TOXIC "
aldehyde dehydrogenase
Formic acid
" TOXIC "
Leads to
CNS depression, metabolic acidosis, permanent neurologic dysfunction, blurring or complete loss of vision, coma, respiratory failure, death
@drugexpert_drx


a
b
c
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Pattern Deviation
Pattern Deviation
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RNFL Deviation Map
Neuro-retinal Rim Thickness
OD
OS
TEMP
SUP
NAS
INF
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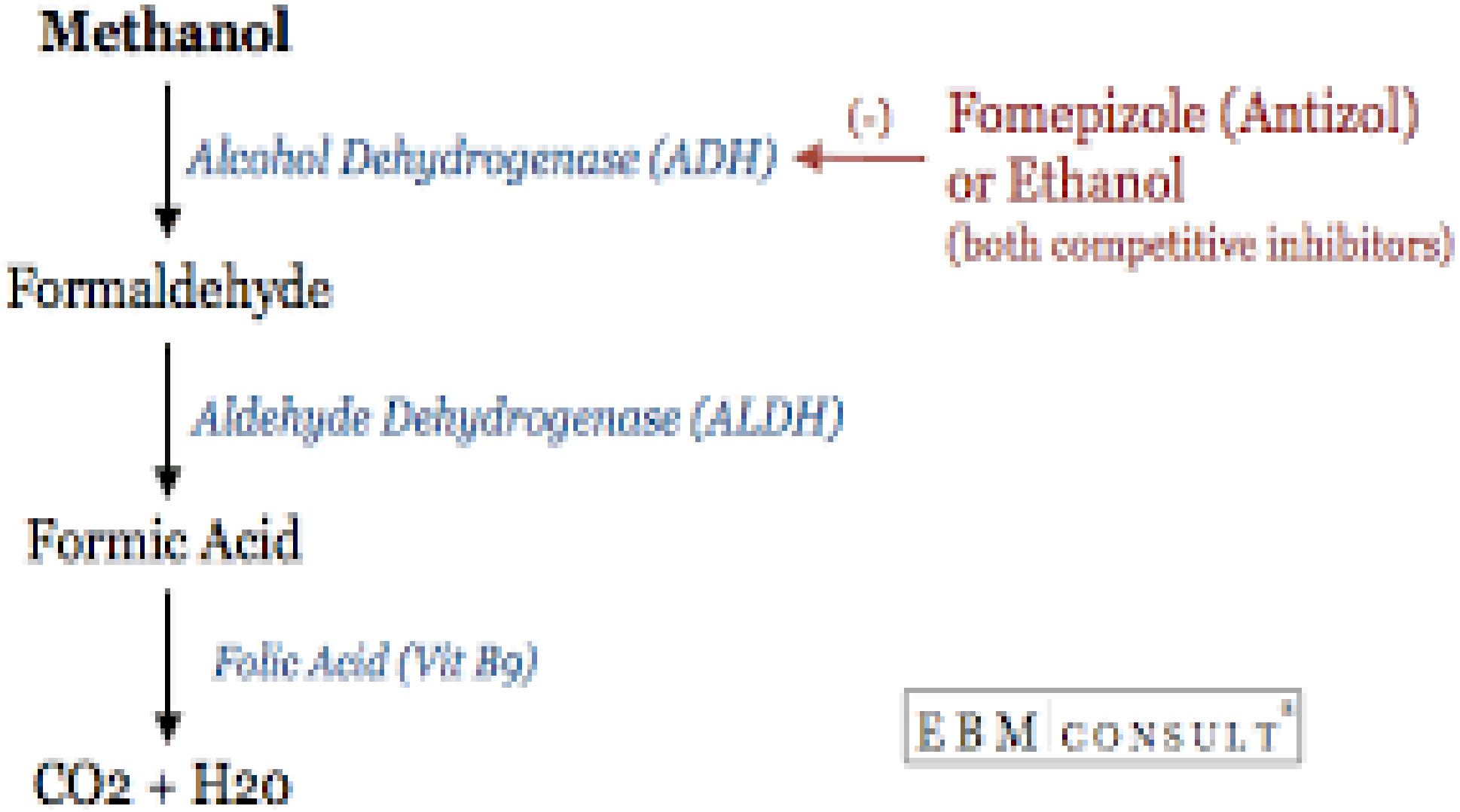
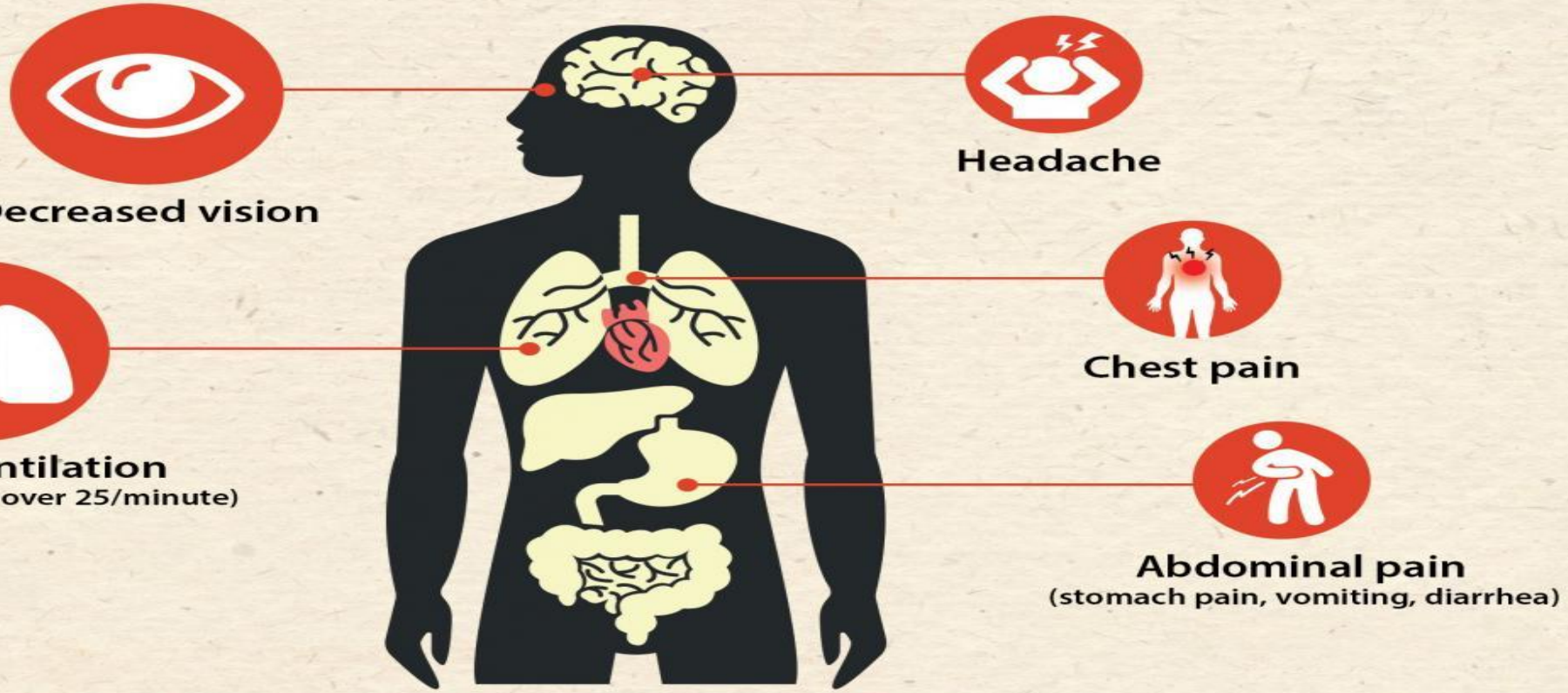
OS Thickness Map
225
150
75
0 µm


Methanol
Alcohol Dehydrogenase (ADH)
(-)
Fomepizole (Antizol)
or Ethanol
(both competitive inhibitors)
Formaldehyde
Aldehyde Dehydrogenase (ALDH)
Formic Acid
Folic Acid (Vit Bg)
CO2 + H20
EBM CONSULT

MEDECINS SANS FRONTIERES
無國界醫生

Methanol is commonly used as an industrial alcohol. It can be absorbed into the body through ingestion, inhalation, and skin contact and metabolised into highly toxic formic acid which can lead to metabolic acidosis.

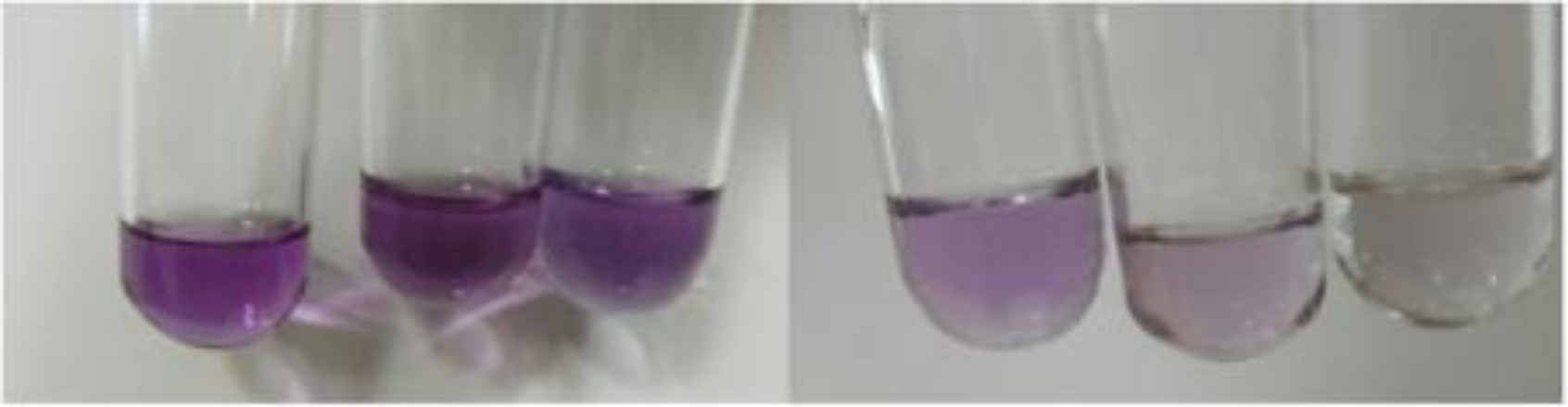
Symptoms of methanol poisoning

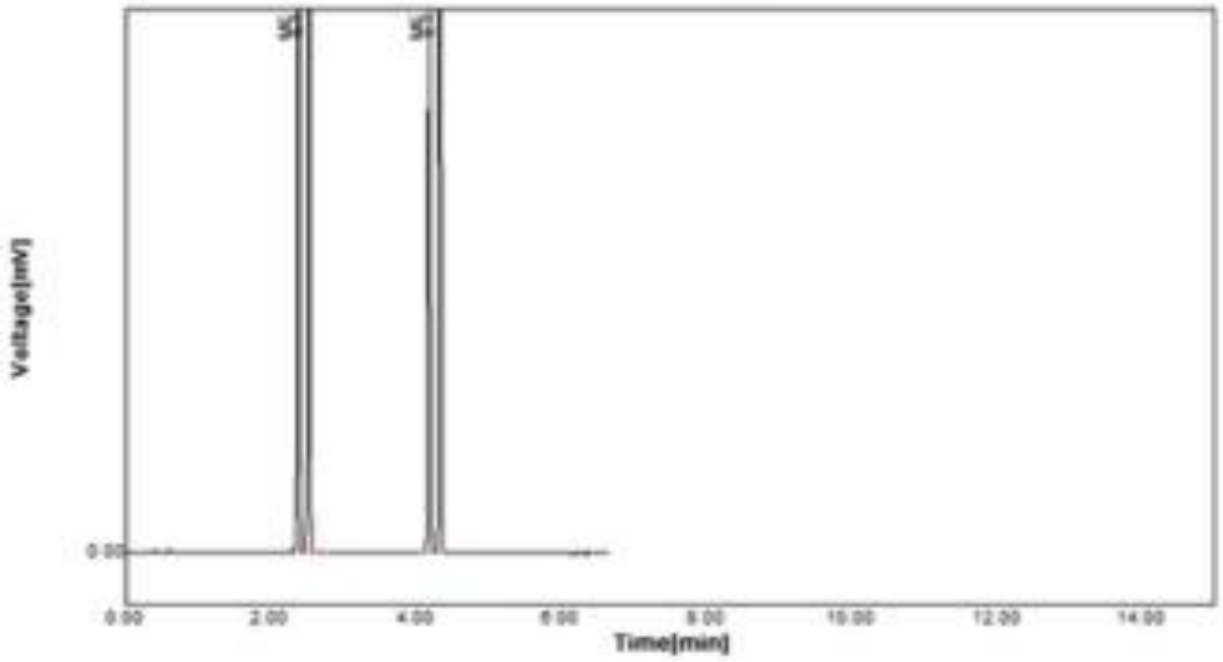


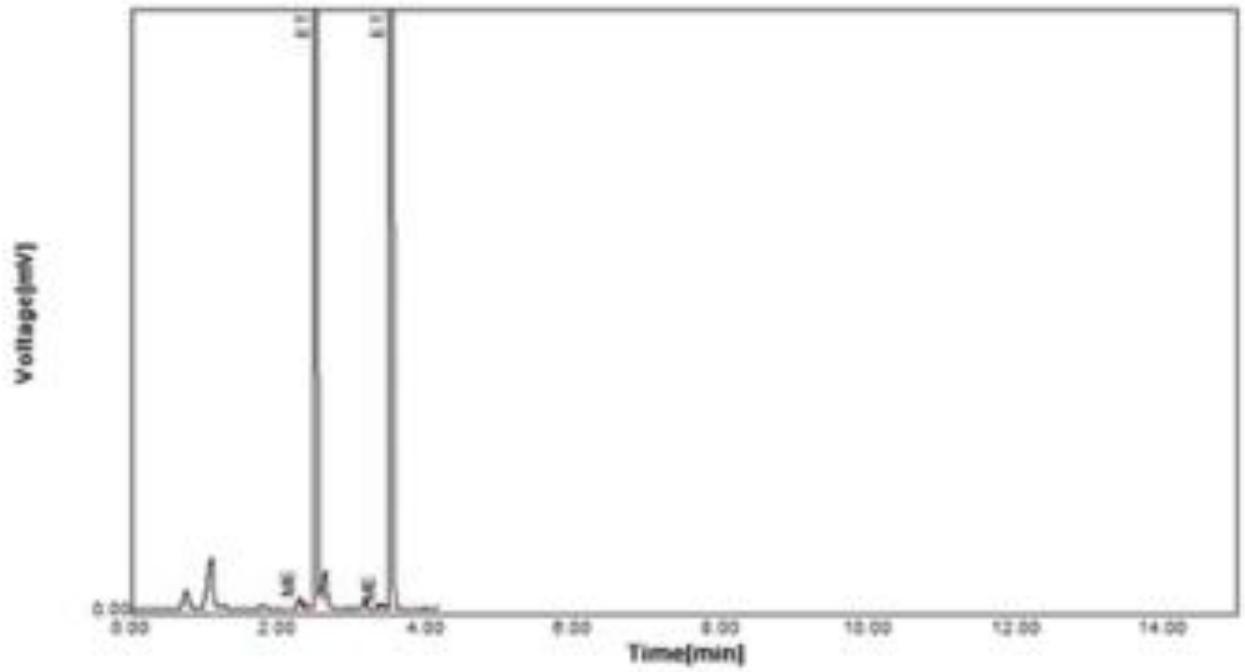
If the above symptoms are identified, please seek medical attention immediately

Test for Methanol:Chromotropic Acid Test:

- 1ml sample + 2ml KMNO4 + 15ml Phosphoric acid in 100ml water, shake well, decolorize permanganate color with sodium bisulphite and add 1 ml of 5% chromotrophic acid followed by 15ml of concentrated Sulphuric acid along the sides.
- Appearance of violet color indicates the presence of methanol.
- For quantitative estimation of methanol, standards are prepared and compared with the unknown sample.Colorimetric method is used
- For Ethanol and Methanol estimation,GC ,GC-MS can also be used.




Voltage[mV]
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Time[min]


Voltage[mV]
0.00
0.00
2.00
4.00
6.00
8.00
10.00
12.00
14.00
Time[min]

Treatment for Methanol Poisoning:

- Ethanol as antidote:10% solution in 500 ml infusion.
- Intra muscular Paraldehyde given for convulsions.
- Morphine to combat pain
- IV Saline-Glucose given
- Gastric Lavage using 5% bicarbonate solution to combat acidosis
- Eyes kept covered to protect from light.
- Fomepizol can be used as antidote.

Fuels:

Petroleum product

- Petroleum is composed from 2 Greek words-
  - Petra means rock
  - Oleum means oil
- The oil which extracted from the rock present below the earth surface is the petroleum.
- It includes petrol, diesel, kerosene etc.

1.2 Adulteration of Petroleum products

- 1.2.1 Introduction:
- Petroleum product is obtained by fractional distillation of crude oil and is a complex mixture of hydrocarbons.Petrol and Diesel are the main fuels or sources of energy used in vehicles in India.
- 1.2.2 Definitions:
- As per "THE MOTOR SPIRIT AND HIGH SPEED DIESEL (PREVENTION OF MALPRACTICES IN SUPPLY AND DISTRIBUTION) ORDER 1993 BY SECTION 3 OF ESSENTIAL COMMODITIES ACT (CENTRAL ACT 1955)

It includes

- LPG and CNG(Liquid Petroleum Gas and Compressed Natural Gas)
- Motor Spirit – all grades and Naphtha
- Aviation Spirit
- Solvents of all types
- Aviation Turbine Fuel (ATF)
- Kerosene
- Diesel Oil

LPG

- Is primarily made of Propane with Butane, Propylene, Butylene & Isobutane;
- CNG – Compressed Natural Gas is primarily made up of Methane
- Bitumen – Is a low grade crude oil which is composed of complex heavy hydrocarbons used industrially.
- In India BIS notifies the specification for Petrol, Diesel, Kerosene etc.
- Alternate fuel present day includes CNG, LPG, alcohol, bio-diesel, methanol, ethanol, diethyl ether etc.

1.2.3 Test for Petroleum Compounds:

1 ml of sample in spot tile+Formaldehyde in con.Sulphuric Acid(1:9 ratio) added.Appearance of violet-brown colour indicates the presence of Hydrocarbons which is positive for a Petroleum compound.

Certain properties of the fuel change when blended with an adulterants.Forensic laboratory, tests for these adulterants.

Hydrocarbon Boiling Range Final Boiling Pt.

- Petrol C5 to C10 35 to180 C 200 C
- Diesel C11 to C18 160 to 350 C 380 C
- (C19&C20 Traces)
- Kerosene C20 TO C30 150 to 260 C 300 C

Density at 15 C Refractive Index Flash Point

- Petrol 0.710 to 0.770 gms/cm3 1.412 to 1.414 -
- Kerosene 0.780 to 0.820 1.435 37 C
- Diesel 0.820 to 0.880 1.465 32 C

1.2.4 WHAT IS ADULTERATION

ADULTERATION: Means the introduction of any foreign substance into Motor Spirit/High speed Diesel, illegally/ unauthorisedly.
MALPRACTICES: It shall include the following acts of ommission, commission in respect of motor spirit and high speed diesel

- Adulteration
- Pilferage
- Stock variation
- Unauthorised exchange
- Unauthorised purchase
- Unauthorised sale

1.2.5 Types OF ADULTERANTS:

- Petrol: Blending small doses of Diesel or Kerosene.
- Blending Industrial solvents whose boiling range is the same as Petrol.
- Blending small amounts of Spent waste Industrial solvents.
- Blending Kerosene or heavier Fuel oils into Diesel.
- Commonly used Adulterants in Petrol are:
- Kerosene,Diesel,Naphtha,Pentane,Hexane,Benzene,Toluene,Industrial solvents and Spent Waste etc.

KEROSENE
Kerosenes are distillate fractions of crude oil in the boiling range of 150-250 °C(max 300 °C) and consists of C_{12}-C_{16} hydrocarbons.
Paraffins are the preferred components of Kerosene because of their excellent burning quality and high smoke point.
Blue Dye (20 ppm) is added to PDS kerosene to differentiate it from non subsidised kerosene

Types Of Adulterants:

- To Diesel:Kerosene or heavier fuel oils added.
- Main purpose of Testing:
- Whether the given sample is Petroleum compound- if yes ,it is Motor spirit or Diesel.
- If adulterated,nature and type of adulterant.
- Fuel adulteration results in the detoriation of engine performance
- Emission of Hydrocarbons,Carbon Monoxide, Carbon Dioxide ,Oxides of Nitrogen bring about pollution.

Tests to detect Adulterants in Petrol:

- Colour Test
- Filter Paper Test
- Density:At 15 C is 0.710 to 0.770 C
- Distillation:Final Boiling Point:200 C

Confirmatory test for adulteration is Research Octane No.

RON for Petrol is 88.

Octane level play an important part in determining the performance,efficiency and suitability of fuel.

If RON is above 88,adulterant will be aromatic hydrocarbon.

Below 88,adulterant will be aliphatic hydrocarbon.

- Analytical Methods:TLC/GC/HPLC/Automatic Density Meter/GC Coupled with Detailed Hydrocarbon Analyser(GC-DHA)

Tests to detect Adulterants in Diesel:

- Density: At 15 C is 0.820 to 0.870 g/cm3
- Distillation:Final Boilng Point 380 C
- Viscosity
- GC

- Tests to detect adulteration in Kerosene:
- Density:At 15 C is 0.780 to 0.820 g/cm3
- Distillation :Final Boiling Point 300 C
- Viscocity:Measured with Viscometer.

Advances in testing Fuel Adulteration:

- Fox FTIR Fuel Analyser is ideal for analysis of commercial fuels since it is portable.

Zeltex ZX 101 CC:Portable Octane Analyser, gives results in less than 20 seconds.Can give separate calibrations for Unleaded Petrol,Leaded Petrol,Kerosene,Diesel.

- Requires less than 250 ml of the sample.

RESEARCH OCTANE NUMBER (RON)

- Knocking :

  Sharp metallic sound similar to rattling of hammer which is produced in IC Engine owing to immature ignition of the air gasoline mixture

  Knocking property is expressed as Octane Number.

1.2.6FORENSIC SIGNIFICANCE

- All Petroleum Solvents are easily characterized
- Hydrocarbon profile gives an idea of nature of adulterant
- Narrow cut Solvents are identified easily using their carbon number and group
- Useful tool to fix the novel fuel adulterant

Cases:

- There are about 4375 fuel adulteration cases in India.
- 1)A 12 member gang was busted in Saharanput for stealing fuel from pipelines.
- 2)In Chennai ,3 men were arrested for adultering Diesel with Hexane.

- 3)Herbal Petrol Case:A person named Ramar was selling herbal petrol and public complained about this as many faced engine failure and a criminal case was registered.Chennai FSD lab detected Benzene,Toluidine,Mineral Turpentine Oil and azo dye.No Chlorophyll was detected.Azo dye was added to impart green colour.

1.3 Cement

- 1.3.1 Introduction :
- FSD receives cement cases under different crime heads like Essential Commodities act, Indian Penal Code and under Cement orders act.
- Cement is one of the most important materials in building construction.
- Testing of Cement is done to check its Purity & Characterization .Hence only a few parameters like soluble Calcium oxide, Silica are determined as per Indian standards specification.
- Concrete & Mortar are referred to FSL in cases of building collapse.

1.3.2 Cement

Portland Cement:

Obtained by intimately mixing together Calcareous, argillaceous or other Silica, alumina and Iron oxide bearing materials, burning them at clinkering temperature & grinding the resulting clinker.

Composition:

Lime CaO 60-67%

Silica SiO2 17-25%

Rest is made up of Oxides of Aluminium, Iron & Magnesium.

The principal cement compound is Calcium Aluminate.

Table 8.4.4. Typical Oxide Analysis of Cement

Oxides	Wt, %
CaO	60 – 67
SiO_2	17 – 25
Al_2O_3	3 – 8
Fe_2O_3	0.5 – 6.0
MgO	0.1 – 4.0
Alkalis	0.2 – 1.3
SO_3	2 – 4

Types of Cement

- Quick Setting Portland cement – Setting time is less
- Rapid Hardening Portland Cement – Particles are grounded finer hence hardening occurs rapidly.
- White Portland Cement – Contains low proportion of Iron Oxide, hence white in color instead of grey.
- Waterproof Portland Cement – Small proportion of Calcium stearate is added at grinding stage.
- Hydrophobic Cement – Grinding Portland cement clinker with Water repellant substance such as fatty acid to reduce the rate of detoriation under favorable storage or transport conditions.

Cement:

Concrete:

- Low heat Portland cement – Heat of hydration is reduced.
- Portland Pozzolona cement – Pozzolonic material like brick powder, fly ash etc are added in the range of 20-40 % & is used in the preparation of plaster materials.

Other building materials include Stone powder, Concrete, Mortar, Sand, aggregate and brick.

- 1.3.3 Other building materials include:
- Stone powder,Concrete,Mortar,Sand,Brick and Aggregate.
- Mortar – Blend of cement & sand in various proportions. Used in brick work in house walls which is 1:4 in proportion.
- Concrete – Blend of cement,air and water, sand & aggregate.i.e.Gravel(10:20:30:40)
- Silica – Mixture of Silicon & Oxygen found in earths crust used to make glass, pottery, ceramics, bricks & artificial stones.
- Aggregate is usually Gravel which is a loose aggregation of rock fragments.

1.3.4 Methods of Analysis:

Cement

- Thymolphthalein Test: – 100-150mg of cement samples taken In a test tube, add 1-2 ml water & 2 drops of indicator, development of blue color indicates presence of cement.
- Heating test: – 0.5 gm of sample taken on a steel plate & heated for 20 mins, Change in color adulterated cement, no change in color unadulterated cement.
- Performance Test: – Make thick slurry of cement with 1 part of cement & 1 part of water in a match box cement gets hardened performance is tested after 24 hrs. if the cement breaks readily, setting properties is poor.
- Determination of Calcium by EDTA titration (By Patton Reeders indicator): – Take 25ml of solution in titration flask, add 50 ml water,5ml 1:1 glycerol with constant stirring,add 5ml diethylamine & 5 to 6 pellets of NaOH ,(PH more than 12).Shake well, add 50mg of Patton Reeders indicator, now titrate against 0 .01M EDTA, color changes from Violet to blue .
- (Patton Reeders Indicator is a blue azo dye)

Instrumental techniques:

- ICP: Inductively Coupled Plasma Mass Spectrometry:

  Used to measure and identify elements within a sample matrix based on the ionization of the elements within the sample.

- XRD:X-Ray Difractometer:A technique employed to determine the underlying crystal structure of a material.

Forensic Significance:

- When the sample is received in the Forensic Department,it has to be ascertained whether the sample received is Cement or not.If its cement, the percentage of Cement.
- Whether adulterated or not,if adulterated,the nature of the adulterant.

Cases:

Concrete buildings should last upto 100 years but recently 20 to 30 year buildings have collapsed.

1) 14 killed in Kurla area in Mumbai as building collapses.

2)70 year old building collapsed in North Chennai when renovation was going on.Many were trapped and only 10 persons rescued.

3)Thane building collapse was the worst, killing 74 persons and injuring 100 severely.

4)A building under construction collapsed near Parrys corner,Chennai killing many workers.

All these cases will be forwarded for analysis to FSD, to find out the quality of cement and adulteration if any.

1.4 Fire Investigation:

- 1.4.1 Introduction:
- Fire investigation deals with examination of fire scene to determine the origin and cause of fire
- A fire scene is extremely difficult to process if there is large scale destruction of material

as a result of the fire as well as due to the fire suppression activities. Every fire scene is investigated as a potential case of arson until proven otherwise.

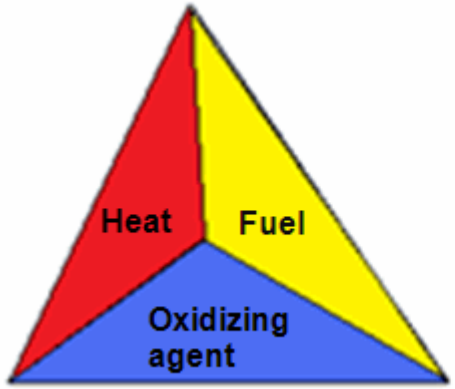
- Arson may be defined as willful and malicious burning of another's property or ones own property. Arson may be committed for concealment of other crimes such as murder or burglary or to defraud an insurance company.
- Crime scene should be secured.
- Fires may be classified as Accidental or Deliberate.

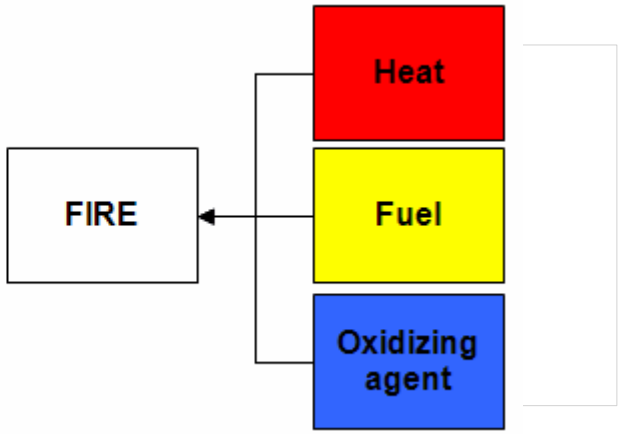
- Electrical Fires: May be caused due to faulty or old electrical wiring, faulty and dangerous appliances or inappropriate use of fuses in electrical appliances.
- Natural causes: such as lightening strikes, volcanic eruptions.
- Deliberate Fires: This type of fire are different in terms of their causes and the motivation behind them. In general, such incidents have been started by some form of flammable material used to accelerate the fire. Motivation often varies and include an attempt to cover up other crimes such as theft, murder or fraud.
- As part of series of crimes of a known arsonist.
- A grudge against particular race or religion.
- Bankruptcy or financial difficulty in order to claim insurance.

1.4.2 Fire:

- Fire can be used for constructive or destructive purposes.
- Three main requirements for a fire to occur are heat, oxygen and fuel.
- Fuel, oxygen, heat and appropriate ignition source comprises of fire.
- After the fire has been established, the fuel, oxygen and heat alone comprises the fire triangle.

Fire Requirement:


Heat
Fuel
Oxidizing agent


FIRE
Heat
Fuel
Oxidizing agent

- Fire is overall a series of oxidative reaction where the fuel present are being oxidized resulting in exothermic reaction.

Eg. Propane, which is a hydro carbon is a fuel that burns with oxygen releasing carbon dioxide and water. This is provided by ignition source which could be lighted match, electrical discharges or spark or chemicals.

- In addition to water and carbon dioxide as major product of combustion, other products including carbon monoxide and oxides of sulfur ,nitrogen and other compounds which may be present and which contribute to smoke.

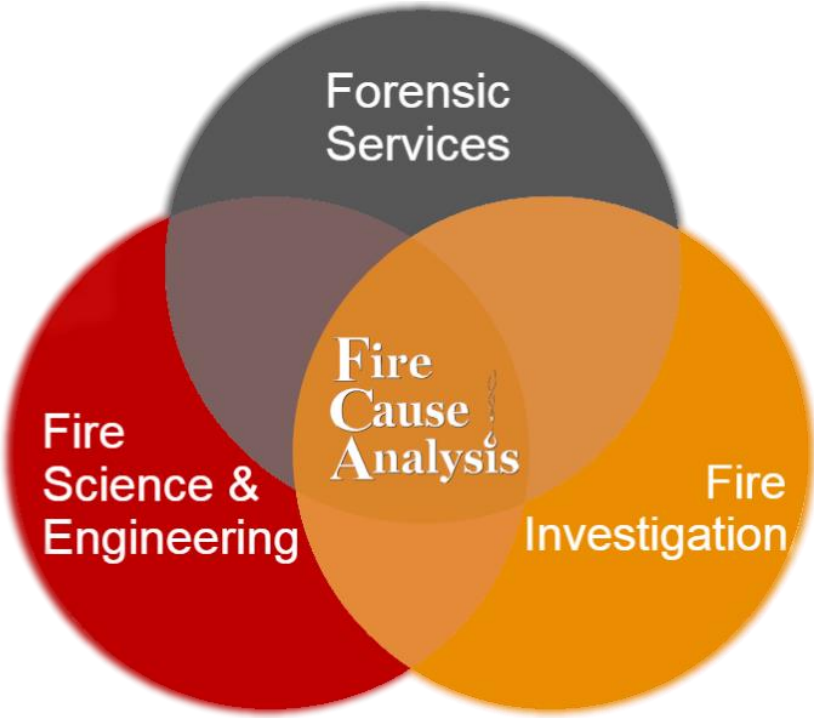
- Types of Fuel: They range from simple hydro carbon gases to chemically complex solid which could be natural, synthetic or semi synthetic . Examples of fuel includes hydrogen, methane, propane, petrol, diesel, kerosene, paint thinner, wood, paper, polystyrene, Pvc, poly urethane.
- Oxidising Agents: Chemicals that supply oxygen is called oxidizing agents. Example oxygen, sodium nitrate, potassium chlorate.
- Ignition sources: May be chemical, mechanical or electrical origin.

Eg. Lighters, candles, matches etc.

Either commercial timers or modified clocks can be used to time in a circuit closer and switches on an initiator.

- A search of the fire scene must focus on finding the fire origin.
- Preliminary investigation is undertaken from outside without disturbing the scene itself.
- This should include a systematic Photographic record, sketches, reference plan of the site to ascertain exact damage, what was stored, where the fire started , who was the last person known to have visited the premises. Witnesses to be examined, interviewed. Where smoke was seen first, color of the flame, color of the smoke, timing etc.
- The largest amount of damage occurs near the point of origin but this is not always the case.
- When liquid is poured over large area, it is highly likely that a portion of it will seep through into porous surface such as cracks in the floor, upholstery, rags, plaster, soil, carpets where enough of it remains unchanged that can be detected in the Forensic Lab.
- Ignitable liquids can be identified with the help of Canine detection teams or with the help of Electronic Sniffers(Portable Vapor Detectors)

- It is important to ensure that any evidence which is to be submitted to the laboratory for analysis has been packaged correctly.
- The packaging material should preserve the volatile residues of accelerants used in Arson and prevent contamination.
- Fire debri may be packaged in sealable ,airtight containers.
- Three samples to be sent to the laboratory.They are Control Container, Control Sample, Fire debri Sample.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1.4.4 Analysis of Sample:

Extraction:

Extraction and concentration of volatile components by
Direct Head Space Analysis

a)Passive Head Space Analysis
b)Dynamic Head Space Analysis

Solid Phase Micro Extraction(SPME)
Head space may contain not only volatized compound but also pyrolyzed products.

Analysis by instrumentation

- Gas Chromatography.
- GC-MS.
- Photo Ionisation Detectors:

Detects hundreds of gases and vapours in low concentration.

PID are non-destructive and will not affect the air sample.

PID is portable and battery powered making it ideal for fire and arson investigation.

Cases:

- 1)Chennai lady Engineer burnt alive with family by a stalker.
- 2)Kumbakonam School Fire:94 children of Krishna English Medium School were killed in 2004 after the school's thatched roof caught fire.
- 3)In 2000,Chennai GPO was gutted in Parrys corner due to old electrical wiring.

Gas Chromatograph-Mass Spectrometer(GC-MS) :

GC Consists of:

- Injection port
- A carrier Gas
- Column
- Detector

MS Consists of:

- An Ion Source
- A Mass Analyser
- A Detector System.

GC-MS:

- The Mass Spectroscope bombards a compound with a beam of high energy electrons that break up the compound and form positively charged particles called ions.The ions are then transported by magnetic or electrical fields to the mass analyser.The mass analyser separates the ions according to the mass to charge ratio.The analyser focuses each of the ions through a slit and into the detector.The detector sends information to a computer that records all of the data produced.The graph obtained is called Chromatogram.
- Library is available where unknown samples can be compared with known samples and arrive at a conclusion.

1.5 OILS&FATS:

- 1.5.1:Introduction:
- Oils and Fats are often adulterated with lower grade,different origin oils (vegetable oil by animal fat and vice versa) or misbranding or contrabranding of products.
- Oils and Fats are used as cooking media and also in industries like paints,varnishes,pharmaceutical industries.
- There may be theft cases or illegal possession
- Samples are sent for examination under EC Act.
- Vegetable Oils include ground nut

  oil,sunflower,coconut,mustard,linseed,palm,sesamese,cotton

  seed,rapseed,soyabean,castor,peanut and rice bran oil etc.
- Vanaspathi-: Is hardened fat obtained from vegetable oil by Hydrogenation.
- Animal Fat-Available in the form of butter,ghee,tallow(fat from cattle and sheep) and lard(pork fat).

1.5.2:Physical and Chemical Tests:

Oils and fats are triglycerides of saturated and unsaturated fatty acids.(Oleic,Linoleic,Linolenic).

They may vary in the % of free acids,sterols,drying properties etc.

Physical Charecteristics involve :Determination of Specific Gravity,

Determination of Moisture and Volatile Substances.

Chemical Charecteristics: Include Acid value,Acetyl value,Saponification value.

Chemical tests are performed to detect the adulteration and rancidity.

Rancidity:Aerial Oxidation of unsaturated fat gives it an unpleasant flavor and odour.

Test For Rancidity:

Kries Test:

5 ml sample+5ml 0.1% Phloroglucinol solution in Diethyl Ether.Shake well.Add 5 ml of Concentrated Hydrochloric acid.Appearance of pink color indicates Rancidity.

- 2)UV Spectro Photometric Method can be employed for determination of rancidity.

- Determination of Physical Properties Of Oils:
- 1)Determination of moisture and volatie substances.
- 2)Determination of Specific Gravity

- Chemical Characteristics:
- 1)Acid Value:Number of mgs of Potassium Hydroxide required to neutralise free fatty
- acid in 1 gm of oil or fat.
- 2)Saponification Value:Number of mgs of Potassium Hydroxide required to saponify 1 gm of oil or fat.
- 3)Iodine Value:Number of gm of Iodine absorbed by 100 gms of oil or fat.

1.5.3:Forensic Significance:

- Whether the sample received is oil or fat and if so the quality and whether adulterated or not.

1.5.4 Adulteration of Oils & fats:

Edible oil and fats are adulterated with low price oils

Coconut oil is adulterated with liquid paraffin, palm oil, palm kernel oil etc.

Mustard oil adulterated with argemone oil and butter yellow

Ghee adulterated with vanaspati

Butter adulterated with banana pulp,molten tallow,wheat and maize dough.

Synthetic colors, castor oil are profoundly used in adulteration of mineral oil , edible oil

High priced sesame and groundnut oil are often adulterated with palm oil.

Palm oil adulterated with Sudan 3 and 4 Azo dyes.

Sunflower oil is adulterated with carotenoids and palm oil.

Olive oil adulterated with soya bean oil, corn, sunflower and sesame oil.

Adulteration of pure cow ghee and buffalo ghee with palm oil, soya bean oil, vegetable oil, animal body fat

Adulteration in oil can cause cancer, paralysis, allergy and liver damage.

Instrumentation:

- GC,GC-MS,UV Spectrometry.

Cases:

- 1)Edible oil adulterated with Argemone Mexican Seed Oil resulting in Epidemic Dropsy that is edema of the extremities.
- 2)1998,Delhi poisoning case:Mustard oil was adulterated with white oil,a petroleum product which caused death of 60 people and illness of more than 3000 people.

It is reported by Food Safety and Standards Authority of India(FSSAI)

that 24% edible oil samples are adulterated.

1.6Acids and Alkalies:

- 1.61:Introduction :
- An acid is a substance which when dissolved in water releases Hydrogen ions.
- Acid has a pH less than 7.
- pH is a measure of acidity or basicity of a solution.
- Measured on a scale of 0 to 14 with 7 being neutral.
- Bases have a pH above 7.
- Alkalies may be a hydroxide or a carbonate of a metal.
- Acids are used as bathroom cleaners,rust removers and in car batteries.
- Alkalies are found in drain cleaners,industrial cleaners and in the manufacture of fertilisers.

1.6 Acids & Alkalies

CORROSIVE : ACIDS AND ALKALIS,METALLIC SALTS

a) Mineral acid (HCl, H_2SO_4, HNO_3)
b) Organic acid (oxalic, salicylic, carbolic, acetic acid)
c) Vegetable acid (HCN)
d) NaOH, KOH

1.6.2 SULPHURIC ACID

Oil of vitriol:It is a colorless, heavy oily liquid which emits no fumes when exposed to air, mixed with water, it evolves much heat

- It chars, blackens the skin, cloth and any other matter it comes in contact with.
- Fuming sulphuric acid has a formula of $H_2S_2O_7$ and is used in the manufacture of indigo dye

Fatal dose: 5-10ml

Fatal period: 12-24hrs

Test:

- pH paper test
- Litmus paper test:Blue litmus paper turns red.
- Test for Sulphate:To the solution,add Barium Chloride followed by con.Hydrochloric Acid.A white precipitate indicates the presence of Sulphate.

Sulphuric Acid:

Cause of death:May be due to circulatory collapse, spasm/edema of glottis, collapse due to perforation of stomach, toxemia, delayed death may occur due to hypostatic pneumonia, secondary infection, renal failure.

Treatment: Avoid gastric lavage or emetics

Acid should be immediately neutralised in situ by giving 1/4th litre of water or milk or milk of magnesia

Alkaline carbonates and bicarbonates which liberate CO2 should not be used as they cause gastric distension and sometimes rupture

- Treatment:

Give demulcent: Olive oil, milk, egg whites, starch water, mineral oil, melted butter maybe given in divided doses to prevent esophageal stricture and shock

Circulatory shock to be corrected

Tracheostomy(if there is edema of glottis) to be performed

Give nothing by mouth

Skin burns are washed with large amounts of water and paste of Magnesium oxide or Sodium carbonate is applied

Eye burns are irrigated with water or Sodium bicarbonate for 10-15mins.

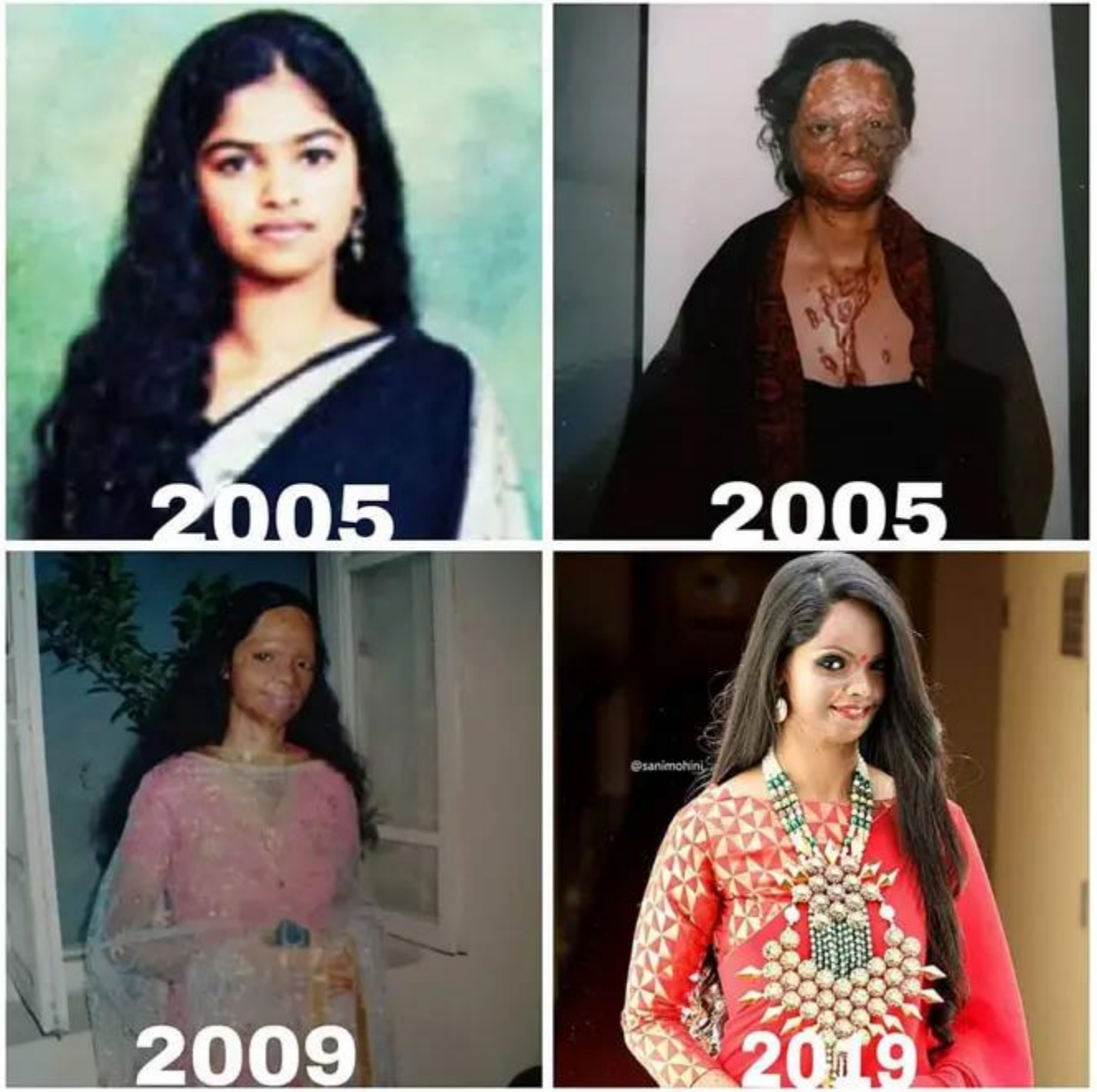
- Treat symptomatically.

VITRIOLAGE(VITRIOL THROWING)

Throwing of Sulphuric Acid on another individual is known as Vitriolage. Jealous or disgruntled persons may throw a corrosive to disfigure and harm their enemies. Burns are painless. They are penetrating burns and acid devitalises the tissues and predispose to infection. Blindness may occur if eyes are involved. Death may result from shock or toxaemia if extensive area is involved

LAKSHMI CASE

Lakshmi Agarwal was only 15 years old when she was attacked by a 32 year old man Neem Khan in 2005 after she refused his proposal.She is a acid attack survivor from New Delhi and filed for public interest litigation in Supreme Court. Her PIL sought framing of a new law or amendment to the existing criminal laws like IPC, Indian Evidence Act and Cr. PC for dealing with the offence besides asking for compensation. In 2013,Supreme Court passed rules restricting the sale of acid.


2005
2005
2009
@sanimohini
2019

1.6.3 NitricAcid

Aqua Fortis, Red Spirit of Nitre: Is a clear colorless, fuming heavy liquid and has a peculiar choking odor. In concentrated form, it combines with organic matter and produces an yellow discoloration of tissue due to the production of Picric Acid(Xanthoproteic Reaction).Greater abdominal distension owing to gas formation. Inhalation of fumes causes lachrymation, photophobia, irritation of air passages and lungs, producing sneezing, coughing, dyspnoea(difficulty in breathing) and asphyxia. Colour of urine is brown. FD and FP are same as that of Sulphuric Acid.

Test: Blue litmus turns Red

Ph paper test

Brown Ring Test: Strong Ferrous Sulphate solution and Sulphuric Acid are added to a solution containing Nitric Acid, a brown ring is formed at the junction of the two fluids.

1.6.4 Hydrochloric Acid:

Muriatic Acid: Is a pungent, colourless fuming acid.It is a natural constituent of the fluid of the Stomach and bowels. It is less corrosive than Sulphuric acid .It destroys the mucous membrane.

FD:15 to 20 ml.

FP:18 to 36 hrs.

Perforation of the Stomach is rare. Acute inflammation and oedema of respiratory passages and lung tissue are common.

Test:

1 Blue litmus turns red.

2 pH paper test.

3 Silver Nitrate Test: A solution of Silver Nitrate and Nitric acid produces a heavy curdy white precipitate of Silver Chloride.

1.6.5 Oxalic Acid:(Salt of Sorrel)

Occurs as colourless, transparent prismatic crystals and resembles Magnesium Sulphate and Zinc Sulphate crystals. Used as a bleach to remove stains or to clean brass or copper articles or leather and for removing writing and signatures illegally.

Systemic :a)Shock: Large doses cause rapid death from shock.

b)Hypocalcemia: It readily combines with Calcium ions in the body tissues and causes it's withdrawal from them.

C)Renal damage: Oxalate produces Tubular nephrosis or necrosis and cause uraemia in 2 to 14 days.

FD:15 TO 20 Gms.

FP:1 to 2 hrs.

Treatment: Stomach washed with Calcium Lactate or Gluconate.

10%of 10 ml i.v. Calcium Gluconate administered.

Dialysis for Renal failure.

Demulcents.

Symptomatic.

Test: A solution of Barium Nitrate gives a white precipitate of Barium Oxalate which is soluble in Hydrochloric Acid or Nitric Acid.

Oxaluria:

Excretion of Oxalate crystals in urine is called as Oxaluria.

1.6.6 Carbolic Acid:Phenol:

- Carbolic Acid(Phenol): Consists of short, colorless, prismatic needle shaped crystals. Has a burning sweetish taste which turn pink when exposed to air. Commercial Carbolic acid is a dark brown liquid containing several impurities, chiefly Cresol.
- Acute Poisoning is called as" Carbolism''.Greyish white discoloration of skin, pain, tingling and numbness will be felt. Pupils constricted.
- Phenol will be metabolised in the liver and the metabolites Hydroquinone and Pyrocatechol are excreted in the urine. Urine turns green in colour on exposure to air due to these metabolites and this condition is called Carboluria.

- Chronic Poisoning: Phenol Marasmus:
- Characterized by anorexia, weight loss, vertigo, dark colored urine.
- Ochronosis: The metabolites hydroquinone and pyrocatechol may cause pigmentation in the Cornea and various cartilages, a condition called Ochronosis.
- Test:1)Turns blue litmus red
- 2)Sample+Ferric Chloride-Gives blue or violet coloration.
- 3)Sample with Bromine water gives white precipitate due to Tribromo phenol formation.

1.6.7 Alkalies:

Commonly encountered alkalies are hydroxides of Sodium, Potassium, Calcium and Ammonium and Carbonates of Sodium, Potassium, Calcium and Sodium Hypochlorite.

- Most of these appear as white powders or colourless solutions.
- Ammonium Hydroxide :Used in paints, dirt remover and as refrigerant.
- Sodium Hydroxide(Caustic Soda):Used as drain cleaner and oven cleaner.
- Potassium Hydroxide(Caustic Potash):Used as drain cleaners and in hearing aid batteries.
- Sodium Carbonate(Washing Soda):House hold cleaner and detergent.
- Sodium Hypochlorite: House hold bleach.
- Usual fatal dose is 10 to 15 gms;15 to 20 ml for Ammonia.
- Mode of Action: Locally alkalies produce liquefaction necrosis and saponification of fats. Ulcer formation is common. Oesophagus more vulnerable than Stomach.

Treatment:

- Alkaline poisons should be neutralised with vegetable acids such as Acetic acid, Vinegar, Citric or Tartaric acid mixed with large quantity of water.
- These should be followed by Olive Oil, White of egg, milk, butter and acidulated demulcent drinks.
- Morphine may be given hypodermically to relieve pain .It may be necessary to perform oesophagostomy or gastrostomy.

1.6.8 Acid Burn Injuries:

- It is a type of Chemical burn injury.
- Injuries :Severe burns,blistering ,damage to eyes,respiratory tract and lungs,
- Acid burns may cause coagulation necrosis due to precipitation of Protein
- First degree burns:Affects Epidermis,that is outer layer of skin.
- Second degree burns:Involves the epidermis and part of the dermis layer of skin.
- Third degree burns:Involves damage to the underlying bones,muscles and tendons. The burn site appears white or charred.No sensation in the area as nerve endings are destroyed.

1.6.9 Forensic Analysis:

- Viscera of the deceased,clothings of the deceased/Victim will be received along with the acid bottles/ containers.Forensic Scientist has to determine the nature of the acid and its strength
- Cases:.
- In another case,sulphuric acid was poured on a male who tried to prevent molestation of his wife.
- Anupama ,another acid victim who was only 13 years old when she was attacked by her stalker who was 12 years her senior.

1.7 Examination of Chemicals used in Trap cases

- 1.7.1:Introduction:
- Law Enforcement Agencies arrange a trap for illegal transaction (bribe) with the help of the complainant where in the accused is given currency notes on which chemical like phenolphthalein or anthracene powder has been applied
- If he keeps these currency notes in his pocket, bag, briefcase or file etc, this chemical is also transferred to these objects (Locards Principle of exchange). In case of phenolphthalein ,the object (hand, bag, pocket etc) are washed with a colorless solution of sodium carbonate (or sometimes with lime water), which becomes immediately pink confirming the touching of currency notes/ transfer of phenolphthalein to the object.
- These washings are being collected and sent to the forensic laboratories along with other relevant articles to establish the presence of phenolphthalein which can be considered as vital evidence in the court

- The pink color of this solution persists for some days or months depending on the quantity of the phenolphthalein and strength of the alkali solution.
- It gradually fades and sometimes becomes colorless at the time of trial in the court.
- This creates unnecessary doubt and investigating officer is put in an awkward position.
- However this phenomenon can be explained by the scientist on scientific basis that the color of the phenolphthalein fades due to its breaking down into 2(4 –hydroxy benzoyl) benzoic acid and phenol in alkali medium.

1.7.2 Test for Phenolphthalein

- 1) **pH Test -** Observe the pH of the solution exhibit with the pH paper. More than pH 9 (pH range 8.3-10) with pink /red color indicates the positive test for the presence of phenolphthalein.
- 2) **Acid –Alkali Test** - Take an appropriate portion of the exhibit solution. Add few drops dilute hydrochloric acid. The pink color of the exhibit disappears. Now add few drops of dilute solution of sodium hydroxide in water, the pink color reappears. If required, this test can also be performed on residue obtained after evaporation of ethanol extract of the exhibit, but in this case first add alkali solution and then acid. Appearance and disappearance of pink color indicates the positive test for the presence of phenolphthalein.
- 3)Thin Layer Chromatography.

- 4) **Instrumental techniques: - Spectrophotometric examination:** Take a portion of the exhibit solution filtered & scanned to note:
- The maximum absorbance value by spectrophotometer in appropriate dilution using a standard solution of phenolphthalein in aqueous alkali (sodium carbonate) for comparison. The pink color of phenolphthalein in aqueous Sodium carbonate solution gives the lambda max in between around 550-555 nm. Aqueous solution of sodium carbonate is used as blank solution for the experiment.
- Other instrumental techniques like HPLC, FTIR,GC, GC-MS are also being used for the detection of Phenolphthalein.

1.7.3 Test for Carbonates,Sodium,Calcium and Potassium.

- Test for Carbonates:
- To the exhibit solution,add dilute hydrochloric Acid.Effervescence observed due to liberation of Carbon dioxide.If a rod dipped in lime water is introduced near the mouth of the test tube,it turns milky.
- Test for Sodium:
- Zinc Uranyl Acetate Test:To the exhibit solution,neutralize with acetic acid and add few drops of Zinc Uranyl Acetate solution.yellow precitate formed.Presence of Sodium confirmed.
- Flame Test:Exhibit evaporated and concentrated hydrochloric acid added to make it into a paste.Introduced into the flame with a glass rod.Golden yellow flame indicates the presence of Sodium.

1.7.4 Forensic Analysis

Involves :

- Detection
- Identification of Phenolphthalein, Sodium, Potassium, Calcium, Carbonate ions.