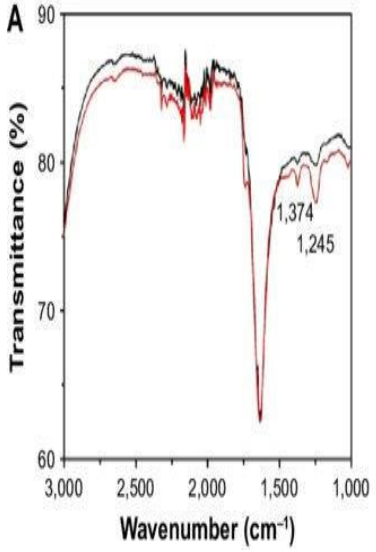
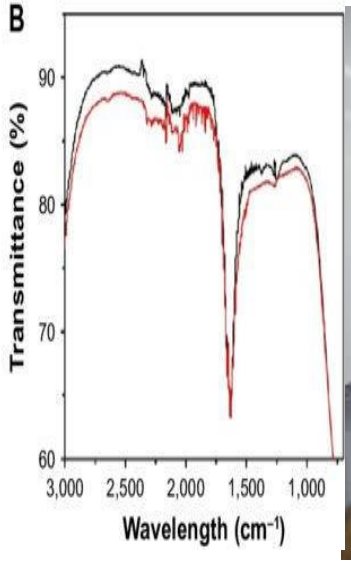
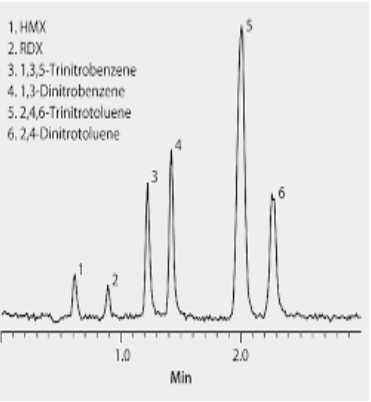




FORENSIC CHEMISTRY



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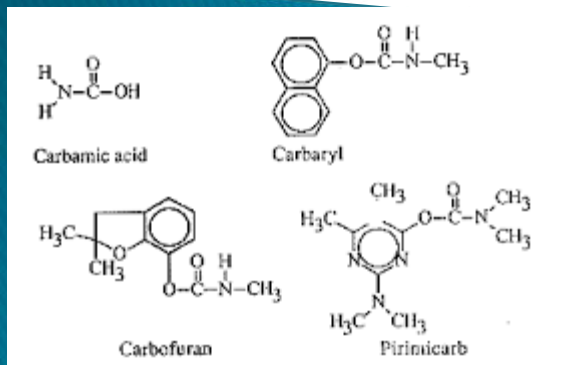
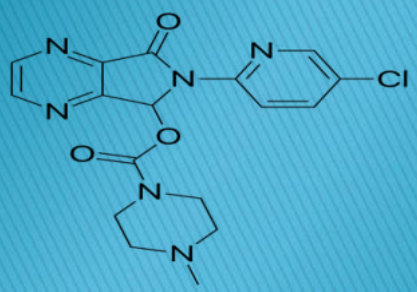
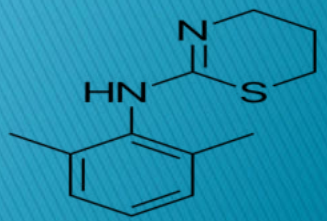






What is forensic science?

- Science in service to the law

- "…the application of science to those criminal and civil laws that are enforced by police agencies in the criminal justice system."

  Saferstein

Locard’s Exchange Principle

- Locard's Exchange Principle states that with contact between two items, there will be an exchange of microscopic material. This certainly includes fibers, but extends to other microscopic materials such as drugs, chemicals , explosives, hair, pollen, paint, and soil.

- What are the consequences of Locard's Exchange Principle?
- The perpetrator leaves evidence behind and also takes evidence away
- The longer you wait before collecting evidence the less there is left
- Every person at the crime scene including police investigators will contaminate it

FORE NSIC CHEMISTRY

- Forensic chemistry is the application of chemistry and its subfield, forensic toxicology, in a legal setting. A forensic chemist can assist in the identification of unknown materials found at a crime scene. Specialists in this field have a wide array of methods and instruments to help identify unknown substances.

- Out of the several disciplines of physical and natural sciences, the principles and techniques of various branches of Chemistry are utilized by forensic scientists to a very great extent. This branch of applied chemistry is called Forensic Chemistry. Forensic Chemistry groups the scientific principles and technical methods of Analytical Chemistry and other branches of Chemistry.

- This generally involves two types of analysis:
- (1) Comparative analysis
- (2) Absolute analysis
- (a) Qualitative analysis
- (b) Quantitative analysis

- Range of samples or exhibits sent for forensic chemical analysis can be of:
- 1.Natural origin: Blood, hair, seminal stains, natural drugs, plant material
- and soil etc.
- 2.Processed Natural Products: Glass, cement, paper, rubber, metals and petroleum products

- 3. Completely Synthetic & Manufactured Products: Drugs, pesticides, plastics, paints, polymers and fibres etc.
-
- Nature of the samples:
- 1. Bulk in large amounts
- 2. Minute sub microgram quantities

- Nature of the samples:
- 1. Normal samples
- 2. Highly admixed, adulterated or contaminated
- 3. Metabolized
- 4. Decomposed
- 5. Weathered

Analytical Methodology

- The analytical methodology to be adopted in forensic analysis depends on factors such as:
- 1. Quantity of the sample
- 2. Purity of the sample
- 3. State of the sample
- 4. Contamination / adulteration of the
- sample
- 5. Impurities in the sample
- 6. Metabolic state of the sample

Aim of the analysis

- To get results which are:
- 1. Unequivocal
- 2. Accurate
- 3. Precise
- 4. Fast
- 5. Reproducible

Methods of analysis

- Most modern instrumental methods of analysis are at the disposal of a forensic scientist.
- However the practicing forensic chemist would use a suitable methodology requiring stepwise progression from simple, general, rapid, widely applicable screening, visual, comparison methods to the more discriminating and specific advanced instrumental methods in order to reach the conclusion about the identity and / or quantity.

- Modern trend in forensic chemical analysis demand results which are:
- Based on proper sampling (Crime & Control)
- Reliable
- Quality assured
- Valid (technically & statistically)
- Admissible & acceptable to courts

Techniques used for analysis

- The techniques used for the analysis in forensic work depend on factors like:
- The quantity of the sample
- Purity of the sample
- Adulteration if any
- Contamination
- The forensic chemist should judiciously use his discretion to select suitable analytical technique (s) & methodology

- Unlike other disciplines of applied analytical chemistry, there is no standard methodology or cook book procedure which could be used for wide variety of sample received in forensic science laboratory. Though methods for some samples of routine nature have been standardized for others standard methods do not suit the various circumstances.

- Suggested standard methods are only recommendatory but not mandatory. Further as most of the time they are carrying out unconventional general unknown analysis they have to use several alternative methods for absolute identification and confirmation followed by quantitation.

- In many of the cases due to very small quantity of the sample or in the case of trace analysis the analyst has to devise a suitable methodology so that the available small quantity of the sample is first examined by general non destructive techniques and later the same sample is subjected finally to a destructive technique.

- This is necessitated in the forensic set up as the chemist can not have a repeat sample of a crime case.
- As an illustration, a single sample of few micro grammes recovered in a crime case
- can go through all the analytical techniques such as visual examination, various microscopic examinations including SEM, X-Ray diffractrometry in the solid state. Later, the same sample can be dissolved in a solvent

- and subjected to HPTLC. On the plate itself, UV or fluorescence spectra can be taken. The spot material can be once again collected, purified subjected to micro
- FT-IR spectrophotometry. The compound in the KBr micro pellet can again be extracted into a solvent to get a UV spectrum and later injected into the HPLC system. The compound fraction eluted can be collected, recovered and once again injected into a GC-MS or LC-MS or LC-MS-MS system to get confirmed unequivocal data.

- Suitable modifications could be made to get the quantitation of the samples. Though this is a typical illustrative case to demonstrate that from a trace sample how a forensic chemist can give his opinion using one or more analytical techniques in tandem at his discretion. It nevertheless shows the ingenuity of the chemist despite several limitations.

- The general nondestructive techniques start with simple optical examination with unaided eyes under various light conditions (day light, artificial light, UV light and IR radiations). Later, starting from simple microscopic observations to various SEM techniques could be used. Non destructive spectroscopic techniques used commonly include absorption and fluorescence. UV absorption and reflectance micro spectrophotometry has extensive use in pigments and colours in paints inks and fibres. It has applications in trace drug analysis.

- The advent of FTIR spectrometers using micro techniques have helped in the analysis of organic materials from fibres, paints, glue, polymers, drugs, greases, oil, inks, paper and toners etc. Fluorescence techniques are regularly being used to characterize and compare the samples of mineral oils, greases, inks and drugs whereas XRF techniques find extensive use in inorganic work dealing with glass, cements, soil, paints and pigments etc.

- SEM-EDX spectrometry has extensive applications in the area of glass, paints, fibres, gunshot residues and polymers. The NAA which was initially used with lot of enthusiasm for glass, metals, gunshot residues and inorganic toxicological analysis has received a setback due to interpretation and contamination problems.

- Among the destructive techniques following array of techniques are routinely used:
- AAS, ICPAES are routinely used for inorganic work. They have found applications in the analysis of hair, paints, finger nails, fuels, lubricants, fibres, polymers, papers, soil, glass, pharmaceuticals, poisons, gunshot residues, explosion residues, counterfeit currency & coins and archaeological specimens. The elemental profiling is used in identifying the source of the material and critical comparison of materials

- Mass spectrometry in its various forms is an indispensable technique in the armamentarium of forensic scientist. It is used in the analysis of metals, soils, drugs, pesticides, natural products, polymers, lubricants and poisons. The MS in its various forms including the hyphenated techniques such as MALDI, TOF, ICP-MS, GC-MS, LC-MS, CE-MS, LC-MS-MS, Py-GC-MS,SIRMS, IMMS, are being increasingly employed in the forensic work giving lot of confidence and unequivocality.

- Though NMR Spectroscopy has been occasionally used, it is not very popular in FSLs. However in the NDPS analysis it is being made a mandatory method along with other Chromato spectroscopic methods.

- Large data forensic data bases for the identification of the compounds are available in the area of spectroscopy. These data bases are incorporated in the software of the various instruments for quick identification by computerized matching.

- UV-Vis Spectrophotometry, FT IR Spectrophotometry (with its various attachments for micro FTIR work such as ATR and DRIFT) GC-FTIR, FT Raman, Raman Spectroscopy, SERR Spectroscopy Spectrofluorimetry and chemiluminescence methods are routinely used for qualitative and quantitative analysis of drugs, pesticides, paints, plant products, dyes, inks, lubricants, fuels and biological material etc.

- Various chromatographic techniques such as TLC, HPTLC, GC (including HS and Py. methods), HPLC, SCFC, and CE are extensively being used for separation, identification and quantifying various forensic samples such as drugs, pesticides, dyes, natural products, poisons, explosives etc.

- These include UV-Vis Spectroscopy, Fourier transform infrared spectroscopy, thin layer chromatography, high-performance liquid chromatography, atomic absorption / Emission spectroscopy, GC-MS, LC-MS, LC-MS-MS and ICP-MS etc.

- The range of different methods is important due to the destructive nature of some instruments and the number of possible unknown substances that can be found at a scene. Forensic chemists prefer using nondestructive methods first, to preserve evidence and to determine which destructive methods will produce the best results.

- Along with other forensic specialists, forensic chemists commonly testify in court as expert witnesses regarding their findings. Forensic chemists follow a set of standards that have been proposed by various agencies and governing bodies, including the Scientific Working Group on the Analysis of Seized Drugs.

- In addition to the standard operating procedures proposed by the group (NABL), specific agencies have their own standards regarding the quality assurance and quality control of their results and their instruments.

- To ensure the accuracy of what they are reporting, forensic chemists routinely check and verify that their instruments are working correctly and are still able to detect and measure various quantities of different substances.

- Forensic chemists' analysis can provide leads for investigators, and they can confirm or refute their suspicions. The identification of the various substances found at the scene can tell investigators what to look for during their search.

- During fire investigations, forensic chemists can determine if an accelerant such as gasoline or kerosene was used; if so, this suggests that the fire was intentionally set. Forensic chemists can also narrow down the suspect list to people who would have access to the substance used in a crime.

- For example, in explosive investigations, the identification of RDX or C-4 would indicate a military connection as those substances are military grade explosives. On the other hand, the identification of TNT would create a wider suspect list, since it is used by demolition companies as well as in the military.

- During poisoning investigations, the detection of specific poisons can give detectives an idea of what to look for when they are interviewing potential suspects. For example, an investigation that involves ricin would tell investigators to look for ricin's precursors, the seeds of the castor oil plant.

- Forensic chemists also help to confirm or refute investigators' suspicions in drug or alcohol cases. The instruments used by forensic chemists can detect minute quantities, and accurate measurement can be important in crimes such as driving under the influence as there are specific blood alcohol content cutoffs where penalties begin or increase.
- In suspected overdose cases, the quantity of the drug found in the person's system can confirm or rule out overdose as the cause of death.

- Forensic Science: Definition – Multidisciplinary
- Forensic Chemistry
- Forensic Toxicology
- Chemistry & Biochemistry
- Analytical Chemistry
- Comparative, qualitative & quantitative analysis
- Nondestructive & destructive analysis

- Conventional & Instrumental analysis
- Nature of sample: Pure, contaminated, adulterated, decomposed – Solid, liquid, gaseous – Elements, compounds and mixtures often complex
- Sample size: Bulk to traces
- Scale: Macro, semi-micro, micro, sub-micro, ultra micro,
- Origin: Mineral, plant, animal. Natural, semi-synthetic & synthetic

- It is the ability of forensic scientist to give an objective and accurate information about the events that have taken place at the SOC or would have affected the body of the individual.
- Locard's principle: Basis of forensic investigation in the form of physical evidence. Analytical variations in the samples, especially minor elements/compounds and impurities, is the key factor in forensic analysis

Types of cases:

- Theft, robbery, accidents, suicides, homicides, rape, white collar crimes, wild life crimes, NDPS, drug/food adulteration, pollution, intelligence, espionage, sabotage, anticorruption and security operations

Forensic Chemical Analysis

- NDPS, therapeutic drugs. foods, pesticides, plant material, plant poisons, industrial chemicals, metals, explosives, firearm residues, arson residues, explosion residues, paints, alcoholic liquors, cosmetics, fibres, dyes, plastics, polymers, soils, dusts, fuels, papers, inks, jewelry, poisons/toxins in the material/body fluids/visceral tissues, art objects, antiques, glasses all in different and varying matrices.
-

- The steps involved in the analysis of the above samples would be:
- 1. Isolation of elements/compounds of
- interest from the materials by using
- various separation techniques
- 2. Identification of the separated
- components
- 3. Confirmation of identity
- 4. Quantification
- 5. Comparative analysis, profiling
- 6. Interpretation
- 7. Reporting the opinion

- 1. Alcoholic beverages: GC,HS-GC,
- Automation, GC-MS, Refractometry
- 2. NDPS/TD: UV-Vis, FTIR,
- Fluorescence,
- Raman spectroscopy, NMR, HPTLC,
- GC, LC, Chiral methods, SCFC, CE,
- XRD,MS, GC-MS,LC-MS, CE-MS,
- GC- FTIR, IMS, SIRMS, SERRS

- 3. Explosives & residues: UV-Vis, FTIR,NMR,
- Fluorescence, FT Raman Spectroscopy,
- SEM-EDX, XRD, XRF,HPTLC, GC, LC,CE,
- GC-MS, CE-MS,LC-MS,IMS, Thermal
- methods, SIRMS, SERRS
- 4. Metals: AAS, ICPAES, ICPMS, Electro
- analytical methods, XRF,SEM-EDX
- microanalysis, NAA, Isotope dilution MS

- 5. Paints: UV-Vis, IR, Fluorescence
- spectroscopy, Micro FTIR,SEM-EDX
- Microanalysis, TLC, GC, Py GC, Py GC- MS,
- AAS,ICPAES, SIRMS, SERRS
- 6. Fibres: Vis,FTIR Spectroscopy, SEM, XRD,
- Py-GC, Py GC-MS,LC, LC-MS
- 7. Paper: SEM, AAS, ICPAES, XRF

- 8. Inks: UV-Vis, HPTLC, LC, GC, SIRMS,
- SERRS
- 9. Cosmetics: HPTLC, GC, LC, GC-MS, LC-MS

10. Art objects and antiques: All the methods

- used for paints, metals, paper and inks

11. Glass: Refractometry, ICP-MS, ICPAES,

- XRF, thermal methods

Toxicological Analysis

- Nature of forensic toxicological samples –
- Blood, urine, saliva, hair, nails, CSF. Vitreous humor, visceral tissues from various organs
- Toxicology of living
- Toxicology of dead (Post mortem)
- Preservation of samples – Decomposition and putrefaction process –Exhumation

Toxicological Analysis

- ANALYTICAL PROCESS:
- 1. Extraction from biological matrices:
- Volatilization, LLC, SPE, SCFE
- 2. Clean up processes for co extractives:
- Columns and cartridges
- 3. Spot tests, colour tests, Immunnoasssays (presumptive)
- 4. Instrumental methods

- 1. Volatile poisons: GC, IR, GC-MS
- 2. Metallic and other inorganic poisons:
- AAS, ICPAES,IC, ICP-MS, CE, NAA
- 3. Drugs & metabolites: UV-Vis, FTIR,
- Spectrofluorimetry, HPTLC, GC,
- LC,CE, GC-MS, LC-MS, CE-MS,
- GC-FTIR, XRD, NMR, Immunoassay
- methods

- 4. Pesticides: HPTLC, GC, LC, CE,
- GC-MS, LC-MS, CE-MS, immunoassay
- methods, spectroscopic methods
- 5. Miscellaneous poisons, Inorganic &
- organic: Molecular and atomic
- spectroscopic methods,
- Chromatographic methods, Mass
- spectroscopic and XRD methods

The Expert Witness

- An expert witness can testify as to his/her opinion of what the evidence indicates
- A lay witness can only testify as to fact
- What is meant by an expert witness?
- An Expert Witness can be anyone with knowledge or experience of a particular field or discipline beyond that to be expected of a layman. The Expert Witness's duty is to give to the Court or tribunal an impartial opinion on particular aspects of matters within his expertise which are in dispute.

- Trial judge must be satisfied that the expert
- Has skill or knowledge that will aid the court in determining the truth
- Education (degrees, courses)
- Training (internship under experienced practitioner)
- Experience (years on the job, publications, professional societies)
- Trial judge is the gatekeeper

- Jury / Court assigns weight to the expert's opinions
- Jury/ Court looks at
- Credentials
- Demeanor
- Whether material is presented simply and clearly
- Jury/Court is the trier of fact

- Admissibility: A Moving Target
- Frye v. US (1923)
- Scientific evidence is admissible only if it has gained general acceptance in the field
- Rejected polygraph opinions

- Coppolino v. State of Florida (1968)
- Doctor accused of poisoning his wife with succinylcholine chloride
- New and unique tests performed specifically for this case
- Detected by-products of metabolism of poison (succinic acid)
- Admissible if based on scientifically valid principles and techniques

- Federal Rule of Evidence 702 (1975)
- Approved by Congress
- More flexible general relevance test for admissibility of opinion testimony by experts
- “If scientific, technical or other specialized knowledge will assist the trier of fact to understand the evidence or to determine a fact at issue, a witness qualified as an expert by knowledge, skill, experience, training, or education, may testify thereto in the form of an opinion or otherwise.”

- Daubert v. Merrell Dow Pharmaceuticals (1993)
- When expert evidence based on “scientific knowledge” is offered at trial, the judge acts as gatekeeper to determine if the evidence is “reliable”
- Four suggested factors in determining reliability
- Testable using the scientific method
- Peer reviewed
- Error rates
- Acceptability to the scientific community
- Trial judge given lots of flexibility
- Muddy waters—what is scientific knowledge?
- What about other types of experts?

- Why Daubert won on appeal
- When Congress passed Rule 702 it ignored the Frye general acceptability criterion
- Frye was no longer “good law”--

- Kumho Tire Co v. Carmichael (1999)
- Daubert factors are extended to non-scientist expert witnesses.
- Daubert factors are not the only ones that can be considered
- Trial judge now has enormous flexibility
- Daubert and Kumho apply to federal cases only
- 18 State Courts have adopted Daubert standards
- Other State Courts have rejected Daubert and still use a modified Frye standard

Testimony

- The standardized procedures for testimony by forensic chemists are provided by the various agencies that employ the scientists as well as SWGDRUG. Forensic chemists are ethically bound to present testimony in a neutral manner and to be open to reconsidering their statements if new information is found. Chemists should also limit their testimony to areas they have been qualified in regardless of questions during direct or cross-examination.

- What is evidentiary value of an expert witness?
- The right of evidence allows an individual to: who is a witness to state the facts related either to a fact in dispute or to the relevant fact, but not to its inference. It covers both criminal and civil law.

- What is Section 45 of the Indian Evidence Act?
- The opinions of experts upon the question whether the symptoms exhibited by A commonly show unsoundness of mind, and whether such unsoundness of mind usually renders persons incapable of knowing the nature of the acts which they do, or of knowing that what they do is either wrong or contrary to law, are relevant.

- The law of evidence is the edifice on which the system of dispensation of justice rests. In fact, the purpose and object of evidence is to guide the Courts to come to a conclusion regarding a case at hand. But, in certain cases, where the questions involved are beyond the range of common experience and knowledge, evidence in form of facts pose problems as the Court may not have sufficient competence to arrive at a conclusion based on those facts.

- Thus, the need arises for experts who have the required ability and knowledge to tender evidences. Section 45 of the In¬dian Evidence Act 1872 deals with expert evidence. It allows an expert to tender evidence on a particular fact in question and to show to the court that his findings are unbiased and scientific. In contemporary times, the reliance on expert evidence has been overwhelming.

- Section 293 in The Code Of Criminal Procedure, 1973
- 293. Reports of certain Government scientific experts.
- (1) Any document purporting to be a report under the hand of a Government scientific expert to whom this section applies, upon any matter or thing duly submitted to him for examination or analysis and report in the course of any proceeding under this Code, may be used as evidence in any inquiry, trial or other proceeding under this Code.
- (2) The Court may, if it thinks fit, summon and examine any such expert as to the subject- matter of his report.

- (3) Where any such expert is summoned by a Court and he is unable to attend personally, he may, unless the Court has expressly directed him to appear personally, depute any responsible officer working with him to attend the Court, if such officer is conversant with the facts of the case and can satisfactorily depose in Court on his behalf.

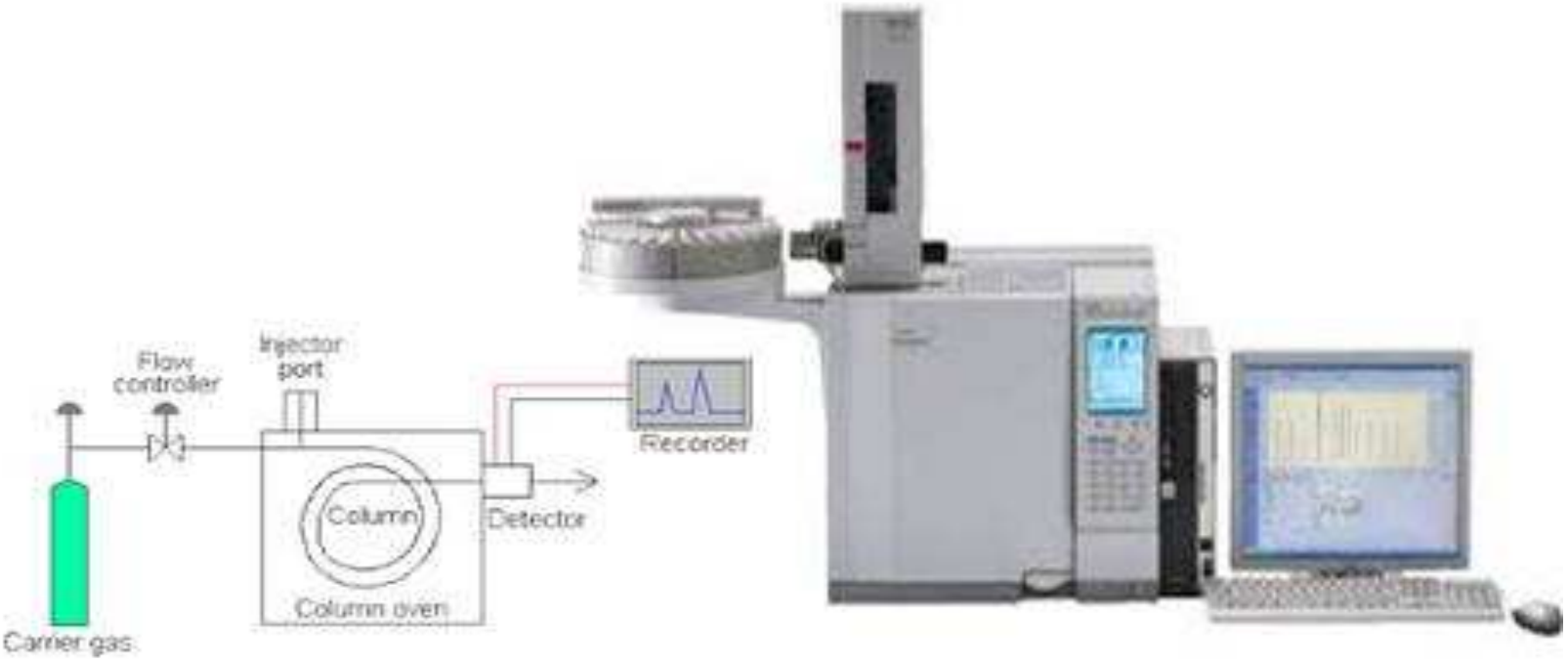
- (4) This section applies to the following Government scientific experts, namely:-
- (a) any Chemical Examiner or Assistant Chemical Examiner to Government;
- (b) the Chief Inspector of- Explosives;
- (c) the Director of the Finger Print Bureau;
- (d) the Director, Haffkeine Institute, Bombay;
- (e) the Director 1 , Deputy Director or Assistant Director] of a Central Forensic Science Laboratory or a State Forensic Science Laboratory;
- (f) the Serologist to the Government.

- Individuals called to testify must be able to relay scientific information and processes in a manner that lay individuals can understand. By being qualified as an expert, chemists are allowed to give their opinions on the evidence as opposed to just stating the facts. This can lead to competing opinions from experts hired by the opposing side.

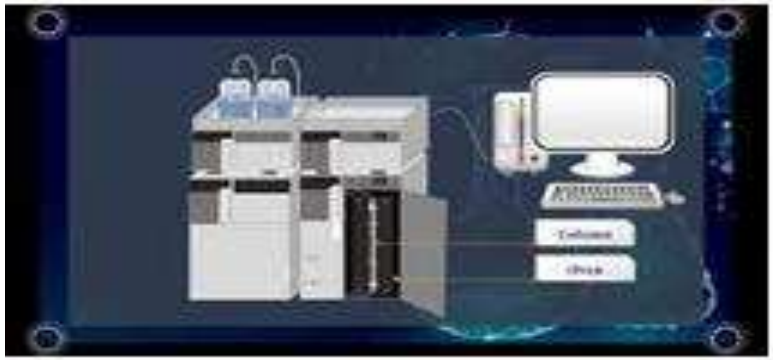
- Ethical guidelines for forensic chemists require that testimony be given in an objective manner, regardless of what side the expert is testifying for. Forensic experts that are called to testify are expected to work with the lawyer who issued the summons and to assist in their understanding of the material they will be asking questions about.

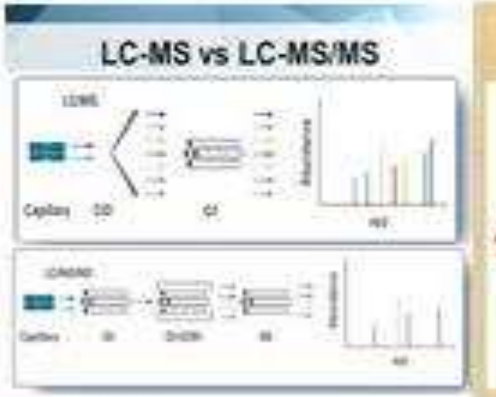
Instrumentation of HPTLC-

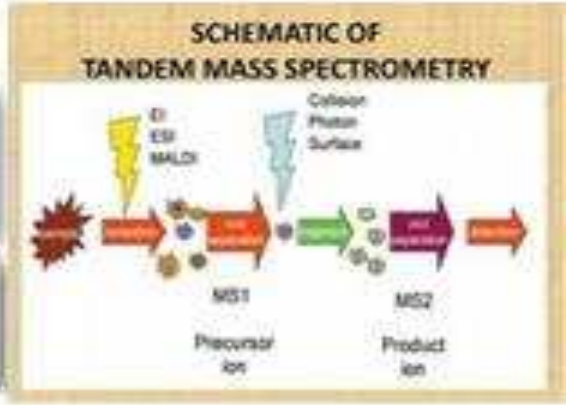
GC


Flow controller
Injector port
Recorder
Column
Detector
Column oven
Carrier gas

HPLC, LC–MS, LC–MS–MS

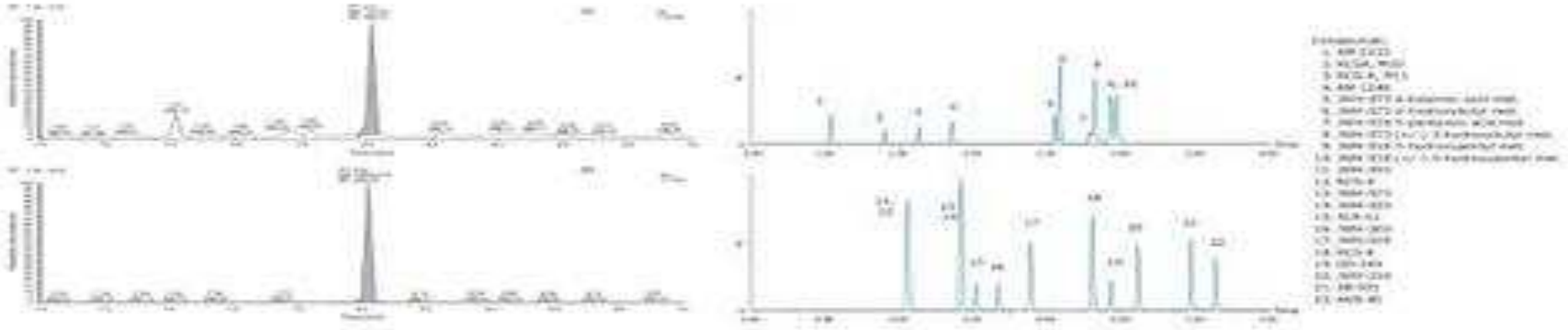


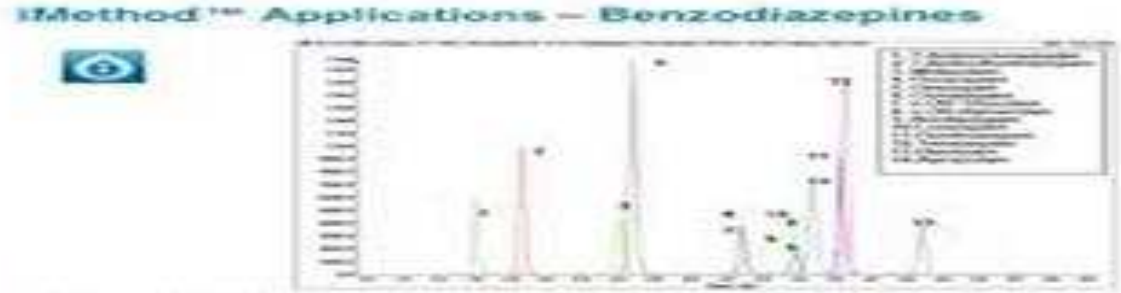




ICP–MS, ICP–OES, AAS, IC & CE

GC– MS, LC–MS, LC–MS–MS





Representative chromatogram of spiked urine at 20ng/mL performed on a 3200 QTRAP® LC/MS/MS system in a 6 minutes run.

Data bases

Mass spectrum

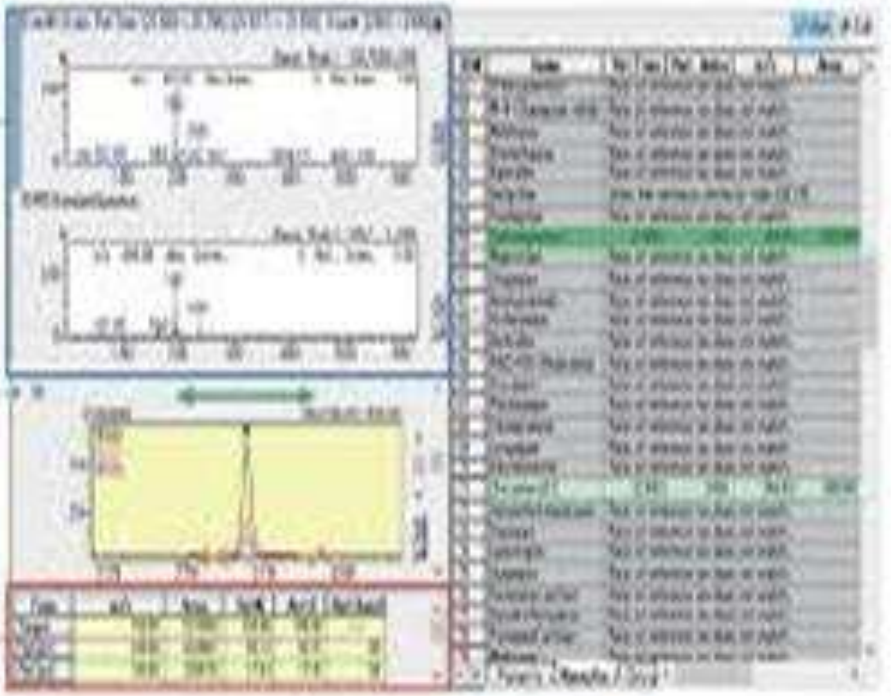
The mass spectrum of the measured sample is compared with the registered mass spectrum in the database.

Retention times

Peaks are searched using corrected retention times.

Mass chromatogram

Peaks are searched characteristic ions and ion ratios




THANK YOU