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Characterization & Instrumental Analysis of Polymers

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Instruemental technique in Polymer Characterisation

1. **Chromatographic Techniques** – GPC/ SEC. HS/ Pyr/ TD with GC/GCMS, LC/ LCMS
2. **Thermal Analysis** – TGA, DSC, DMA
3. **Microscopy** - Optical / Electron microscopy (SEM/ TEM)
4. **Spectroscopy**- Infra-Red spectroscopy (FTIR) with ATR, FTIR microscopy, Raman spectroscopy and Raman microscopy, UV/Vis spectrometry, Nuclear Magnetic Resonance Spectroscopy (NMR)
5. **Elemental Analysis**- AAS, ICP-OES/MS. IC , XRF
6. **Rheometry**

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Gas Chromatography in Polymer characterisation

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Content

- **Chromatography**
- **Basics of chromatography**
- **Gas Chromatography**
  - Inlet systems in chromatography
  - Sample introduction
  - Injection systems
  - Columns
- **Detection systems**
  - Classification
  - Applications
- **Sample Introduction Technique for polymer samples**

History

- *1906-Tswett described the use of glass columns packed with adsorbent for separation*
- *1941-Martin and Synge- Gas could replace liquid as mobile phase*
- *1952- First GC- Martin and James*
- *1954-Ray-Thermal conductivity detector*
- *1955-First Commercial GC*
- *GC-Powerful analytical tool in modern laboratory*

History

Mikhail Tswett, Russian Botanist, 1872-1919

In 1906 Tswett used to chromatography to separate plant pigments.

He called the new technique chromatography because the result of the analysis was 'written in color' along the length of the adsorbent column.

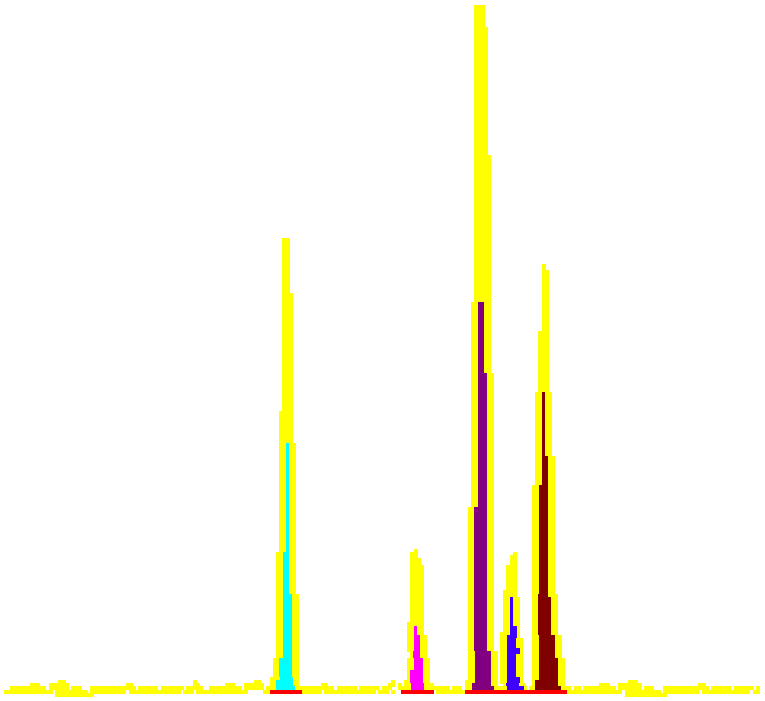
Chroma means “color” and graphein means to “write”

Chromatography

A separative technique

Physical separation of components:

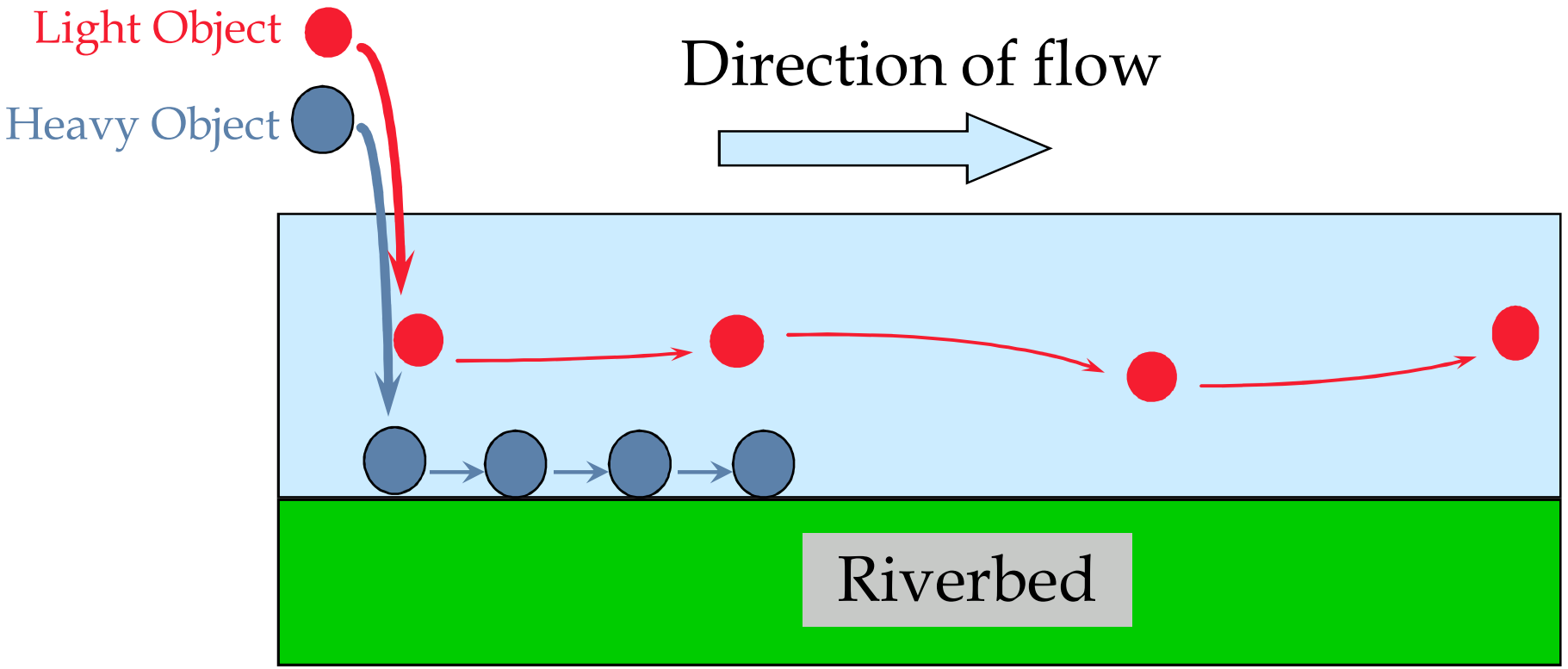
Gas, Liquids, Solids



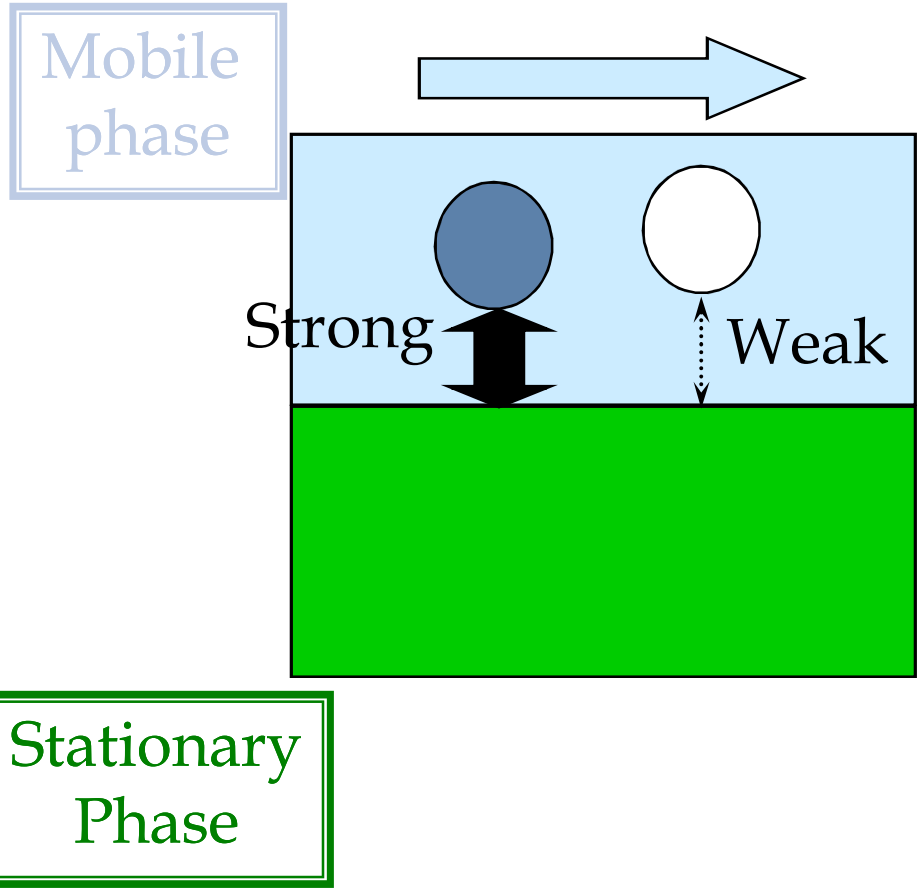
What is chromatography?

Chromatography is a dynamic separation process based on the selective distribution of the different components between two phases. One of the phases, the stationary phase, is held immobilised inside the column while the other phase, the mobile phase travels through the column, flowing through the stationary phase. Compounds that exhibit a higher affinity for the stationary phase will travel more slowly than compounds exhibiting a lower affinity. The different sample components travel at different speed through the column and are eluted from the column at different times.

Comparison of Chromatography to the Flow of a River



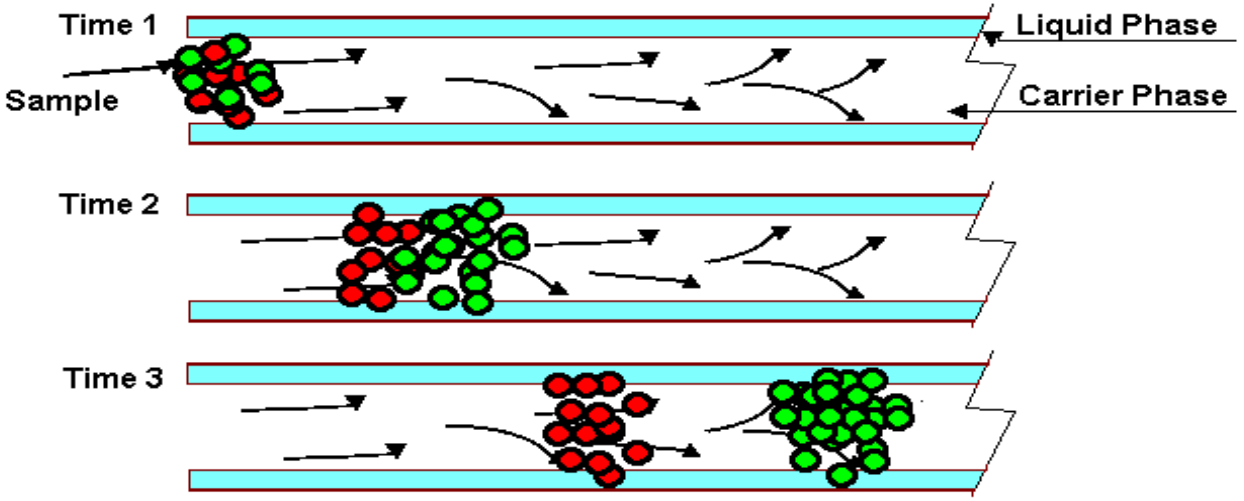
Stationary Phase and Mobile Phase



- Mobile phase and stationary phase contact through phase boundary
- Different analytes have different affinities to stationary phase and mobile phase.

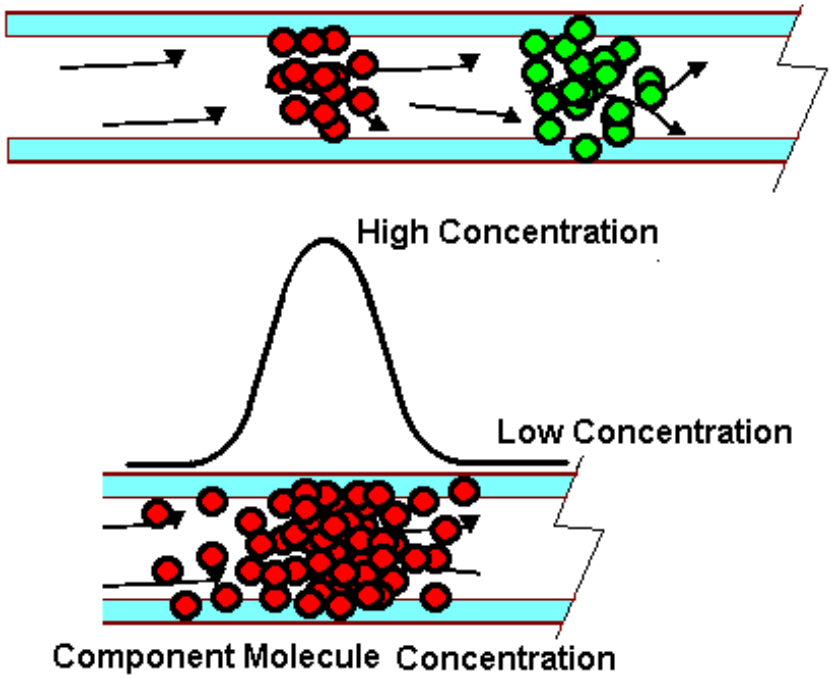
→ Difference of moving velocity results in separation!

The chromatographic process



Two different substances are partitioned between two phases.
Depending on their affinity (toward the stationary phase) will spent different times adsorbed by the stationary phase.

The chromatographic process

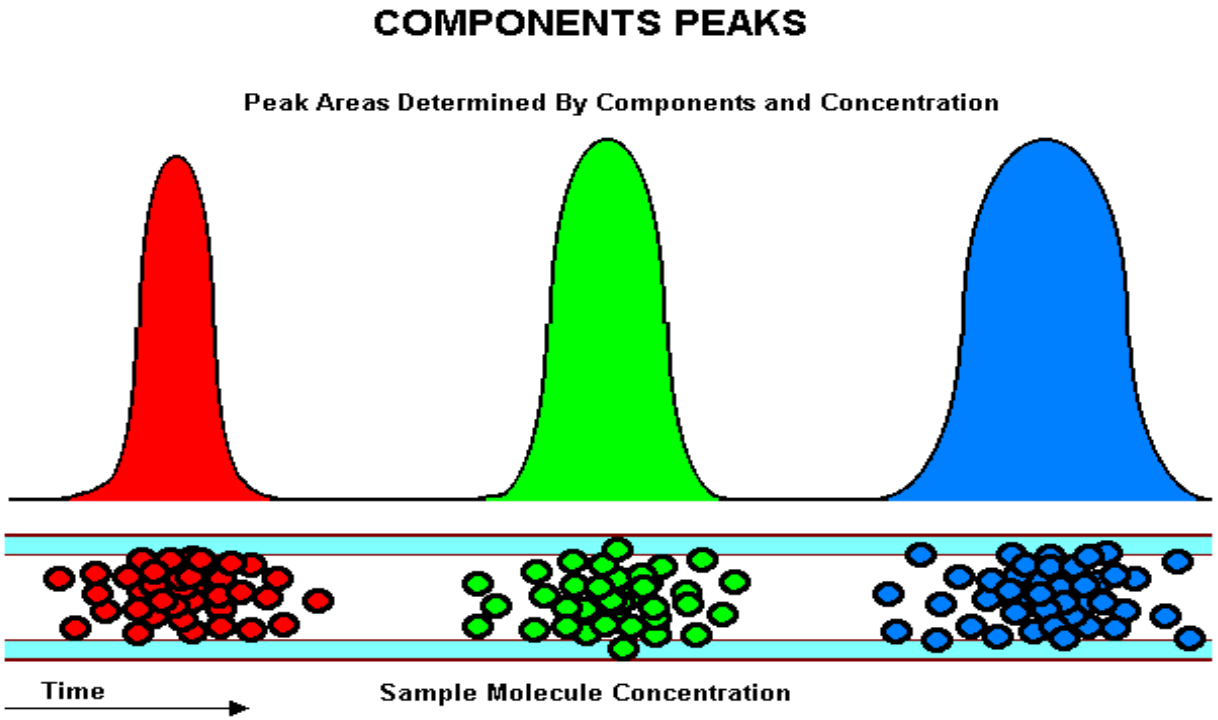


These bands will be most concentrated in the centre due to column effects

If a plot of the sample component concentration is made, a symmetrical random distribution results.

This concentration plot is called Gaussian Curve or Peak

The chromatographic process



•Each component is detected and it exits or elutes from the column.

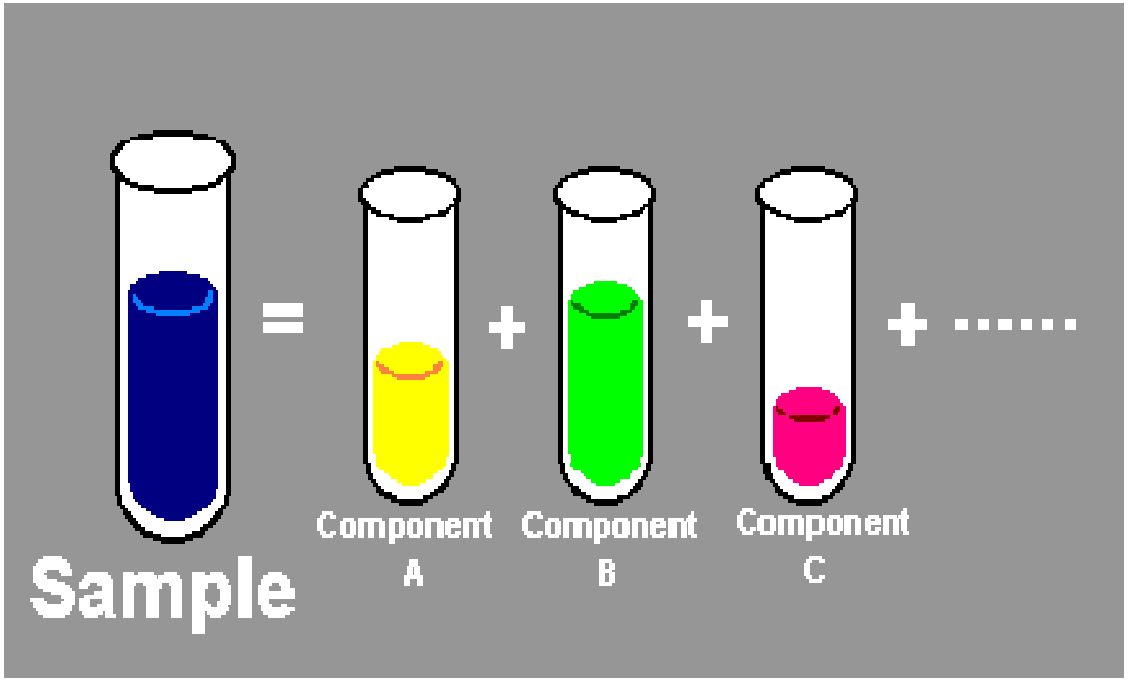
•The detector send a signal to a plotter

Chromatography: Qualitative and Quantitative

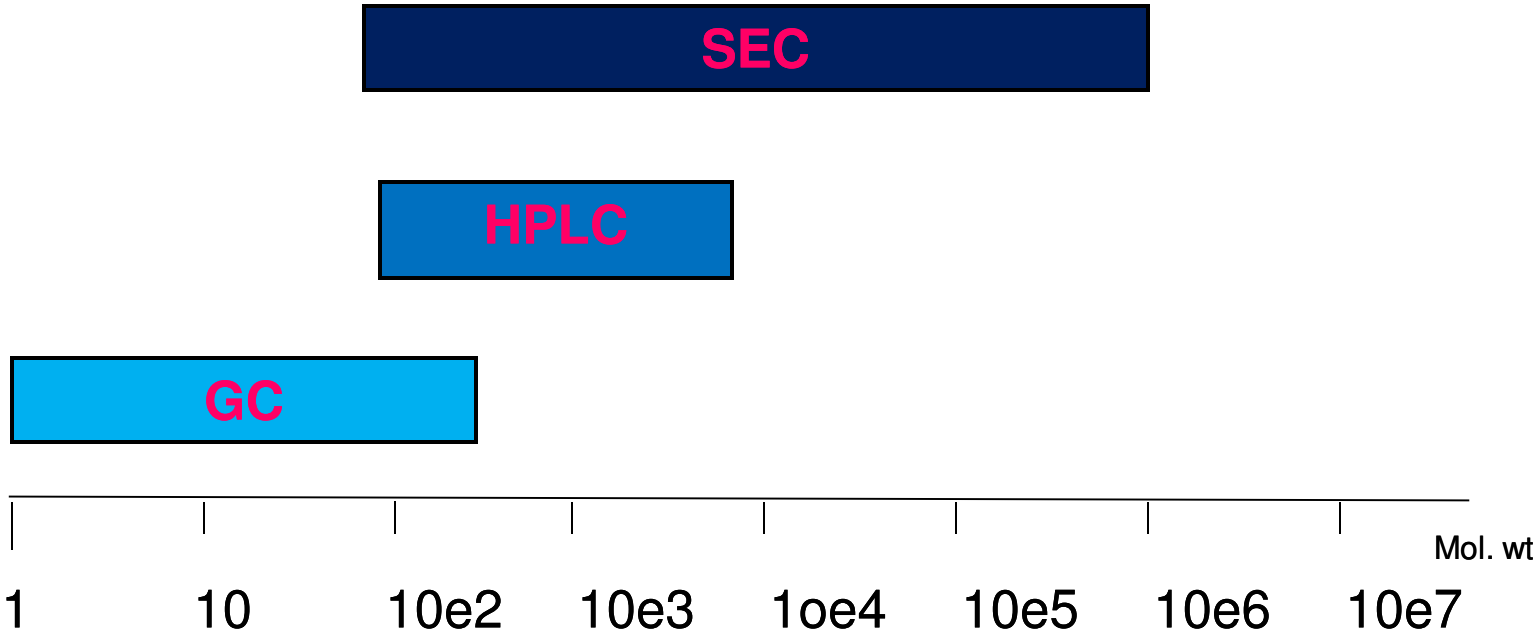
- Identification- Which are (the components)?

and

- Quantitative-How much (of the single component)?



Chromatographic Areas



Chromatographic Modes

Stat. Phase / Mobile Phase	Solid	Liquid	Liquid (ionic)	Solid (Pores)
Gas	**G.S.C.**	**G.L.C.**	**------**	**G.S.C.**
Liquid	**L.S.C. T.L.C.**	**L.L.C.**	**I.E.C.**	**G.P.C. S.E.C.**

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Gas Chromatography

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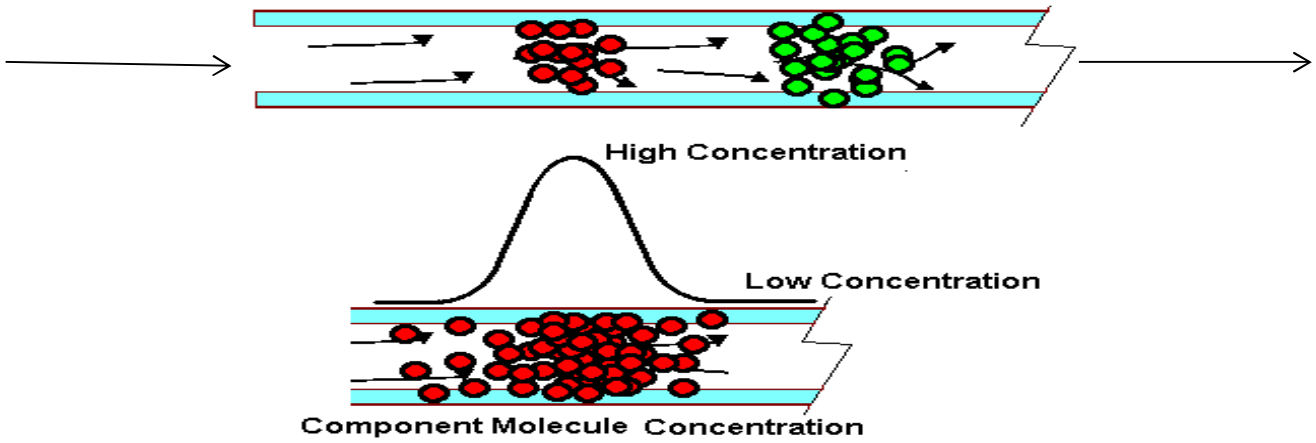
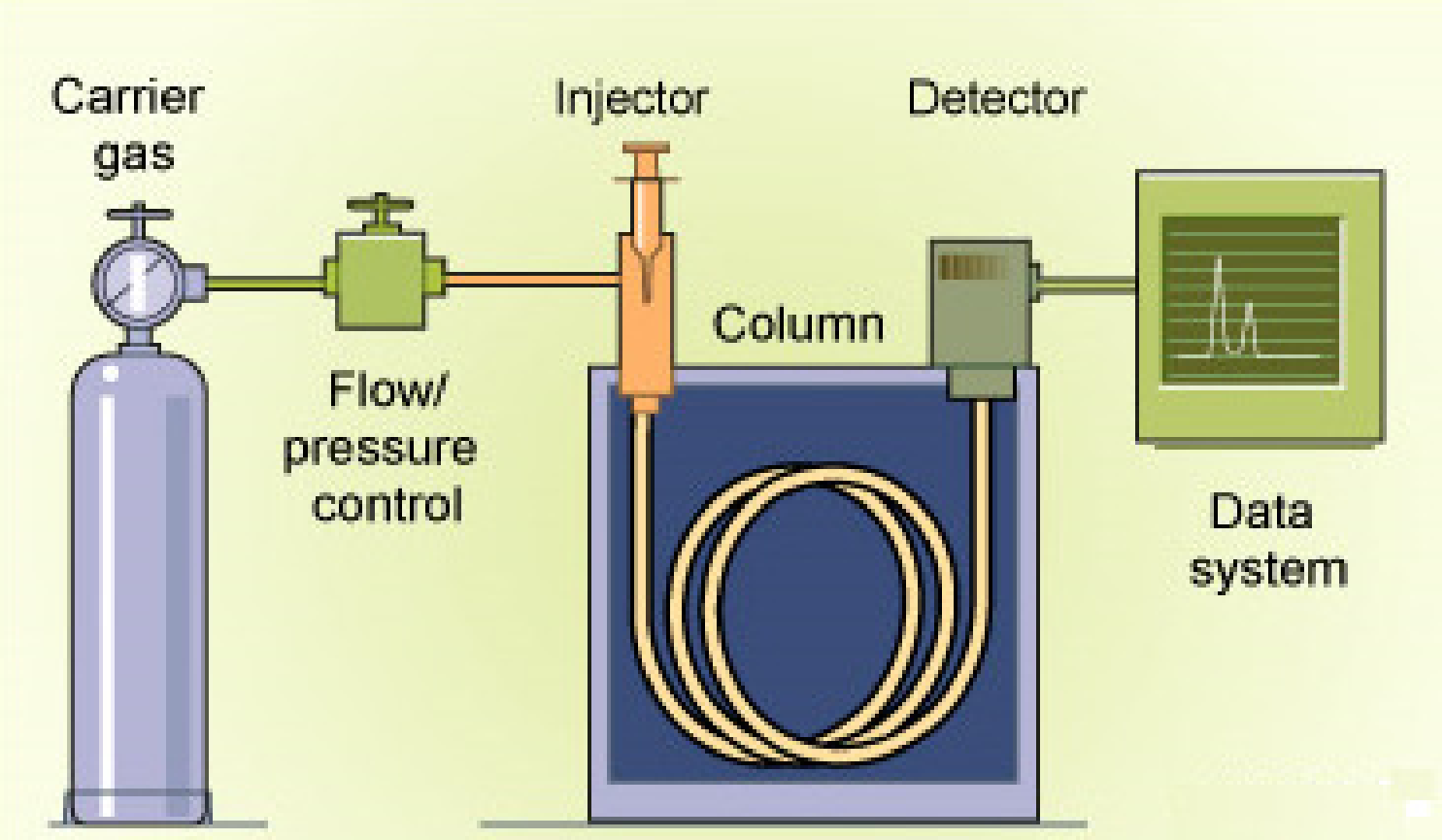
CHROMATOGRAPHIC PROCESS

- *The sample injected onto the column and are carried through the column by an inert gas (carrier gas).*
- *The different component of sample is partitioned between the carrier gas and the stationary phase.*
- *The stationary phase selectively retards the sample components according to their partition coefficient.*
- *The components separate as they pass through the column and eventually elute from the column one after another and are recorded as a function of time*



Gas Chromatographic Equipment



CARRIER GAS IN GAS CHROMATOGRAPHY

Carry injected sample through the column
Commonly used carrier gases are: N_2, He, H_2
Carrier gas is inert and does not interact chemically with the injected solute or analyte

Choice of Carrier Gas in GC-The choice of carrier gas does depend on the Mainly by :
(a) Cost (b) Safety (c) Dryness (d) Freedom from Oxygen (f) Inertness
(g) Availability (h) Type of Detector Used

Secondary purpose of Carrier gas------→ "Suitable matrix for detector to measure the sample component signal."

--Below are the choice of Carrier gas for various GC detectors

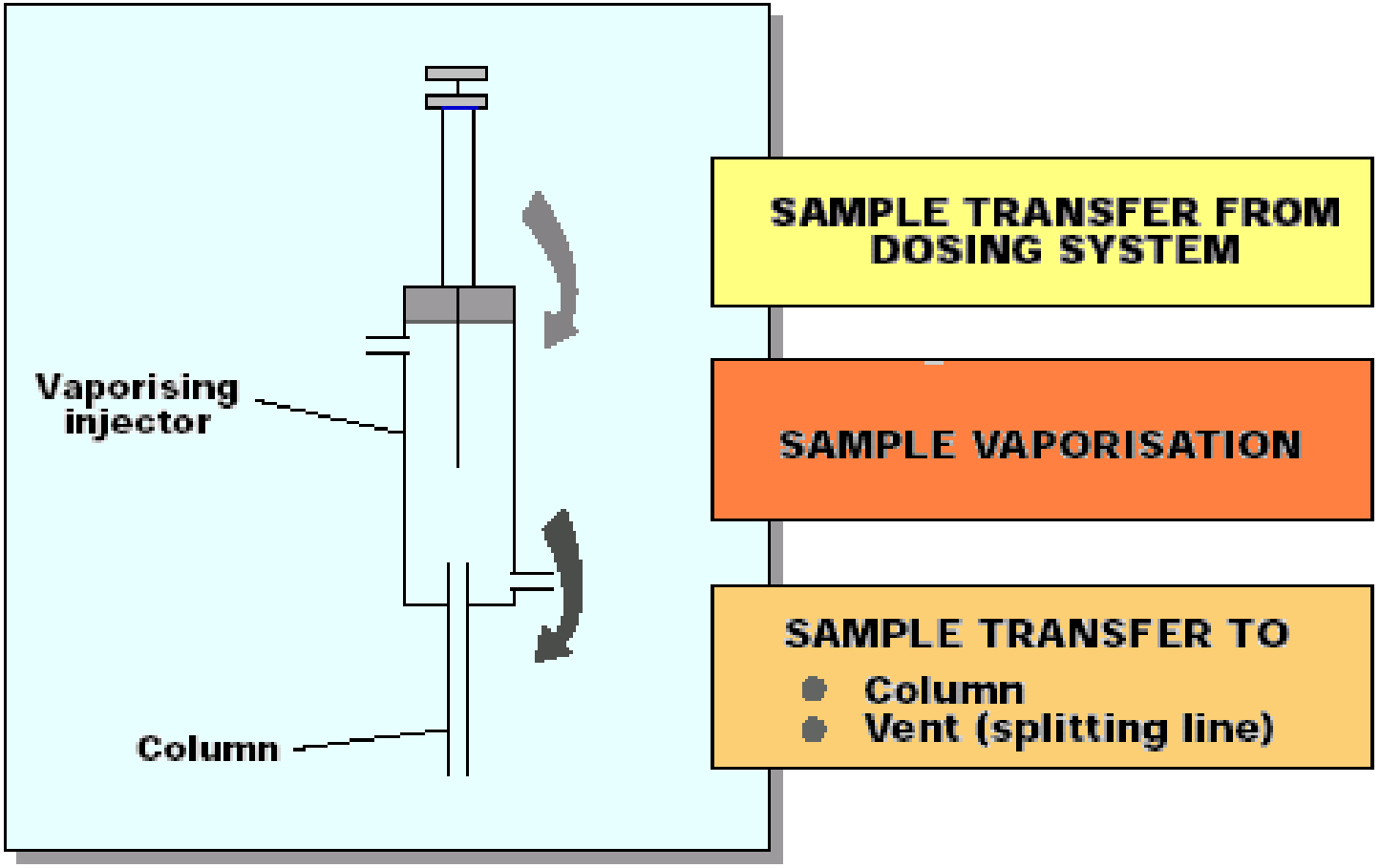
Detector	**Carrier Gas**
Thermal Conductivity	**He**
Flame Ionization	**He or N_2**
Electron Capture	**Very dry N_2/Ar, 5% CH_4**

Sample Introduction in Gas Chromatography

- Liquid introduction by syringe
  - Most commonly used technique
  - Different injector types and techniques are available

- Other techniques and devices
  - Sampling valve (gas or liquids)
  - Head-space (liquids or solids)
  - Purge and trap (water)
  - Thermal desorption (solids)
  - SPME (vapours, liquids or solids)
  - Pyrolizer (solids)
  - ……..

Sample Transfer Process

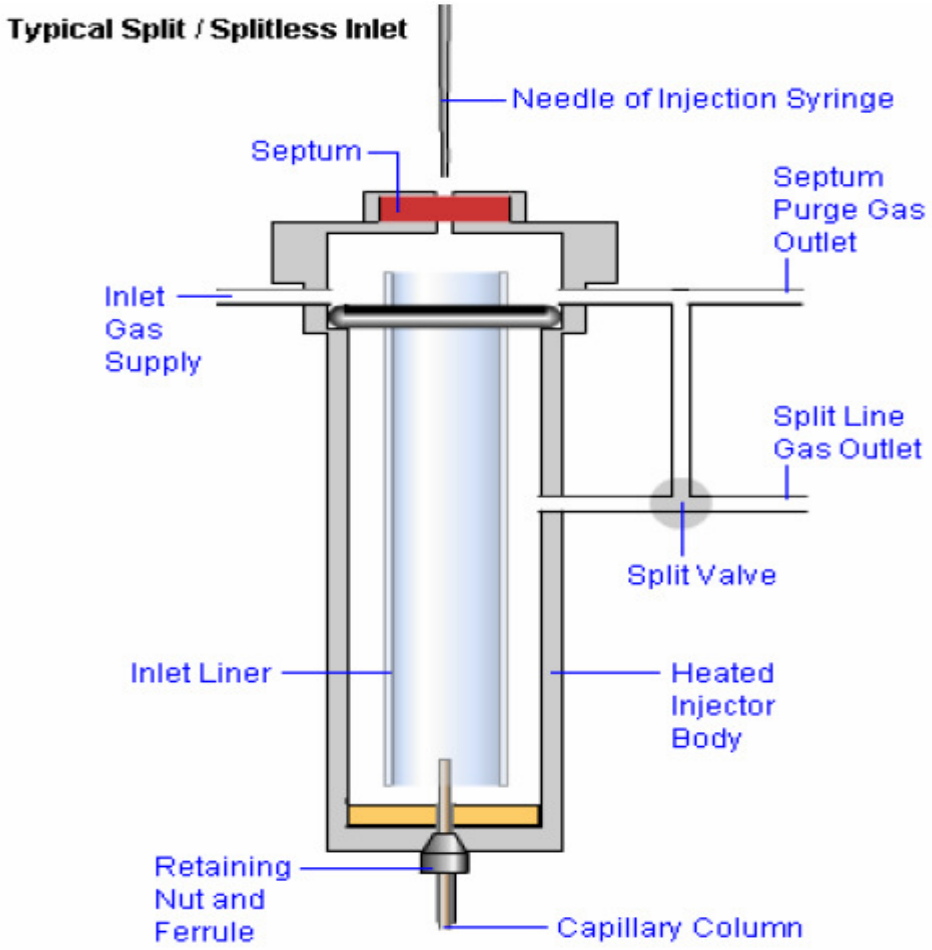


Split / splitless inlet

- Most common inlet
- Vapourising inlet
- 2 mode:

  split injection

  splitless injection



Split / splitless injection

- Splitless injection: Complete transfer of the sample amount.

  Some time cause overloading on column & band broadening.

  Highly reproducable.

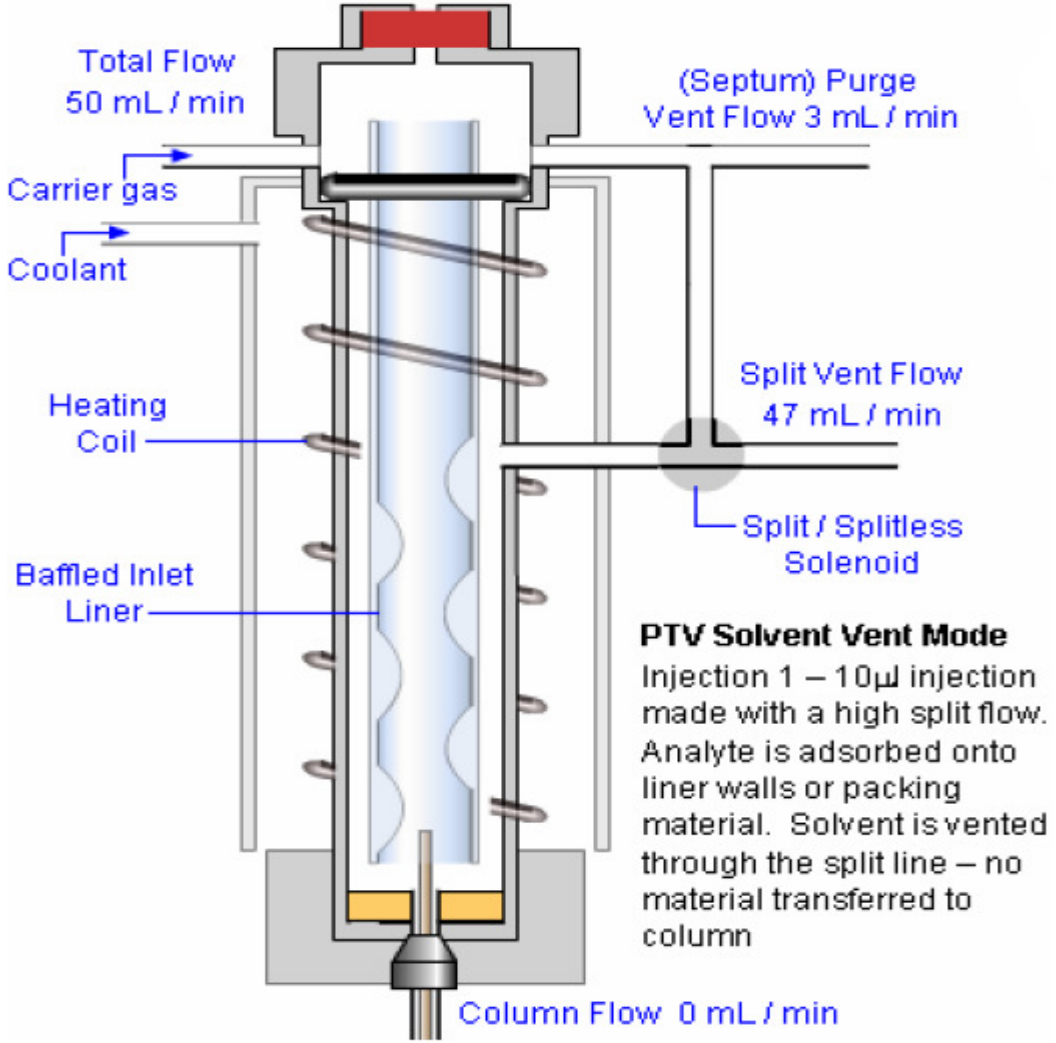
- Split injection: Transferred amount related to the split ratio.
  - Pressure and flow transients in the inlet during injection may change the actual splitting ratio
  - Loss of sample as liquid through the split line.
  - Not suitable for trace level detection.

PTV injection

- First describe by VOGT in 1979.
- Closely resemble to split/splitless inlet. 2 main differences:
  - inlet is kept cool during injection- allowing the analyte to condence inside the liner, while solvent is vented via split.
  - Inlet has very low thermal mass, allow rapid heating for analyte transfer

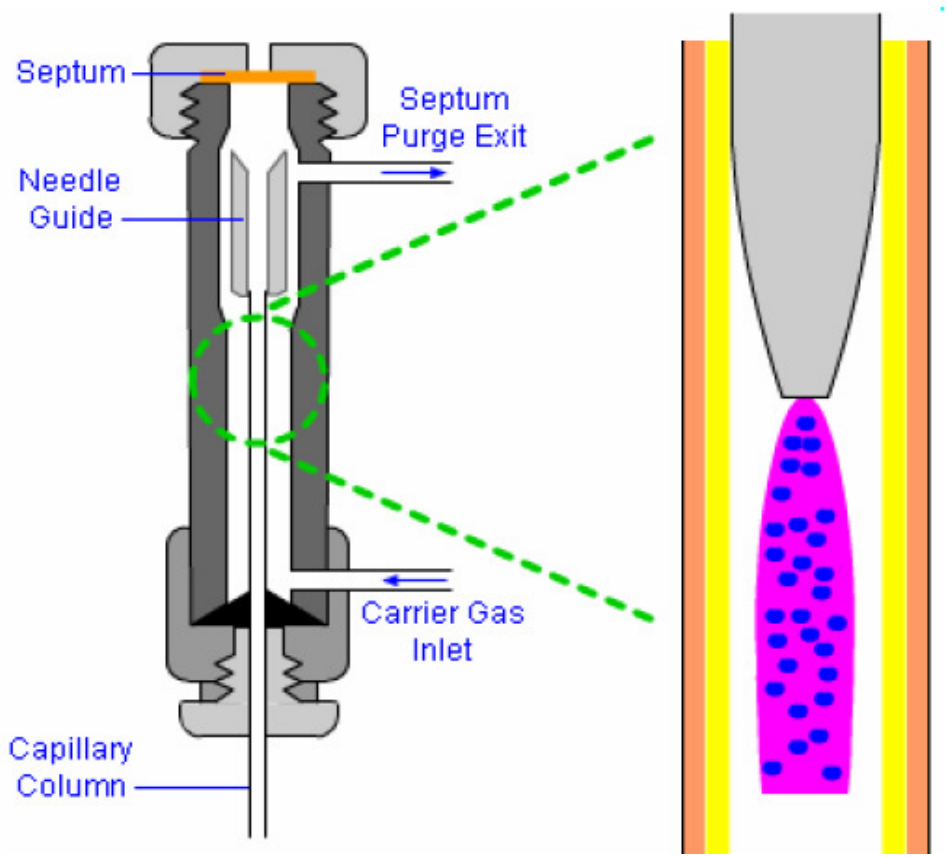
  Large volume may be injected at control speed into the inlet allowing the injection of very large volume.

PTV



Cool on column injection

- The sample solvent is directly injected directly into column using a small diameter needle. (does not use flush vaporisation).

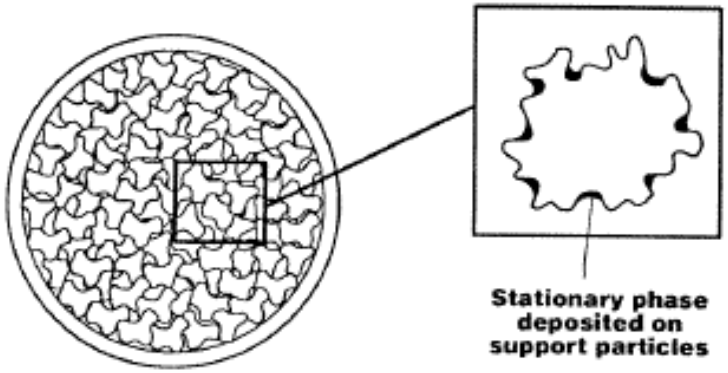


Column type

Column type	Internal diameter	Carrier flow
Capillary column	0.25 – 0.32 mmID	3 - 4 ml/min
wide bore column	0.53 mmID	5 – 10 ml/min
Narrow bore column (e.g. UFM)	0.1 mmID	1 – 1.5 ml/min

GC Columns main characteristics

PACKED COLUMNS



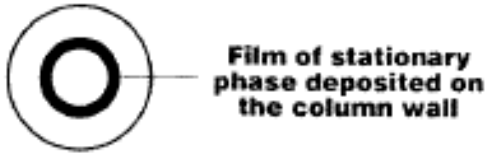
$d_{col} = 1 \div 6$ mm

$L_{col} = 0.2 \div 10$ mm

$d_p = 0.1 \div 0.4$ mm

% Stationary phase = $1 \div 30$

CAPILLARY COLUMNS



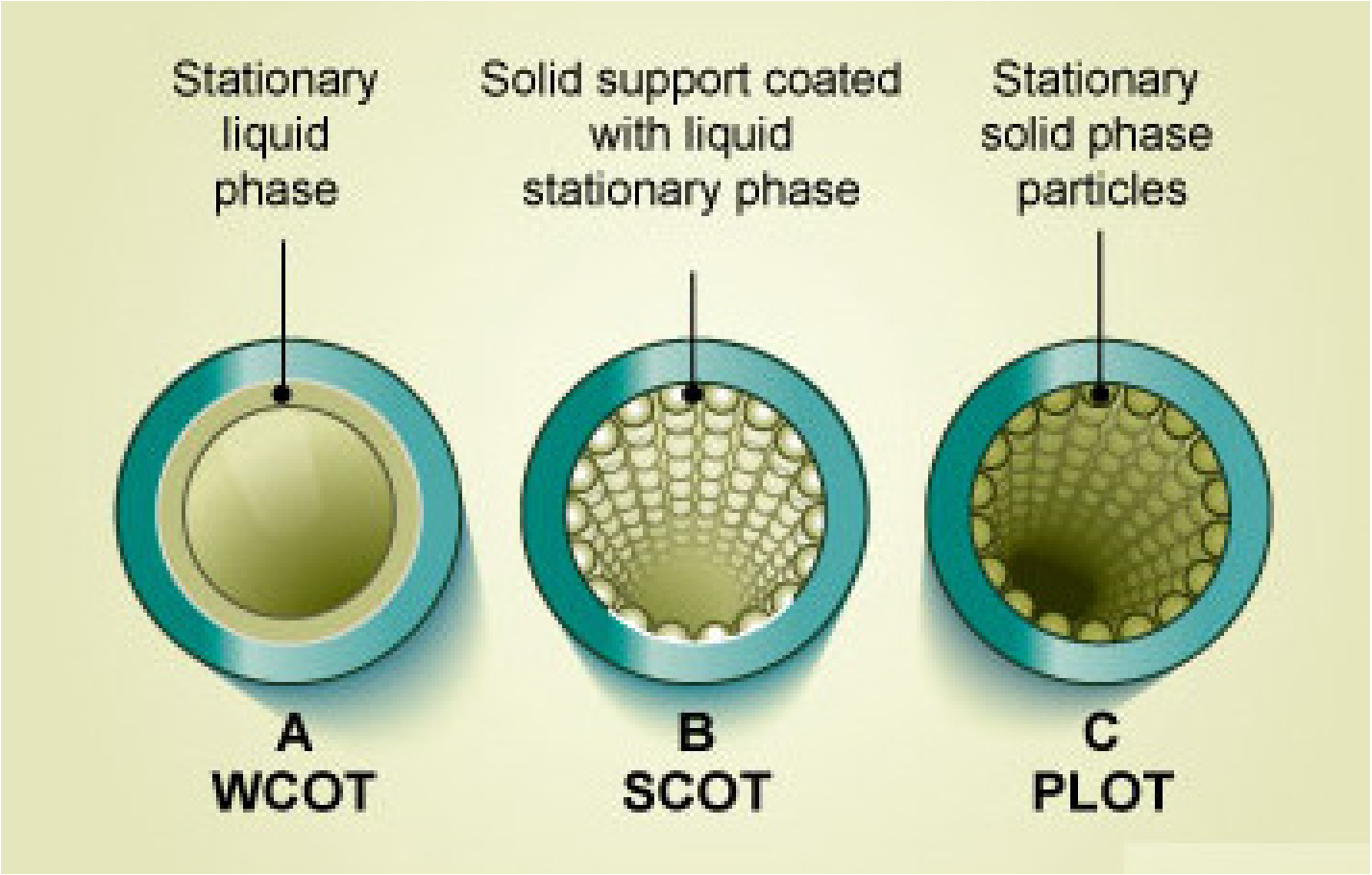
WCOT	Wall coated open tubular column
PLOT	Porous layer open tubular columns

Stationary phase thickness = $0.1 \div 10$ µm

$L_{col} = 2 \div 50$ m (100m)

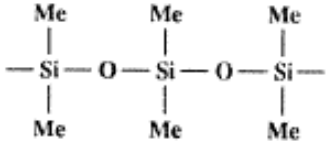
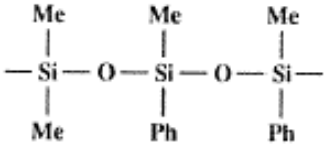
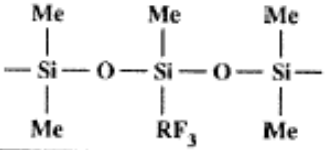
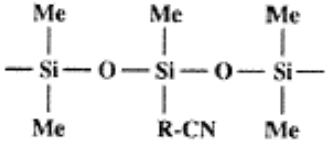
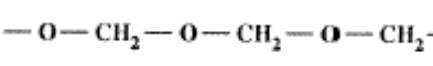
d_{col} (mm)	
Narrow bore	$0.02 \div 0.1$
Conventional	$0.2 \div 0.32$
Wide bore	$0.5 \div 0.6$

Cross-Section of capillary column



Main Stationary Phases in Capillary GC

POLARITY

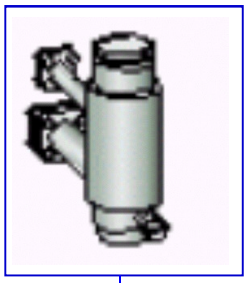
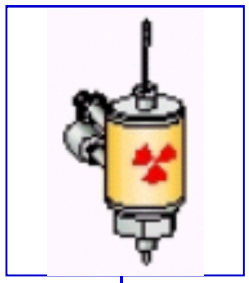
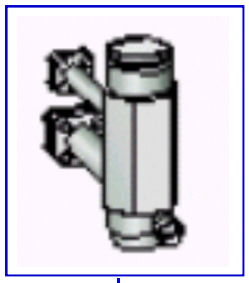
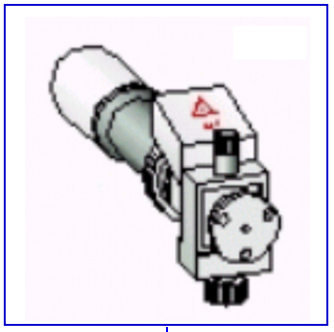
Type	Molecular structure	Code
Dimethyl silicones		OV-1, OV-101
Methyl phenyl silicones		OV-17, OV-61, OV-73
Trifluoropropyl methyl silicones		OV-210
Cyanopropyl methyl silicones		OV-225, OV-275
Polyethylene glycols		Carbowaxes

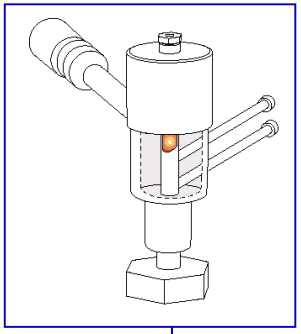
MAIN TYPES OF STATIONARY PHASES USED IN HRGC

Efficiency

- The efficiency of a column is the capability of the system to maintain the subtance's molecules dispersed in small phase volumes.
- The efficiency depends on different parameters
  - diameter
  - length
  - linear rate

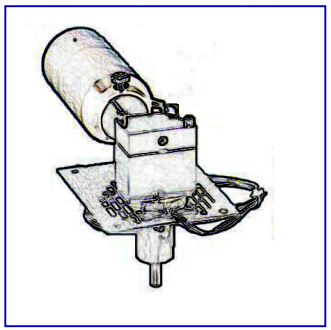
NPD ECD FID FPD PID PDD



TCD

PFPD



Up to three detectors can be mounted and controlled

Detector Response Characteristics

Sensitivity (or Response Factor RF)

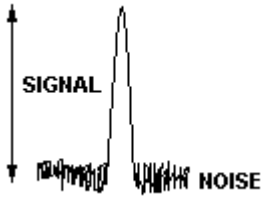
Detector efficiency to convert the sample in an electrical signal

Noise

Short term: high frequency baseline fluctuation
Long term: low frequency baseline perturbation

Minimum Detectability

Amount of sample for which the peak height is three times the noise (S/N=3)



Dynamic Range

Range of sample concentration for which the detector can provide a detectable signal variation with analyte amount

Selectivity

The ratio of the detector sensitivities of a given compound over a potentially interfering compound

Detectors classification

Universal

They respond to everything eluting from the column

- TCD
- PDD
- (FID)

Selective

They may be element selective, structure/functional group selective or selective to other properties

- FID (very broad selectivity)
- ECD
- PID
- PDD

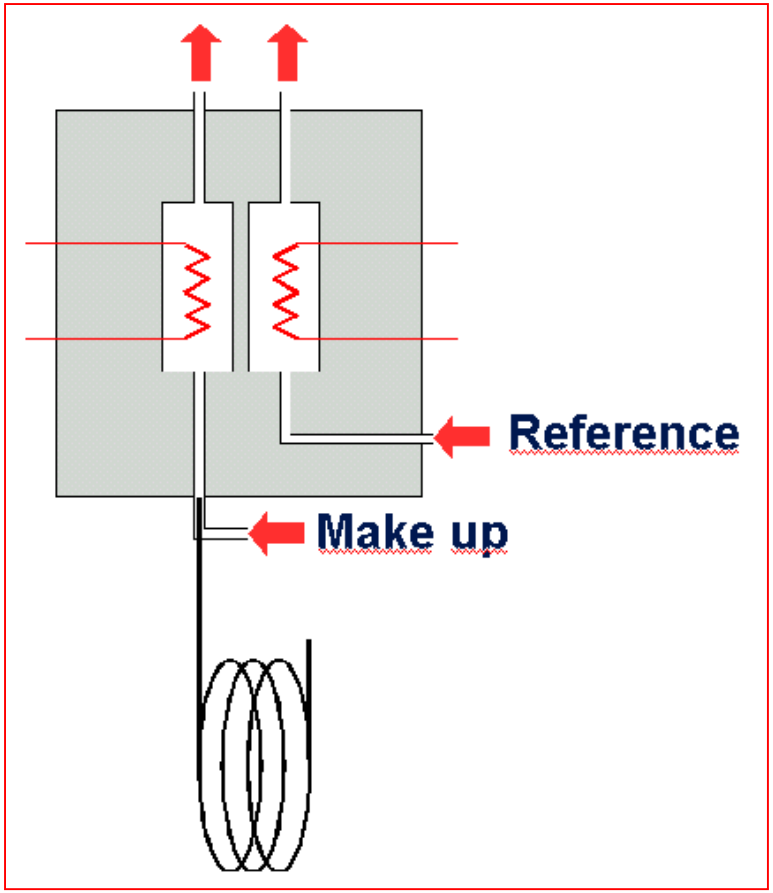
Specific

They are so selective to distinguish particular structures or elements

- NPD
- FPD
- PFPD

Thermal Conductivity Detector

- universal response
- non-destructive
- physical detection principle
- concentration-dependent detector
- two sensitive filaments
- flow-through design



Thermal Conductivity Detector

Application fields

- Petroleum industry
- Chemicals (gas analysis)
- Semiconductor industry

Sensitivity in the ppm - % range

Flame Ionization Detector

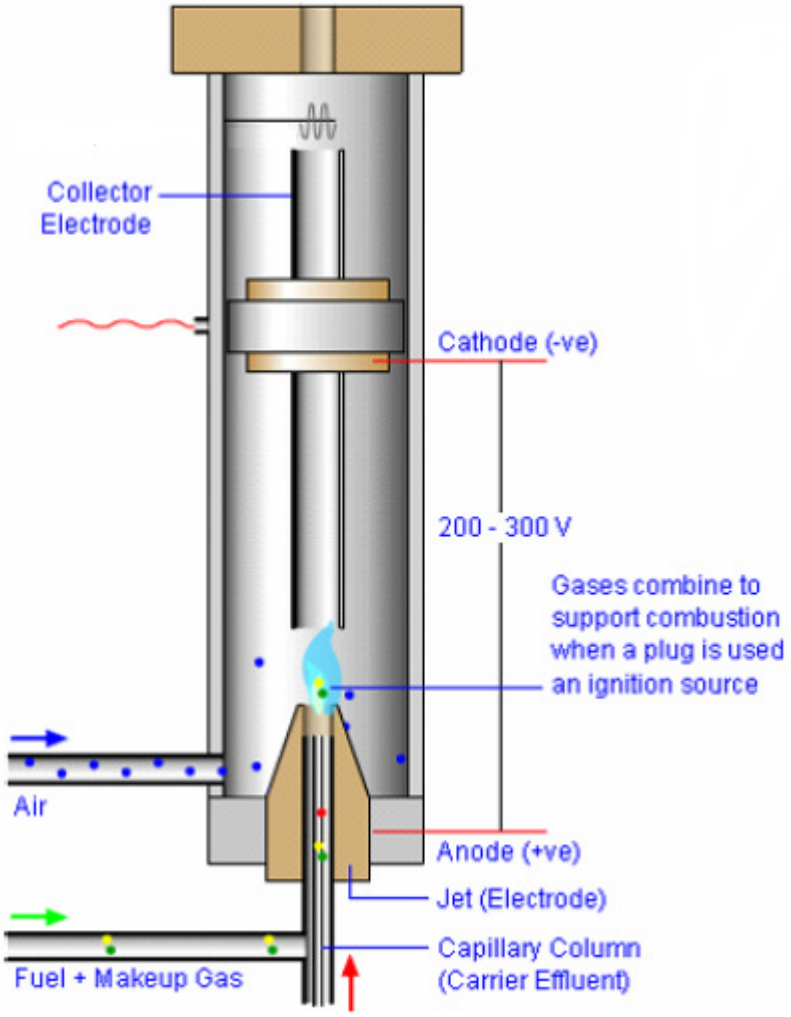
Selective response (broad range)

Ionization detection

Destructive

Process:

- Hydrogen is mixed with gas stream at bottom of jet and air or oxygen is supplied axially around the jet
- Hydrogen flame burns at the tip, which also functions as anode and it is electrically insulated from the body
- Collector electrode is above the burner tip



Flame Ionization Detector

Principle of operation

Combustion of organic compounds in a oxidizing flame

$CH + O \longrightarrow CHO^+ + e^-$

Electric field between the jet and the collector electrode
Voltage -300V

Collection of the ions generated into the flame
Current pA

A good combustion step is the prevailing factor to get the best performances

Flame Ionization Detector

Application fields

- Petroleum industry
- Enviromental
- Pharmaceuticals
- Food and flavors

Sensitivity in the ppm - % range

Electron capture detector (ECD)

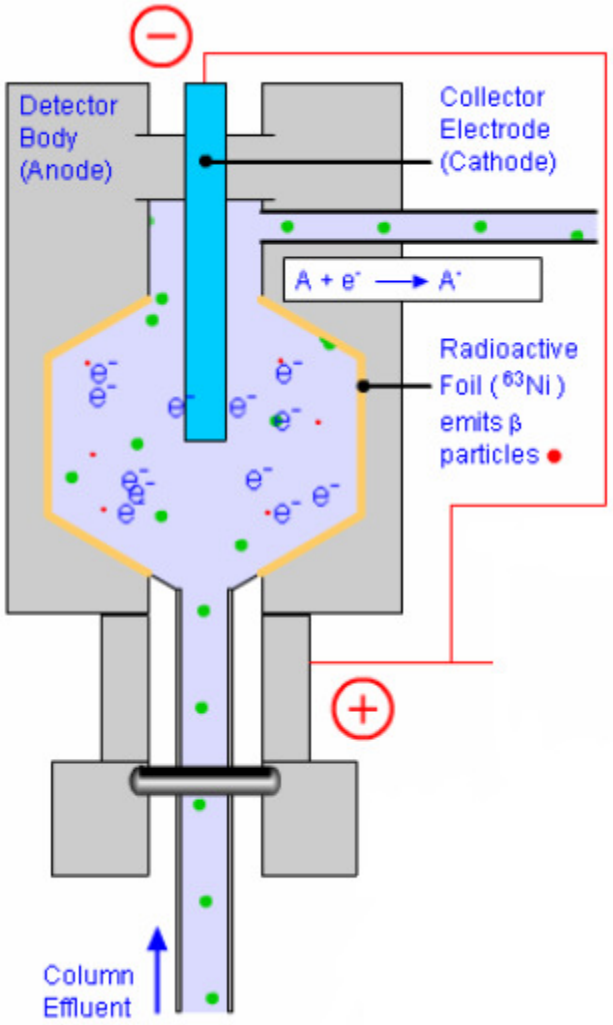
- Non- destructive
- Selective detector

- Measure electrical conductivity of the effluent after exposure to ionizing radiation.
- Sensitive to ‘electron capturing species’- halogens.
- Radioactive 63Ni foil emit low energy electron (beta particle)

$$^{63}Ni \rightarrow \beta^{-}$$

- These β particle collide with carrier to produce high energy electron

$$\beta^{-} + N_2 \rightarrow 2e^{-} + N_2^{+}$$



ECD

- This establishes a high current flow between detector body (foil) and centrally located collector.
- Halogenated analyte elute and 'capture' some of the electrons

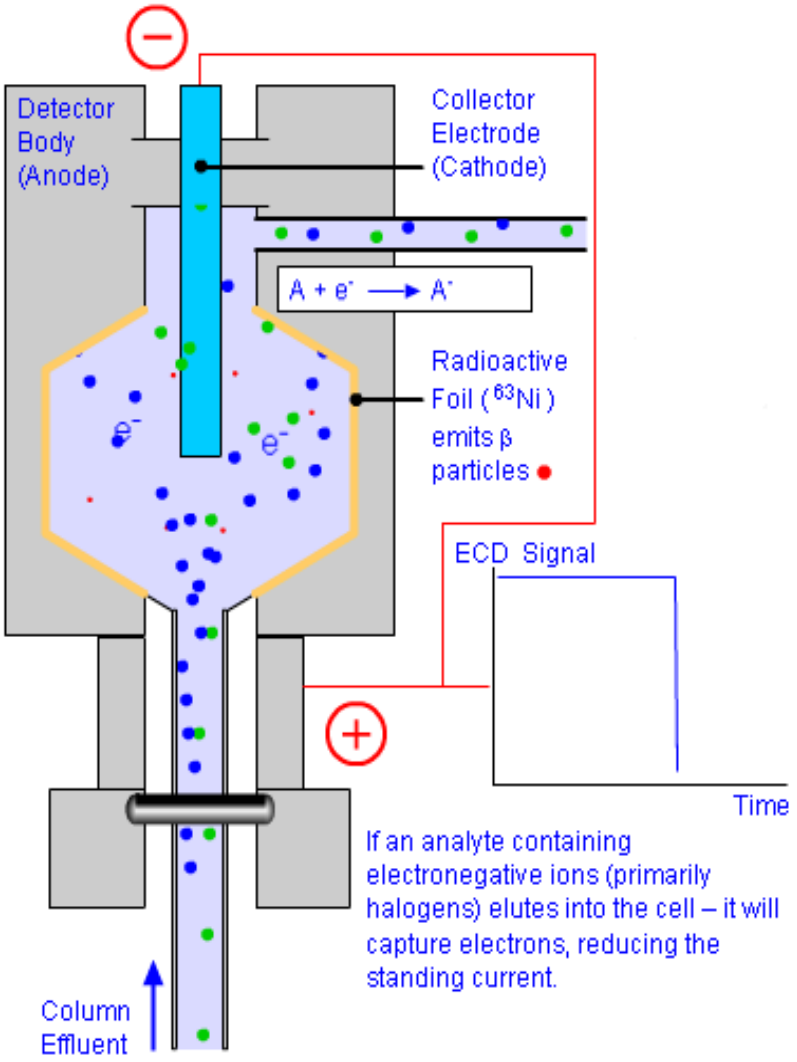
$$A + e^- \longrightarrow A^-$$

- Negative ions formed are low energy and are not collected on the electrode.
- Reduction in the current flow.

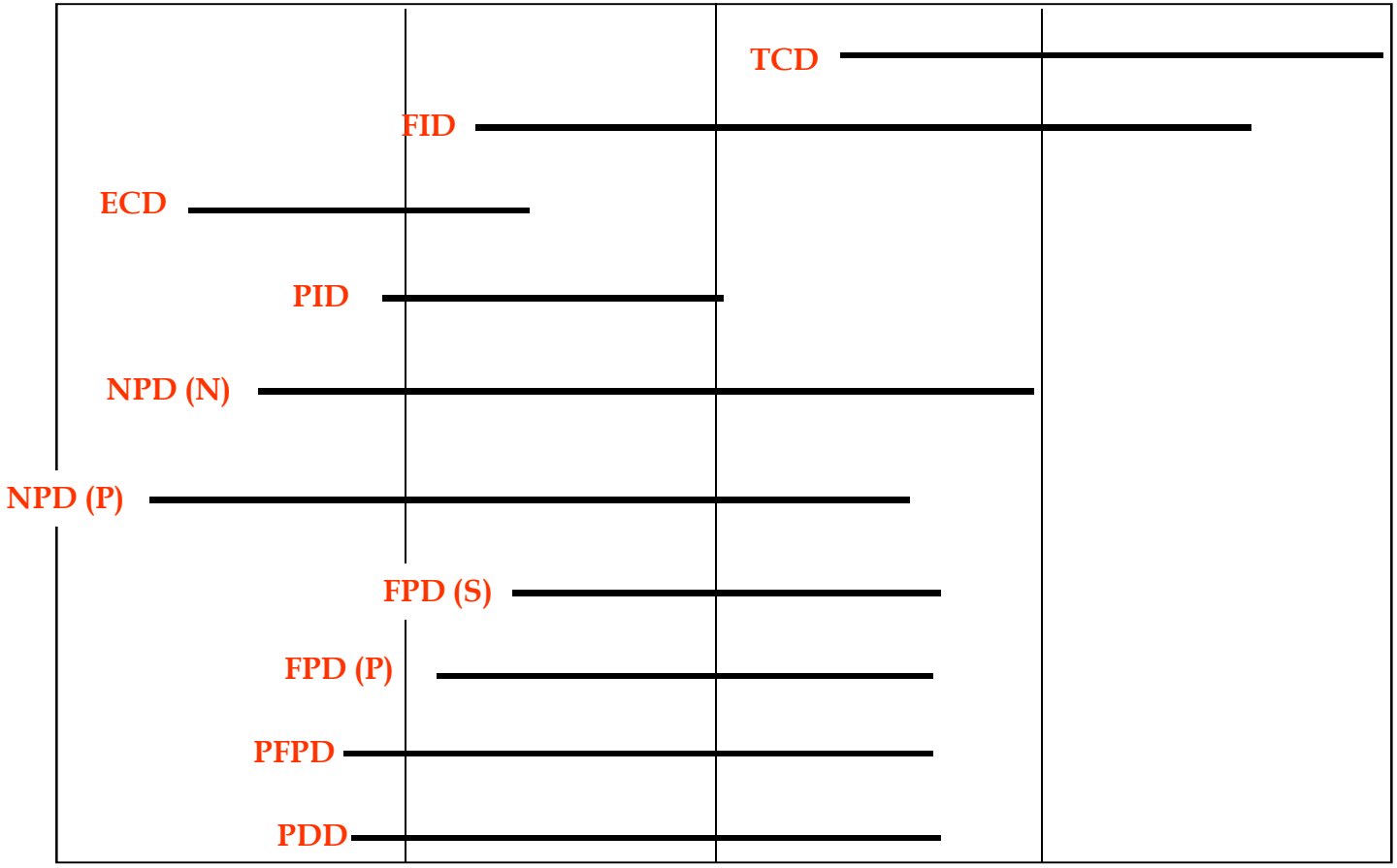
Characteristic:

Minimum detectability: ~ 10^{-9} - 10^{-12}g

Response: selective to halogen containing compound



Detectors dynamic range and sensitivity



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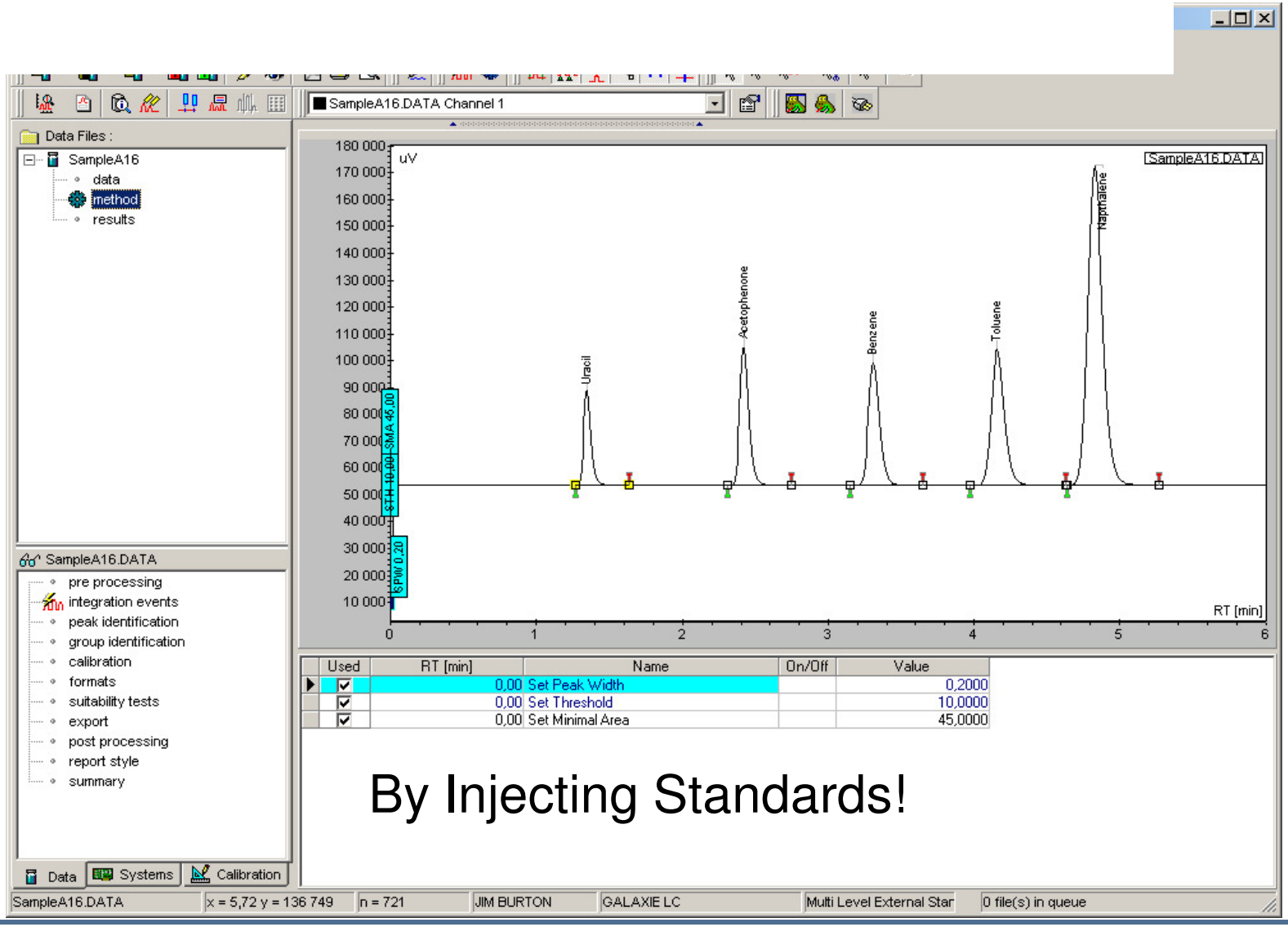
Matching a sample with a GC detector

Fixed gases	TCD, PDD, PID
Hydrocarbons	TCD, FID, PDD, PID
Halogenated compounds	ECD, TCD, FID
Nitrogen containing compounds	NPD, TCD, FID
Sulfur containing compounds	FPD, PFPD, TCD, FID
Phosphorous containing compounds	FPD, PFPD, NPD, TCD, FID
Oxygen containing compounds	TCD, PDD, FID

How to identify in GC ?



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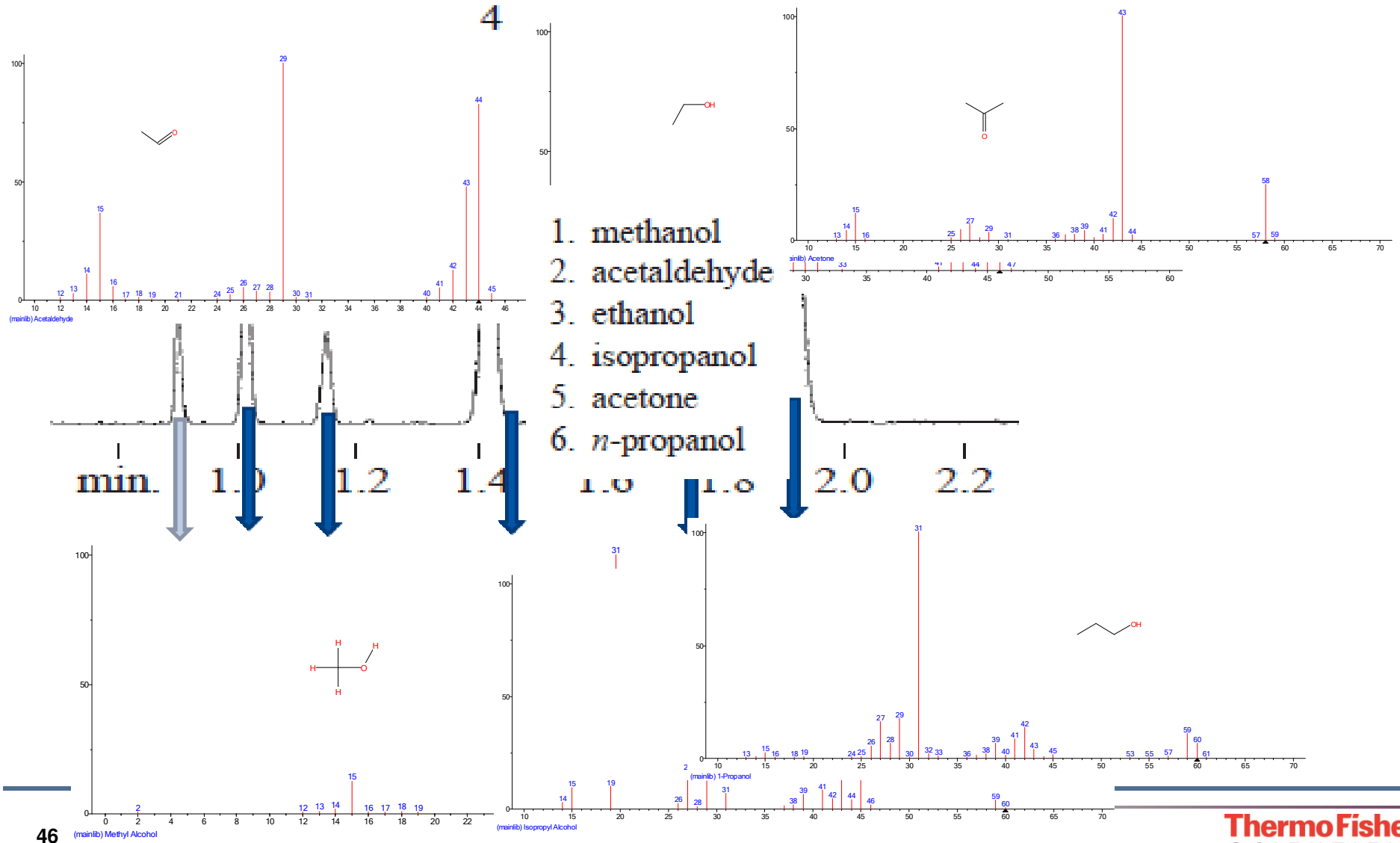
Sample screening by GCMS



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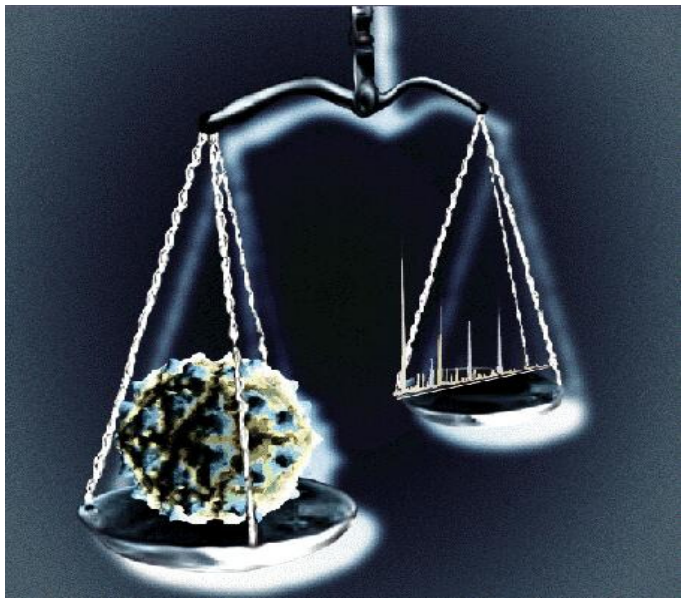
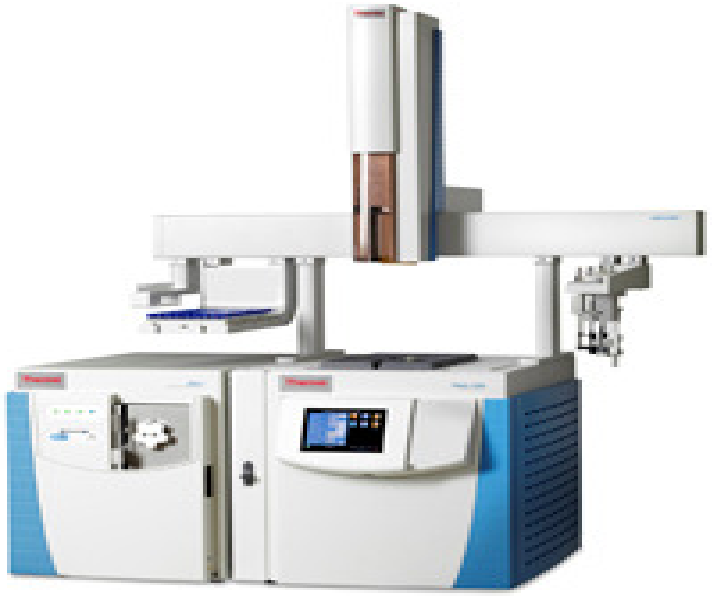
GC-MS why?

- Nearly Universal and specific
- Sensitive
- For compound identification with standard or library spectrum and mass interpretation
- Interference-free quantitation
- Combines separation (GC)and identification techniques (MS).Nothing but hyphenation GC-MS
- Provides both qualitative and quantitative information about sample

What is Mass Spectrometry?

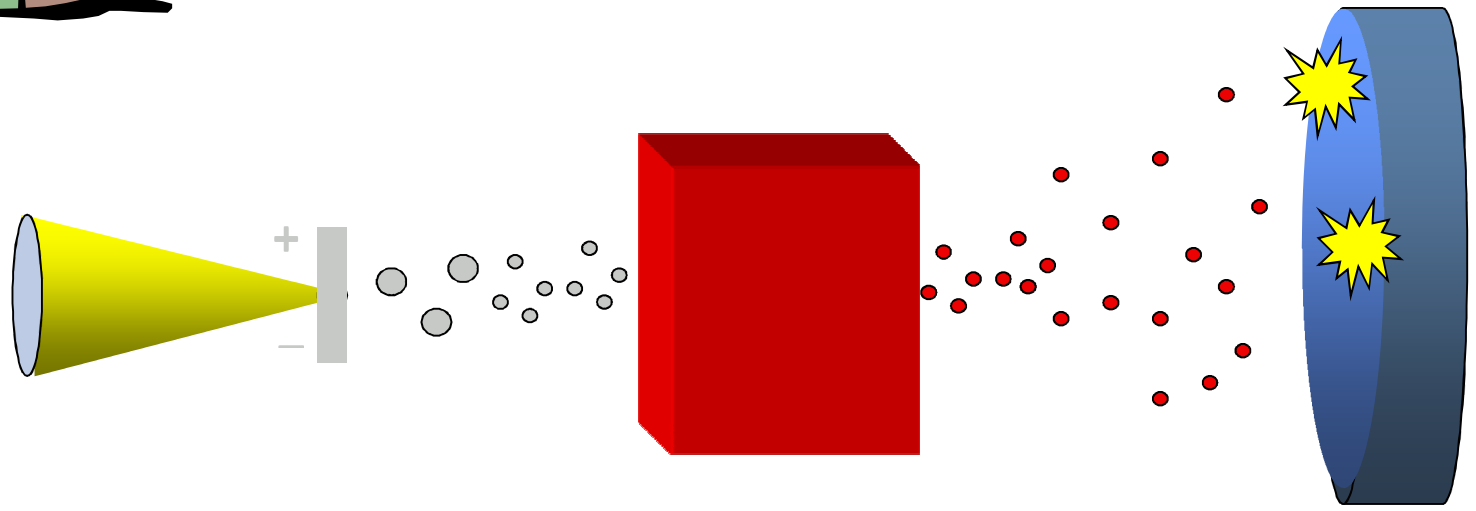
"The basis of MS (mass spectrometry) is the **production of ions** that are subsequently separated or **filtered according to their mass-to-charge (m/z) ratio** and detected. The resulting mass spectrum is a plot of the (relative) abundance of the produced ions as a function of the m/z ratio."





Mass Spectrometer

…Introduction of mass ions in a separation field…



Ion Source Mass Analyzer Detector

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GC & GC-MS Product Portfolio

Increasing Analytical Specificity

TRACE 1300 Series

Instant Connect Modular GC

Detection with Multiple Detectors

Pesticides, PCBs, Volatiles

Petrochemical and Chemical

ISQ Series

Single Quadrupole MS

Confirmation by Mass Spectrum or SIM

EPA Regulated Methods (524, 525, 8260, 8270)

Forensic chemistry and toxicology

ITQ Series

External Ionization 3-D Ion Trap MS

Mass Spectrum and MS^n

EPA Regulated and PBMs (524, 525, 8260, 8270)

Academic research and teaching

TSQ Duo

Single / Triple Quadrupole MS

High performance, easy to use MS/MS for non-experts

Screening & confirmation Analysis in Complex Matrix

Pharma, Chemicals, Toxy/Forensic

TSQ 8000 Evo

Triple Quadrupole MS

High speed and high capacity MS/MS and SRM

Target Analysis requiring ultimate sensitivity/selectivity

Pesticides Multiresidual, Dioxin, POPs

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Automated Sample Introduction techniques in GC for polymer samples

The world leader in serving science

Sample Introduction Techniques

- Head-space (gas, liquids or solids)
- Pyrolizer (solids)
- Thermal desorption (solids)
- SPME (vapours, liquids or solids)

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Static or Equilibrium Headspace sampling technique

Principles of Headspace Analysis

- Gas Chromatography- Investigation of volatile component
- Complex solid samples - Indirect method e.g. Monomers in polymers.
- Gas phase in contact and in equilibrium with an essentially non volatile (or lesser volatile) sample as the headspace (HS) and its investigation as headspace analysis (HSA)

Principles of Headspace Analysis

- Headspace analysis refers to the analysis of the gas (vapor) phase of a binary heterogeneous system in equilibrium.
- The other phase may be a liquid or solid - condensed phase.
- HSA is an extraction procedure
  - Gas is used instead of a liquid
  - Gas is an 'ideal solvent' for highly volatile compounds
- GC is well suited for analysis of HS vapours (HS-GC)

Types of Headspace analysis

- Dynamic HS analysis-Purge and trap method
- Static or equilibrium HS analysis-One step gas extraction

Dynamic HS analysis-Purge and trap method

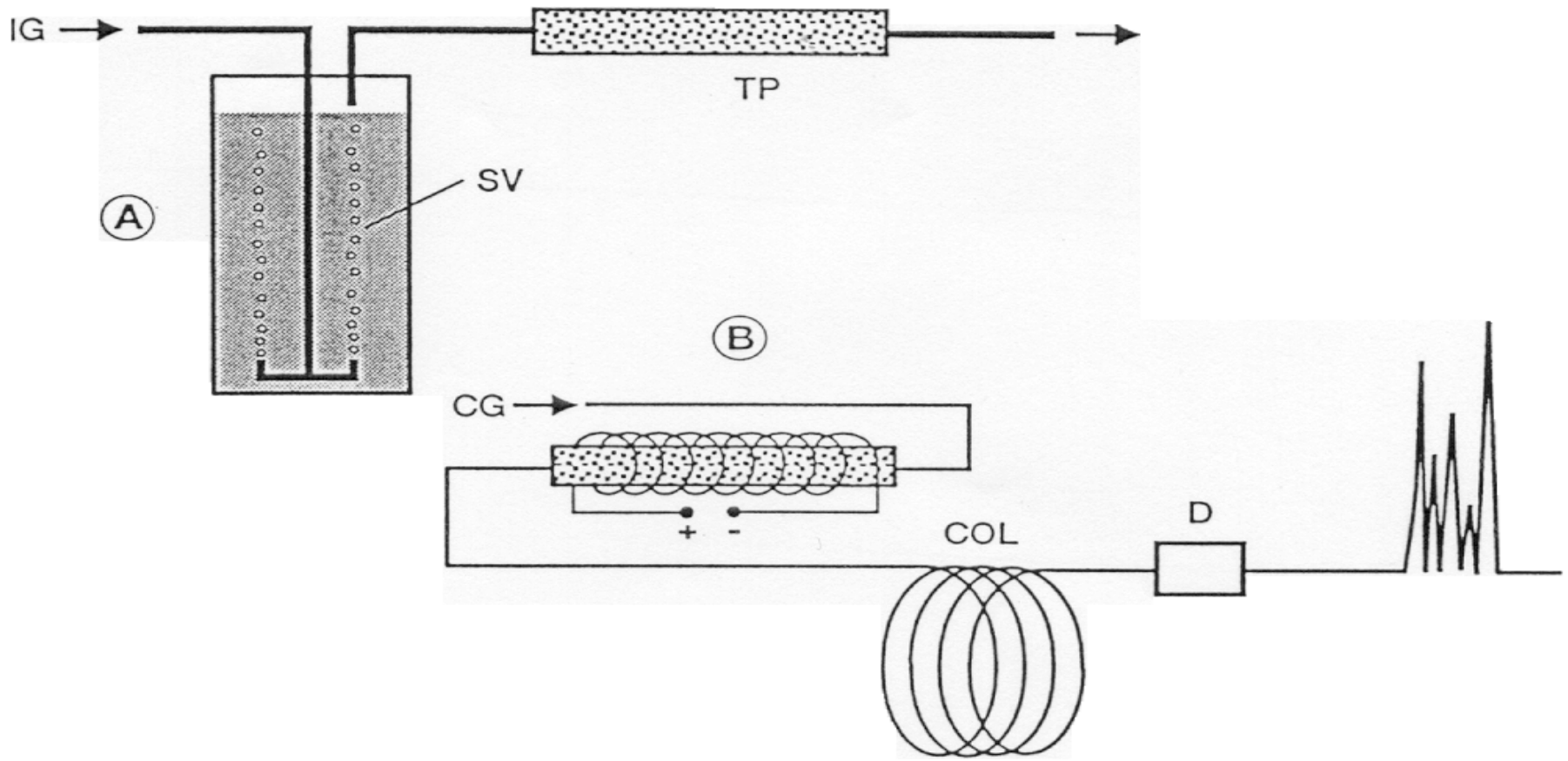


Figure 1.2 Principles of dynamic headspace–gas chromatography ("purge-and-trap"). (A) sample purging and collection of the removed volatiles in a trap and (B) desorption from the trap and transfer into the gas chromatograph. *IG* = inert purge gas, *CG* = carrier gas, *SV* = sample vessel, *TP* = trap, *COL* = gas chromatographic column, *D* = detector.

Static or equilibrium HS analysis-One step gas extraction

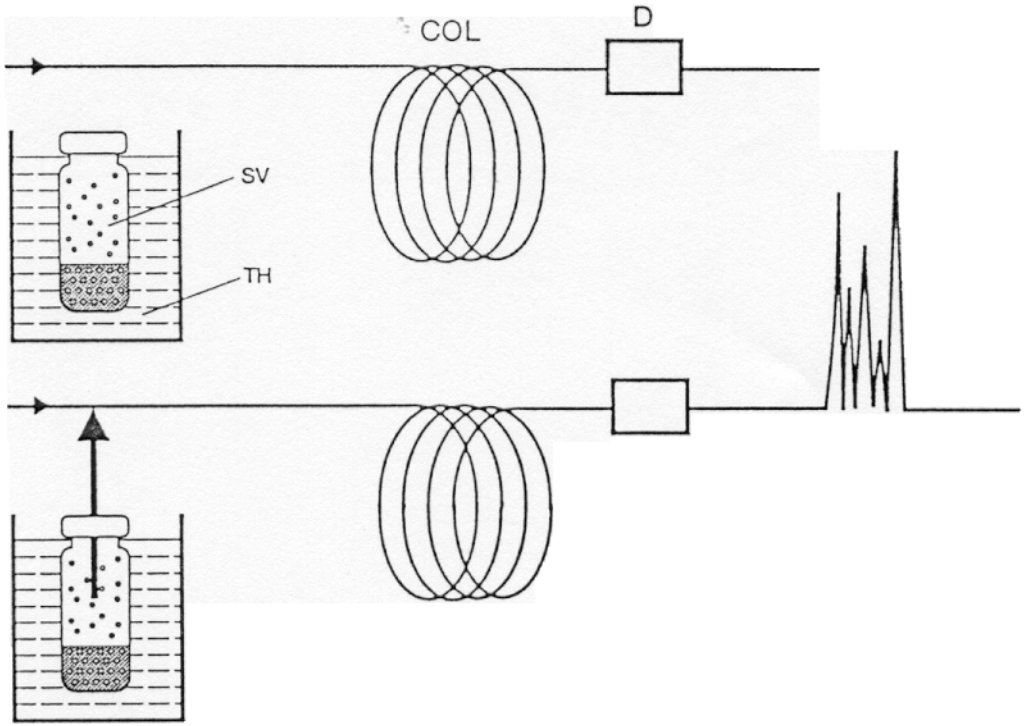
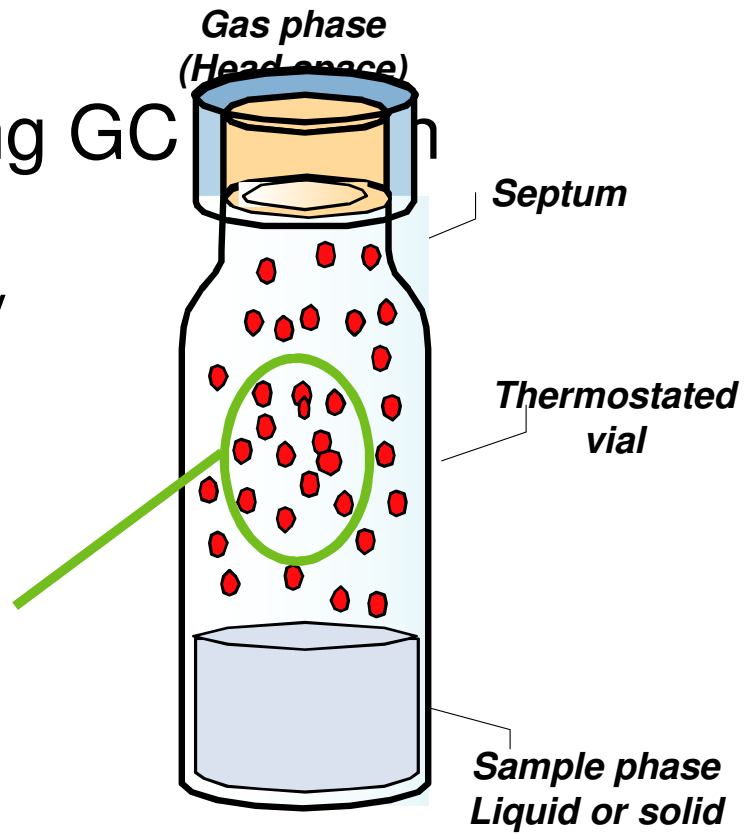


Figure 1.1 Principles of static (equilibrium) headspace–gas chromatography. (A) equilibration and (B) sample transfer. *CG* = carrier gas; *SV* = sample vial, *TH* = thermostat, *COL* = gas chromatographic column, *D* = detector.

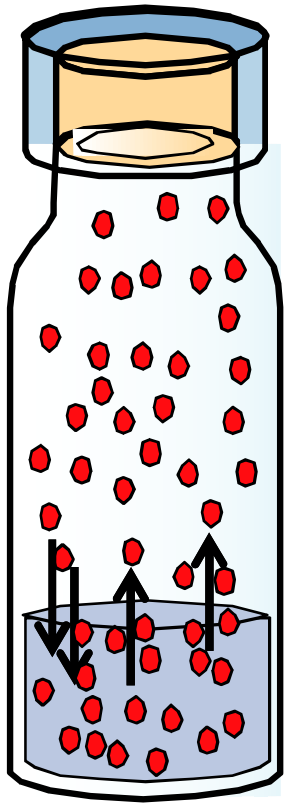
Why use Headspace?

- Investigating volatiles in many matrices
  - Avoid extraction
  - Eliminates losses
  - Avoids non-volatiles entering GC
- It's Simple and Clean
- Highly automated - saves time and money
- Extremely Robust – Enhance Uptime
- Non-detectable carry-over
- Enhanced accuracy
- Excellent repeatability



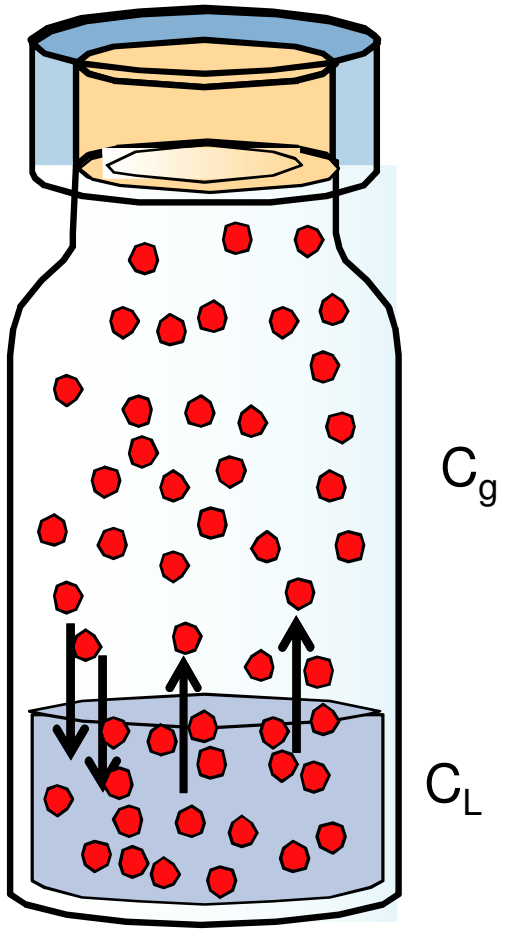
What is Headspace Analysis?

- Concentration of volatiles reaches a dynamic equilibrium between the two phases
- Volatiles concentration in gas is proportional to the volatiles concentration in liquid phase
- An aliquot of headspace is representative of the concentration of analytes in liquid and gas phase
- Sample matrix left behind
- Non-volatiles do not contaminate column



Headspace is solvent free, automated sample preparation.

Headspace principle: Partition Equilibrium



$$K = C_L/C_g$$

K = Partition coefficient
C_L = Concentration in the liquid phase
C_g = Concentration in the gas phase

Factor:

- Time
- Temperature
- Shaking
- Matrix modifiers

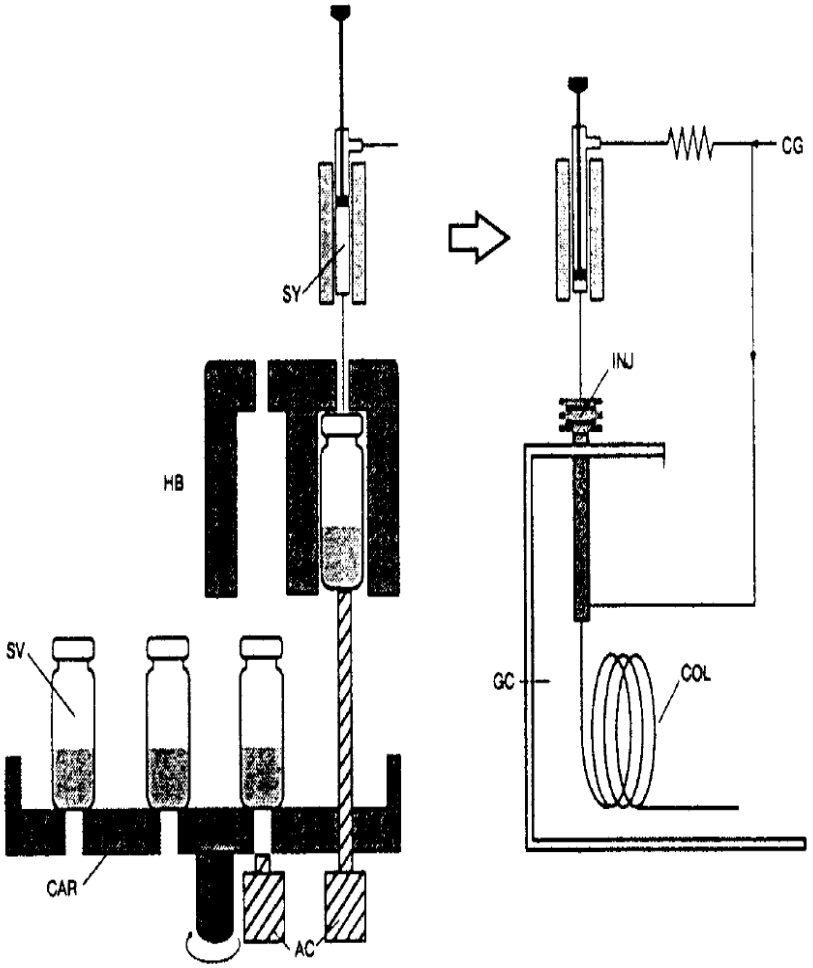
Partition Coefficients in Water

COMPOUND	50°C	60°C	80°C
ETHANOL	1220	630	240
n-PROPANOL	520	350	150
IPA	445	250	120
t-BUTANOL	280	150	60
ACETONE	270	110	55
ETHYL ACETATE	42	30	18
BENZENE	1.2	0.4	0
TOLUENE	0.8	0	0
TRICHLOROETHYLENE	0.7	0	0

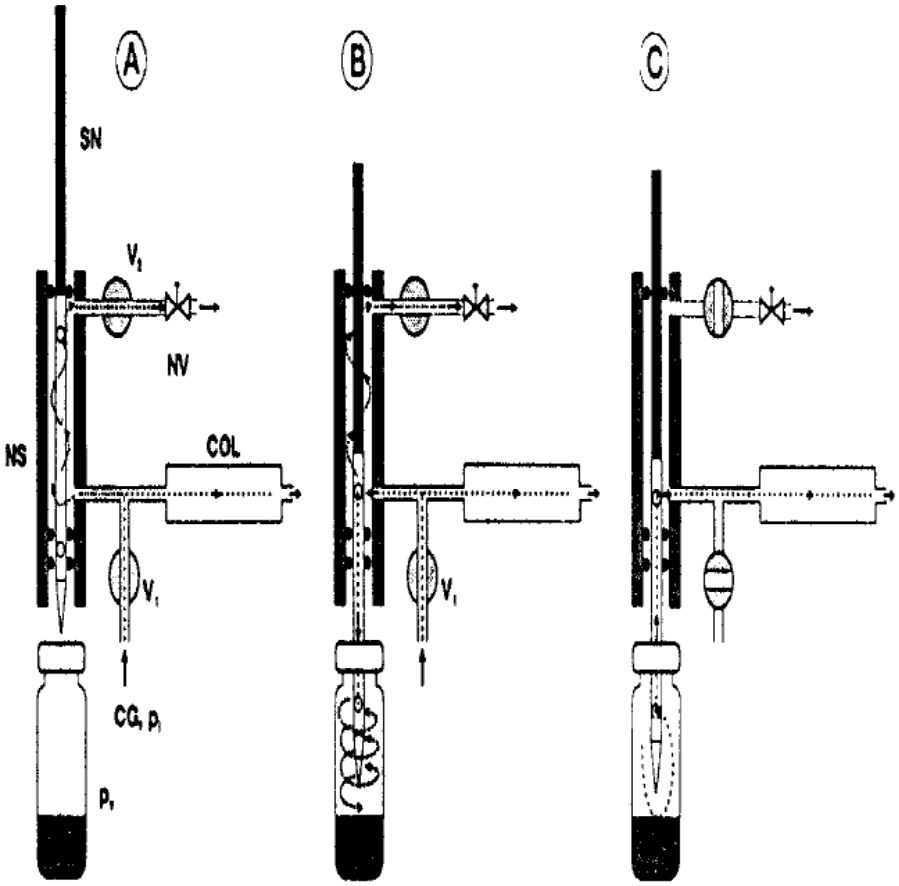
Headspace Sampling Technique in Static HSA

- Gas Tight Syringe
- Time controlled balance pressure system
- Solid phase microextraction (SPME)
- Pressure loop system

Headspace vapour injection



HS GC based on Syringe Injection



HS GC based on Pressure balanced time mode

Solid Phase Microextraction (SPME)

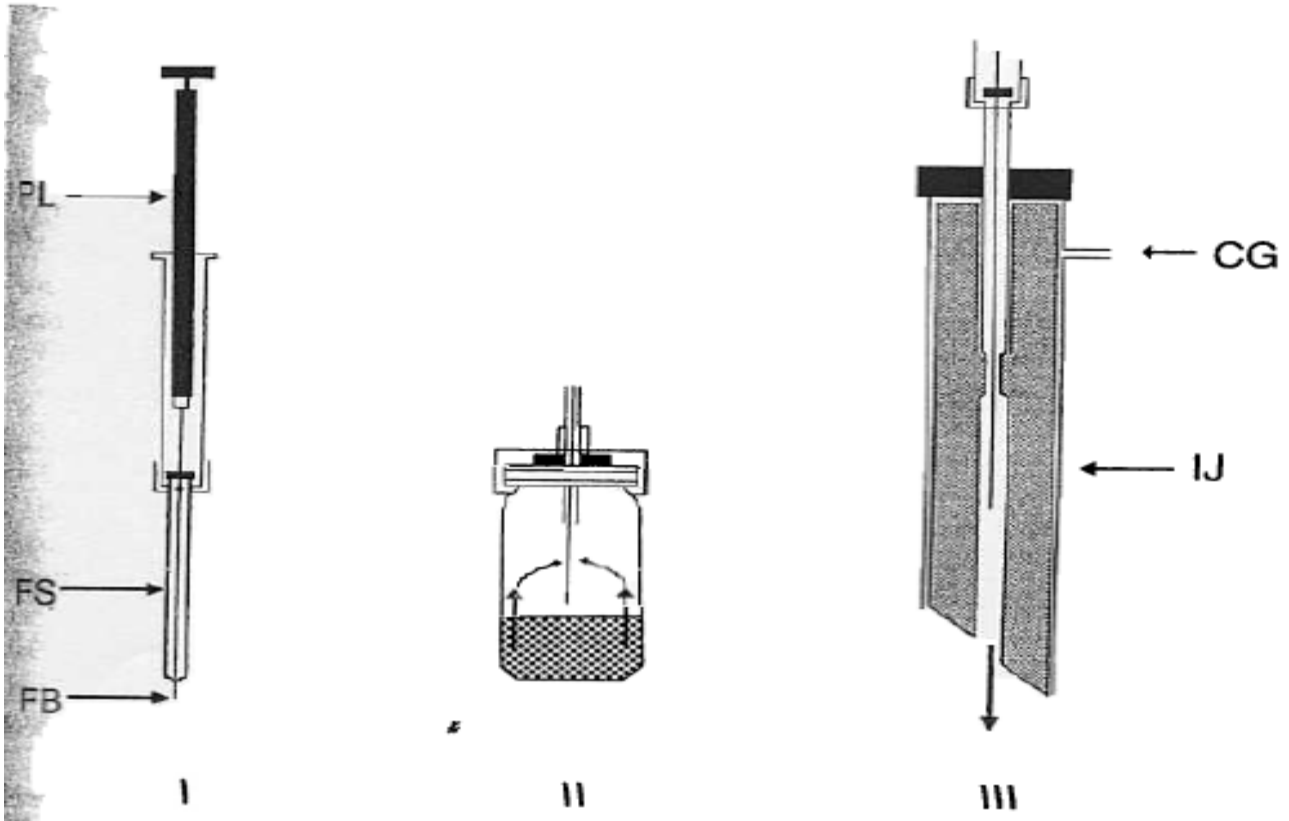


Figure 5-11. Schematic of the solid phase microextraction headspace sampling system. (HS-SPME). *I* = SPME fiber holder, *II* = headspace absorption, *III* = desorption and injection. *PL* = plunger in the sampling syringe, *FS* = fiber sheath (pierces septum of sample vial and GC injector), *FB* = SPME fiber, *IJ* = GC injector, *CG* = carrier gas.

Pressure/Loop System

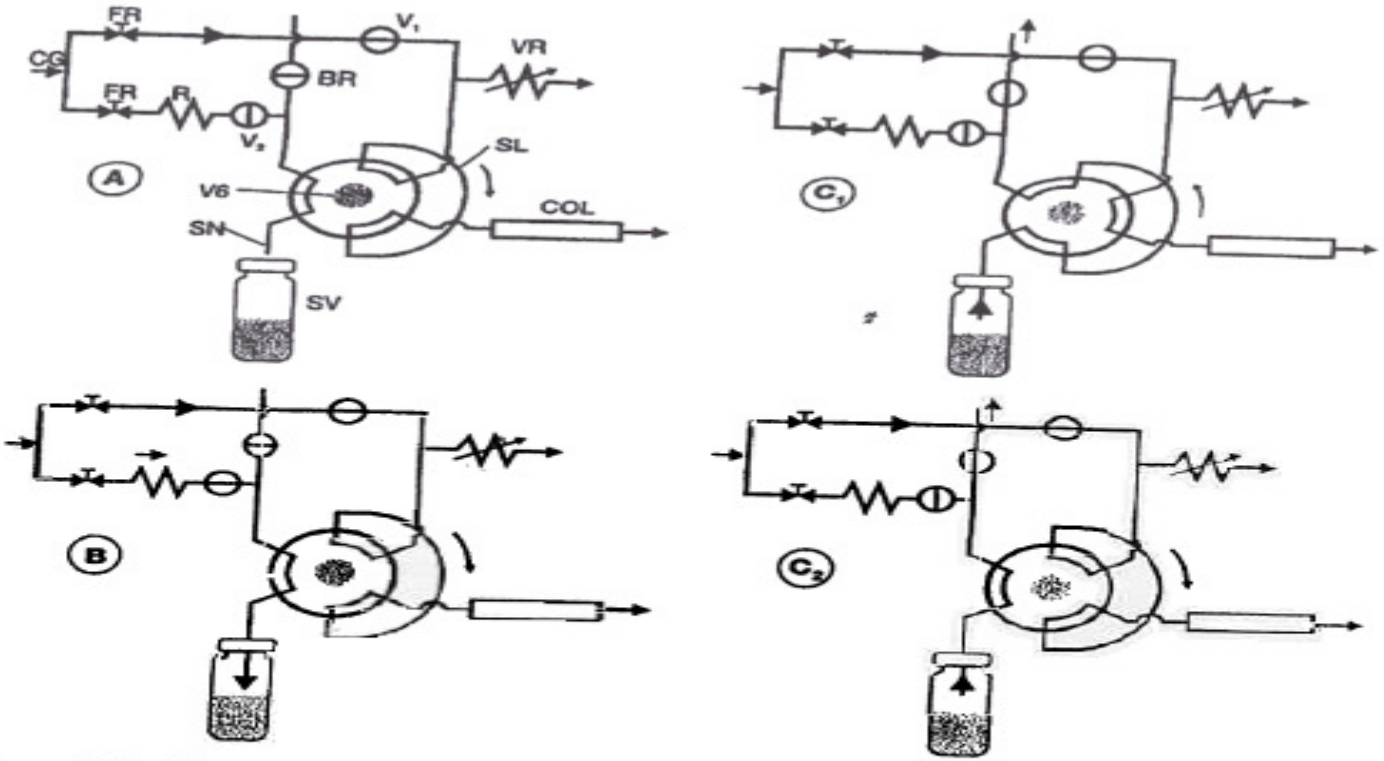


Figure 3-15. Principles of the pressure/loop system for headspace introduction into the gas chromatograph [41]. (*A*) equilibration (standby), (*B*) pressurization (C_1) loop filling, (C_2) injection.
CG = carrier gas, *FR* = flow/pressure regulator, *R* = restrictor, *V* = on/off solenoid valves, *BR* = backpressure regulator, *VR* = variable restrictor, *V6* = six-port valve, *SL* = sample loop, *SN* = sampling needle, *SV* = sample vial, *COL* = column.

Regulatory methods utilizing static HS GC

- Polymers
  - ASTM, APME, CEN
- Environmental
  - Water (German and Japanese Methods)
  - Soil, Sludge, Waste (US and German Methods)
- Blood alcohol
  - US DOT
- Pharmaceutical
  - Extractable and Leachable testing
  - USP 467 Method (IV) Official from July 2008
  - European Pharmacopea
- Brewery quality control of beer
  - European Brewing Convention (EBC)

Regulatory methods utilizing static HS GC

ASTM Methods

- D 3680 Test Method for Residual Vinyl Chloride Monomer Content of Poly(Vinyl Chloride) Resins, Compounds, and Copolymers by Solution Injection Technique.
- D3749- Standard Test Method for Residual Vinyl Chloride Monomer in Poly(Vinyl Chloride) Resins by Gas Chromatographic Headspace Technique

D4322- Standard Test Method for Residual Acrylonitrile Monomer Styrene-Acrylonitrile Copolymers and Nitrile Rubber by Headspace Gas Chromatography

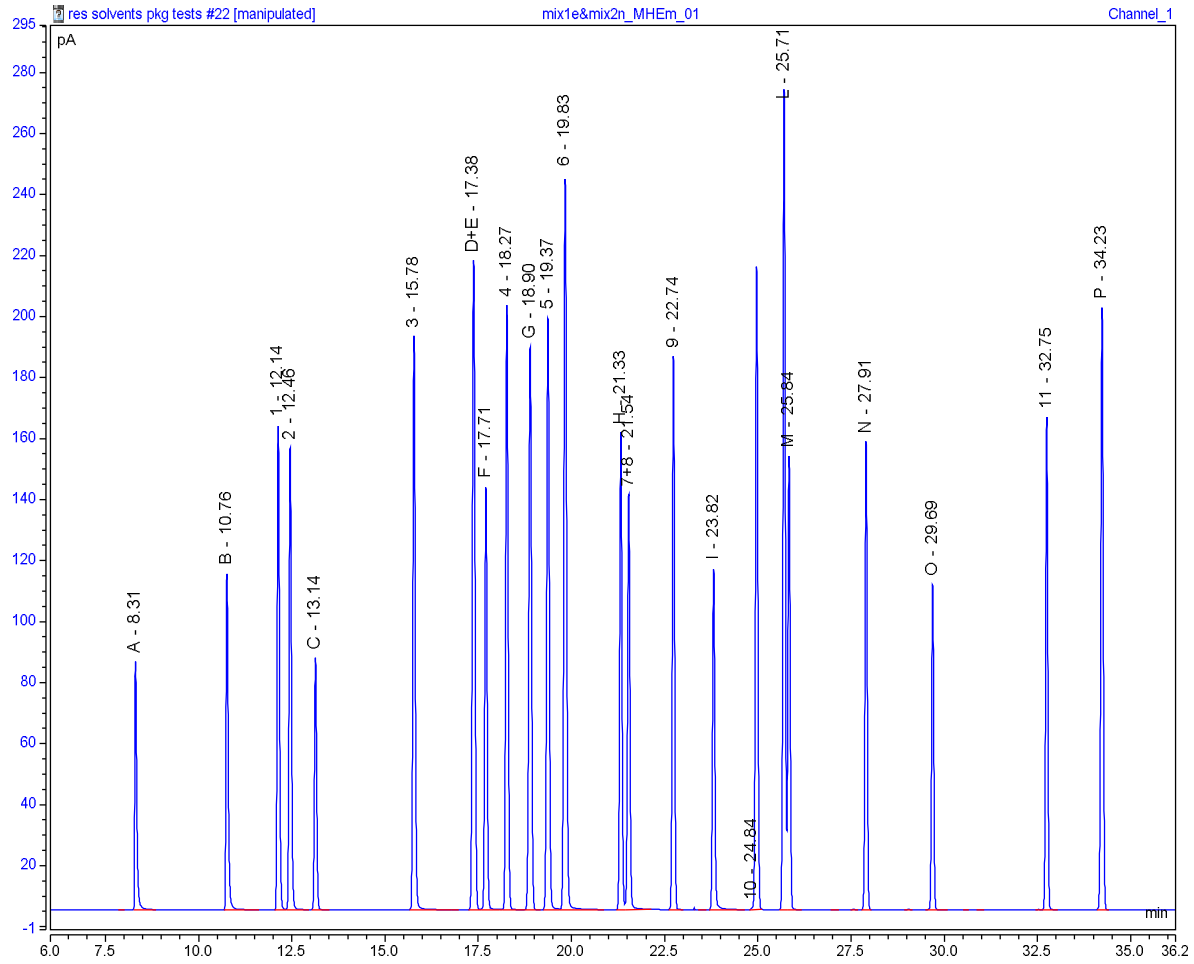
- D 4443 Test Method for Analysis for Determining Residual Vinyl Chloride Monomer Content in PPB Range in Vinyl Chloride Homo- and Co-Polymers by Headspace Gas Chromatography
- D4526- Standard Practice for Determination of Volatiles in Polymers by Static Headspace Gas Chromatography

ISO Standard

ISO 6401-1985 Determination of Residual Vinyl Chloride Monomer in Homopolymers and Copolymers by Gas Chromatography

Static HS analysis of residual solvents in flexible packaging (EN 13628-1)

Standard mixtures and elution order



Peak	RTs (min)	compound
A	8.32	Methanol
B	10.76	Ethanol
1	12.147	Acetone
2	12.463	2-Propanol
C	13.15	Methyl acetate
3	15.78	1-Propanol
D+E	17.39	Ethyl acetate & 2-Butanone
F	17.72	2-Butanol
4	18.275	Tetrahydrofuran
G	18.91	Cyclohexane
5	19.367	2-Methyl-1-propanol
6	19.833	Isopropyl acetate
H	21.33	1-Butanol
7+8	21.533	1-Methoxy-2-propanol & 2-Methoxyethanol
9	22.738	Propyl acetate
I	23.82	2-Ethoxyethanol
10	24.97	4-Methyl-2-pentanone
L	25.71	Toluene
M	25.84	Isobutyl acetate
N	27.91	Butyl acetate
O	29.69	2-Methoxyethyl acetate
11	32.748	2-Ethoxyethyl acetate
P	34.23	Cyclohexanone

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Static Headspace

Advantages

- Easy sample handling
- No apparatus to clean
- High throughput
- Sample thermostatting
- Lower contamination

Disadvantages

- Cannot detect less than 1 ppb
- Small fraction of sample extract injected
- 1-10% efficiency

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CDS Pyrolyser

The world leader in serving science

Why is Pyrolyser required ???

- GC separation is designed for compounds that can be made volatile while passing through the GC column.
- Materials such as tire rubber, textiles, dried paint, glue, natural and synthetic polymers are unable to be analyzed by GC because of their high molecular weight and low volatility.
- Through the use of pyrolysis these compounds can be broken down into smaller, more volatile compounds to be analyzed using GC.

Theory of Pyrolysis

- Pyrolysis can be a preparatory step for high molecular weight, low volatile samples prior to GC analysis
- Bond breaking needs to be reproducible in order for this to be a useful means for analysis (same polymer should yield the same pyrrogram every time)
- There are three types of bond breaking observed depending on relative bond strengths of the compound (chain scission, side group scission, unzipping)
- Useful to understand bond breakage patterns when interpreting pyrograms

Theory of Pyrolysis

- Chain Scission (Random Scission)
- - all the bond strengths are relatively the same (carbon chain)
- - bond breaking occurs along the backbone of a polymer chain
- - bond breaking is random, fragments still consist of monomers
- Ex: polypropylene yields propylene trimer, tetramer, pentamer

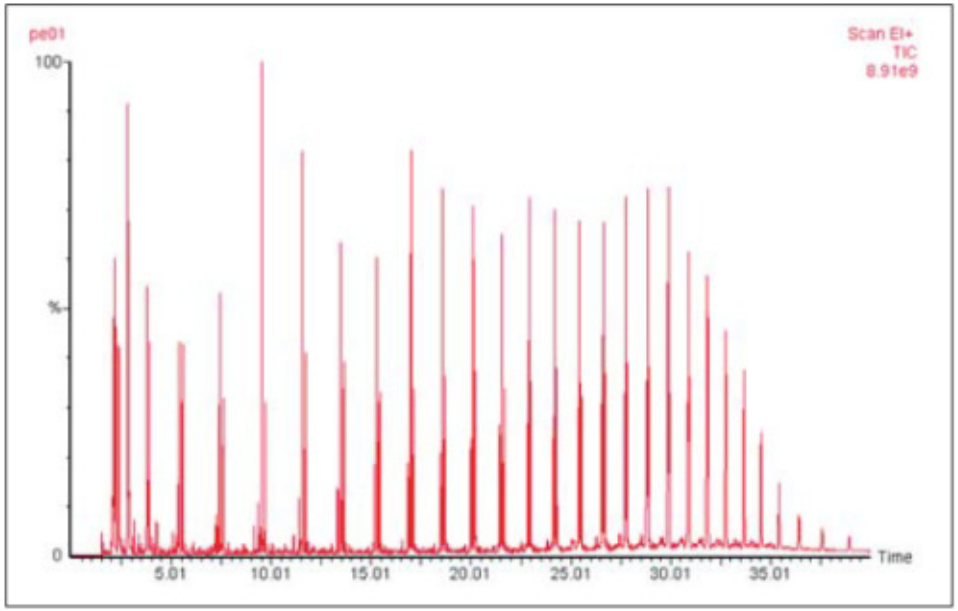

Figure 1. Total Ion Chromatogram resulting from pyrolyzing polyethylene at 750 °C for 15 seconds.

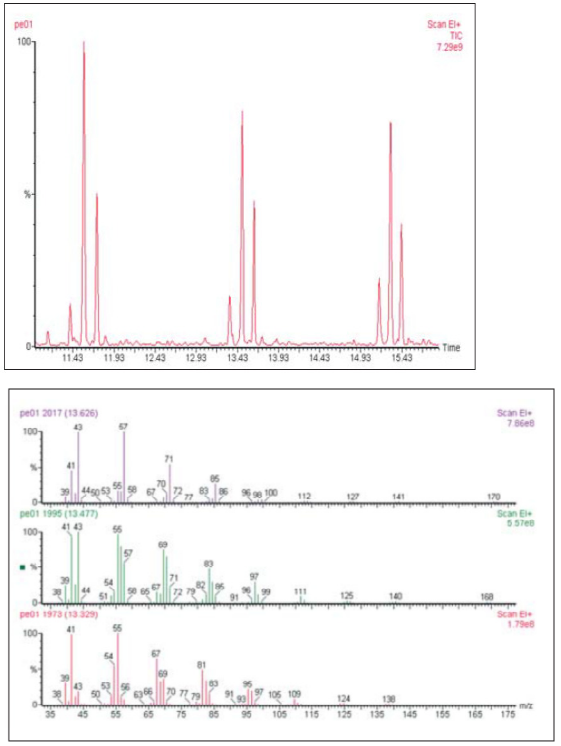

Figure 3. Mass spectra of peaks between 13.3 to 13.6 minutes (Figure 2). Identified using the Wiley 7 library as dodecadiene, dodecene and dodecane.

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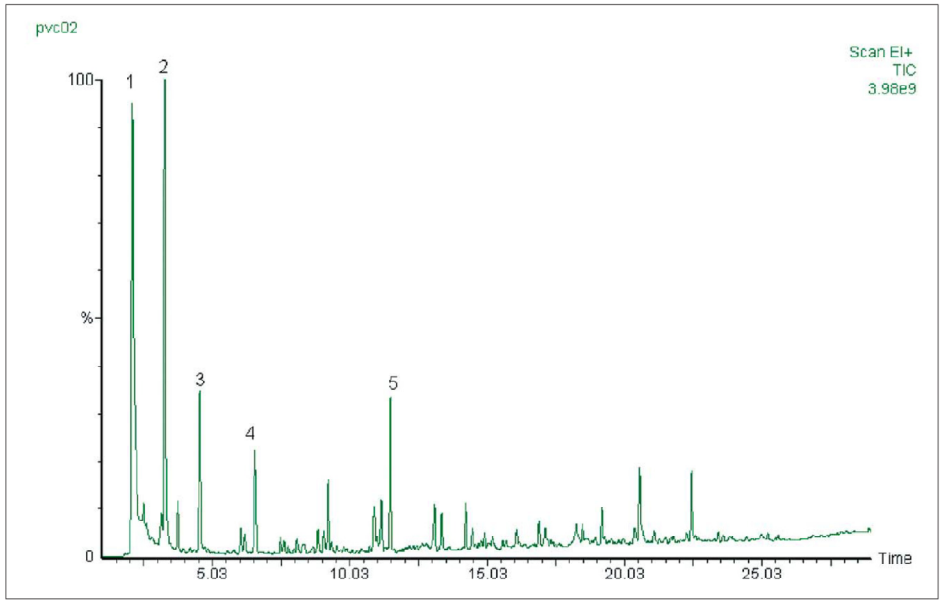
Theory of pyrolysis

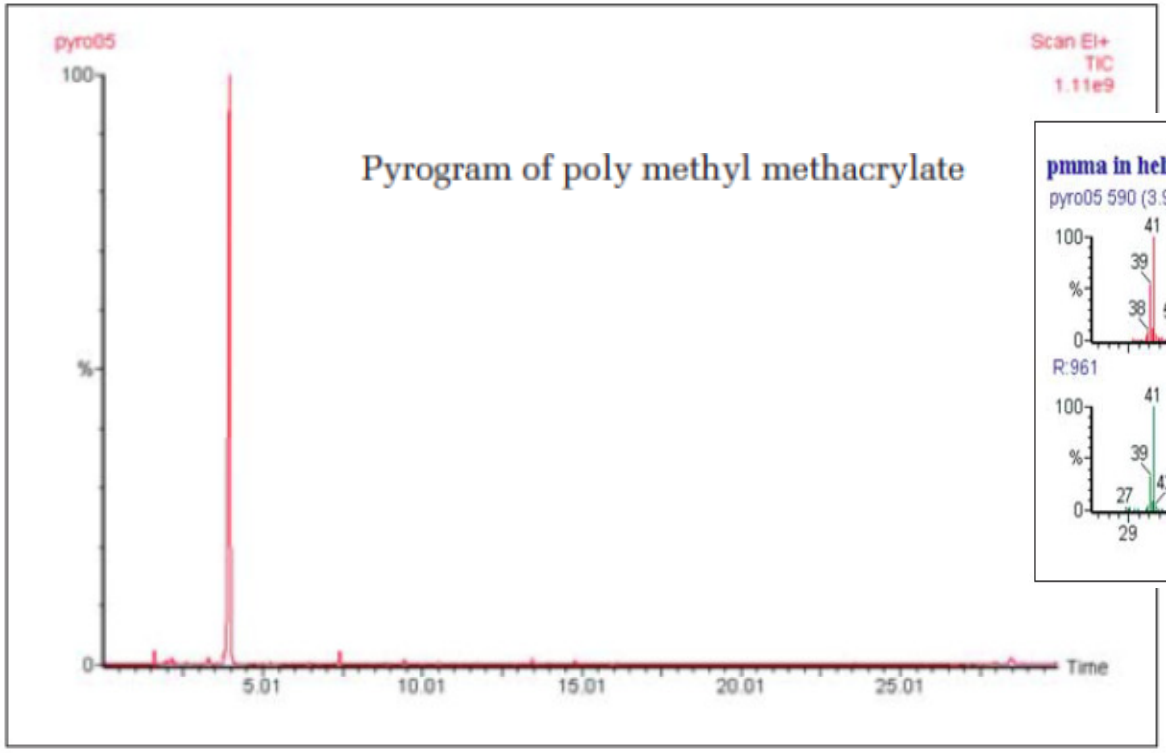
- Side Group Scission:
- bonds attached to polymer backbone are weaker
- Side groups are split off
- Altered backbone pyrolyzes further
- Example: polyvinylchloride (PVC) yields HCl, backbone reconfigures to aromatics (Benzene, Napthelene)



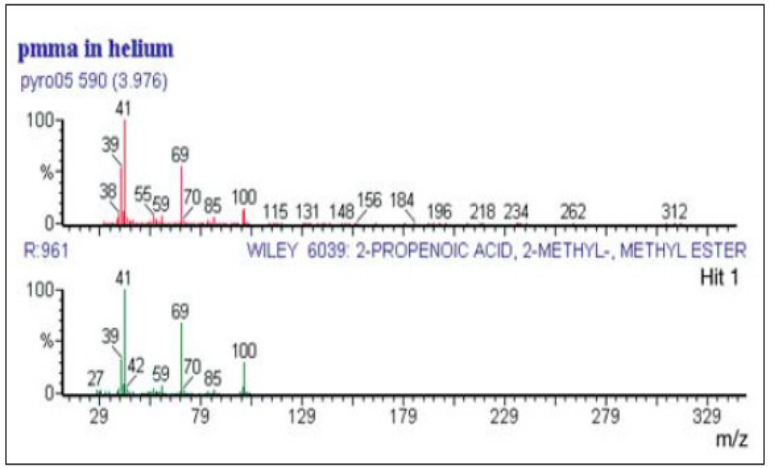
Pyrogram of poly vinyl chloride. Peak identification: 1 - HCl, 2 - Benzene, 3 - Toluene, 4 - Xylene, 5 - Naphthalene

Theory of pyrolysis

- Unzipping (Monomer Reversion):
- - bonds connecting the monomers are the weakest
- polymer to revert back to monomers
- Fragments are almost entirely consisting of monomers
- Ex: polymethyl methacrylate will revert back to methyl methacrylate monomers



Pyrogram of poly methyl methacrylate



monomer, methyl methacrylate.

Theory of pyrolysis

- Bond breaking is reproducible when the following parameters are constant:
- 1. Temperature
- 2. Heating Rate
- 3. Time of Heating

- Pyrolyzers are instruments that rapidly heat and pyrolyze samples

- Each pyrolyzer offers different options when trying to adjust for the optimal temperature, heating rate, and time of heating

Pyrolysers

- Pyrolyzers:
- - capable of heating up to 1400℃
- - operate between 500 and 800ºC for most analytical work
- - designed to connect directly to GC
- - three basic types (each with its own advantage and disadvantage)

- Types of Pyrolyzers include:
- 1. Microfurnace
- 2. Curie-Point Filament (Inductively Heated)
- 3. Resistively Heated Filament

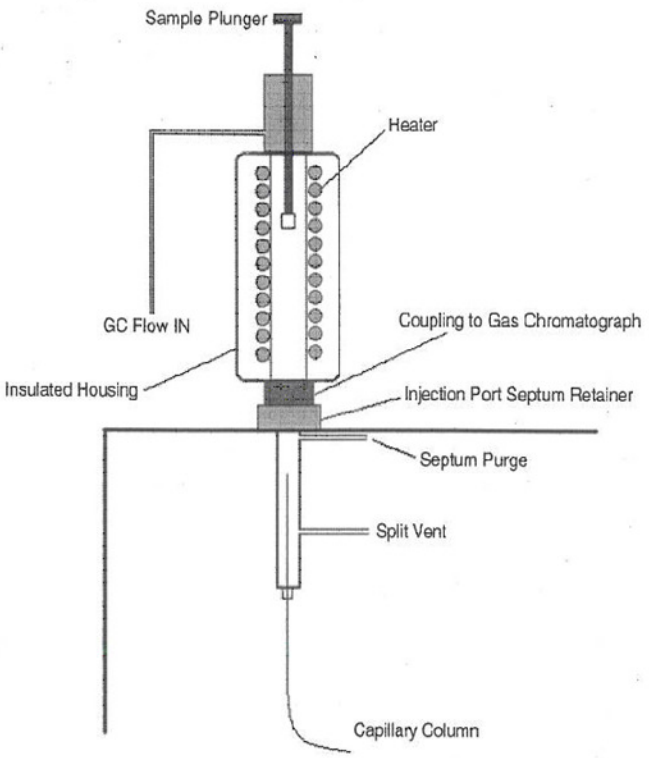
Pyrolysers- Microfurnace pyrolyzer

- Pyrolysis zone is set to a constant temperature.
- Sample Loading:

1. into a boat or tube and dropped into pyrolysis zone (solids, liquid)
2. syringe injects sample directly into pyrolysis zone (liquid only)

- Advantages:
- inexpensive, easy to use, no temperature
- ramping, vaporizes liquids very quickly,
- no condensation

- Disadvantages:
- large pyrolysis chamber increases volume (band broadening), increase flow to account for band broadening (wastes sample, need higher split ratio)

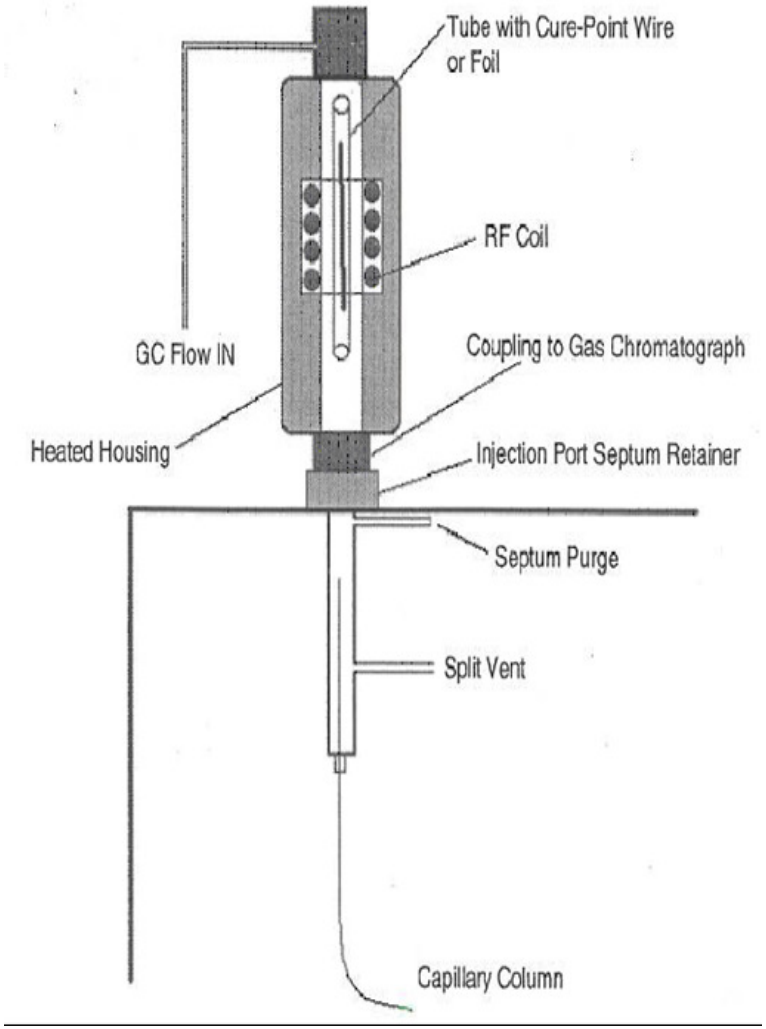


Pyrolyzers- Curie-Point Filament

- Electric current induced into a wire made of ferromagnetic metal
- Wire heats until it reaches its maximum temperature (Curie-Point), no further current can be induced

- <u>Sample Loading:</u>
- sample either coated onto (dipped in soln. or applied with syringe) the wire or wrapped in ferromagnetic foil, dropped into pyrolysis zone

- <u>Advantages:</u>
- final temp is set (no calibrating), very rapid heating, reproducible heating, sample insertion simple
- <u>Disadvantages:</u> temperature optimization difficult (only set temperatures available), no adjusting the heating rate (need resistively heated filament)



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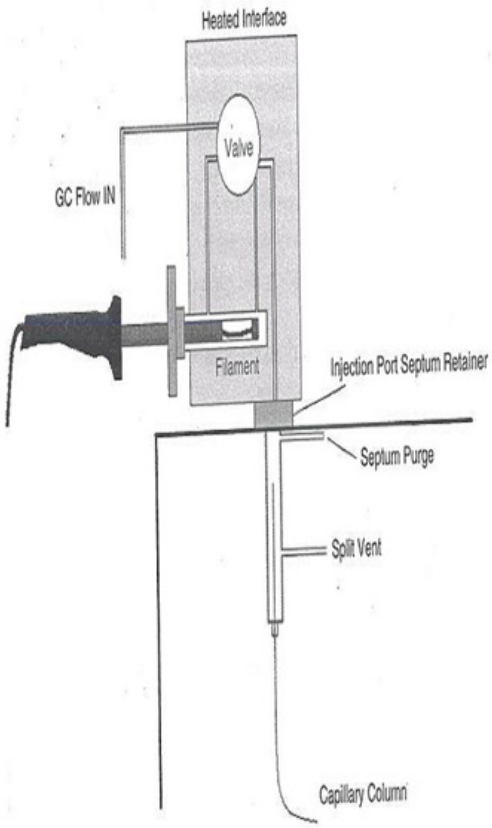
Pyrolyzers- Resistively Heated Filament

- Current supplied directly to filament (typically platinum)
- Temperature and heating rate are controlled and monitored

- <u>Sample Loading:</u>
- similar to Curie-point, typically coated onto the filament using a syringe (liquid), melted in place (solids), quartz tube with quartz wool (solids)

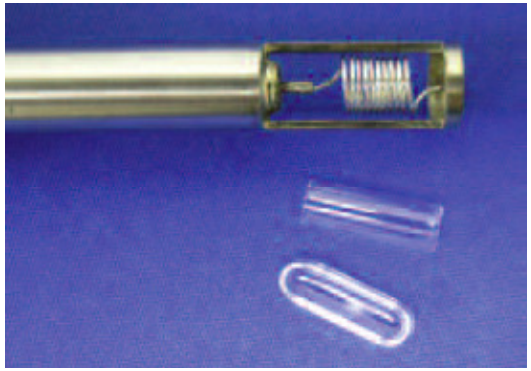
- <u>Advantages:</u>
- temperature optimization, heating rate optimization

- <u>Disadvantages:</u>
- temperature monitoring based on current through entire filament loop, (not localized, may be inaccurate), area where filament is housed is heated (heats sample prior to pyrolysis)



CDS- 5150 Pyrolyzers

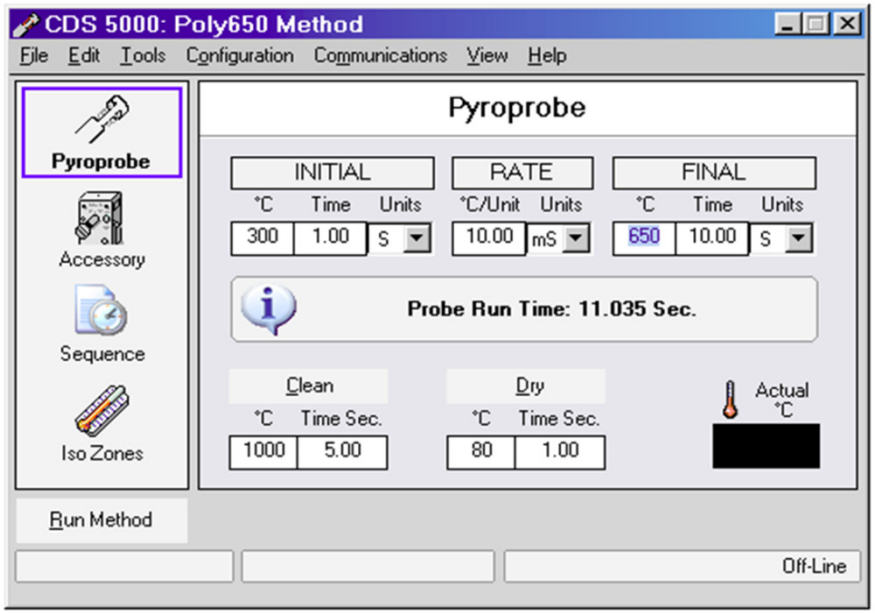
- **Specifications:**
- FILAMENT TEMPERATURE: Settable in 1 ℃
- increments to 1400 ℃
- TIMES: Settable in units of 0.01 second to 999.99 sec. or in units of 0.01 minute to 999.99 min.
- HEATING RATES: Settable in units of 0.01 ℃/millisecond
- from 0.01 to 20.00 ℃/mS, or
- 0.01 to 999.99 ℃/Second, or
- 0.01 to 999.99 ℃/Minute
- INTERFACE TEMPERATURE: Settable in 1 ℃ increments to 350 ℃
- TIMES: Settable in units of 0.01 minute to 999.99 minutes
- HEATING RATES: Settable in units of 0.01 ℃/minute to 60.00 ℃/minute.
- DRY MODE: User selectable
- CLEAN MODE: User selectable
- SEQUENCE: Up to 8 methods, each with GC start



CDS- 5150 Pyrolyzers

- **Alignment Tool**
- **Comes w/ all new 5000 instruments**
- **Will help to extend life of coil probes**
- **Allows easy loading of quartz tubes**

- **Pyroprobe 5000 Software**



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Applications

TYPES OF SOLID MATERIALS ANALYZED

- Plastics – films, foams, fibers, molded parts
- Paints – alkyd, latex, art, varnish
- Rubber – tires, bumpers, building materials
- Adhesives – rubber, acrylic, urethanes
- Petrochemicals – resins, waxes, asphalts, oils
- Printing – ink, toners, coatings
- Consumer goods – cosmetics, surfactants, food, soaps, detergents

Vulcanized Rubber

Figure 1 Total Ion Chromatogram

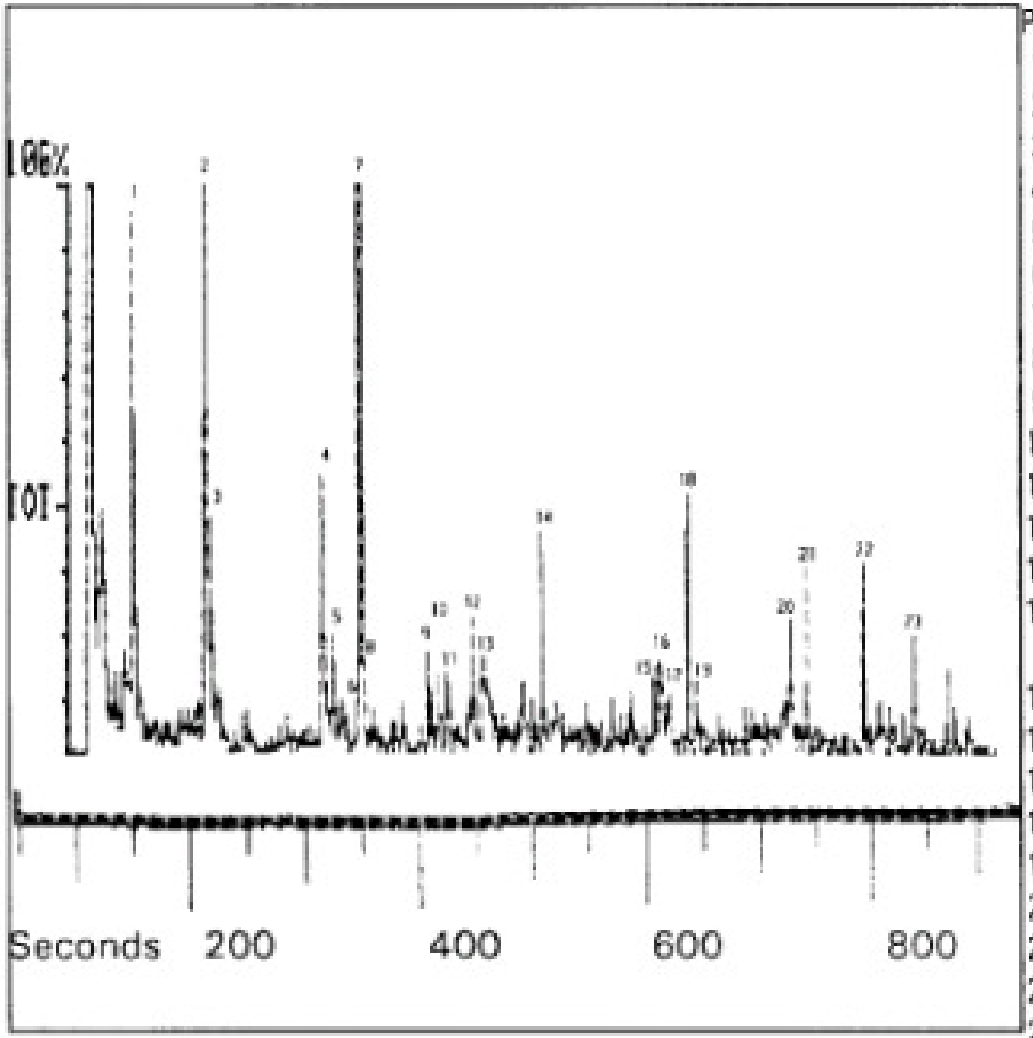
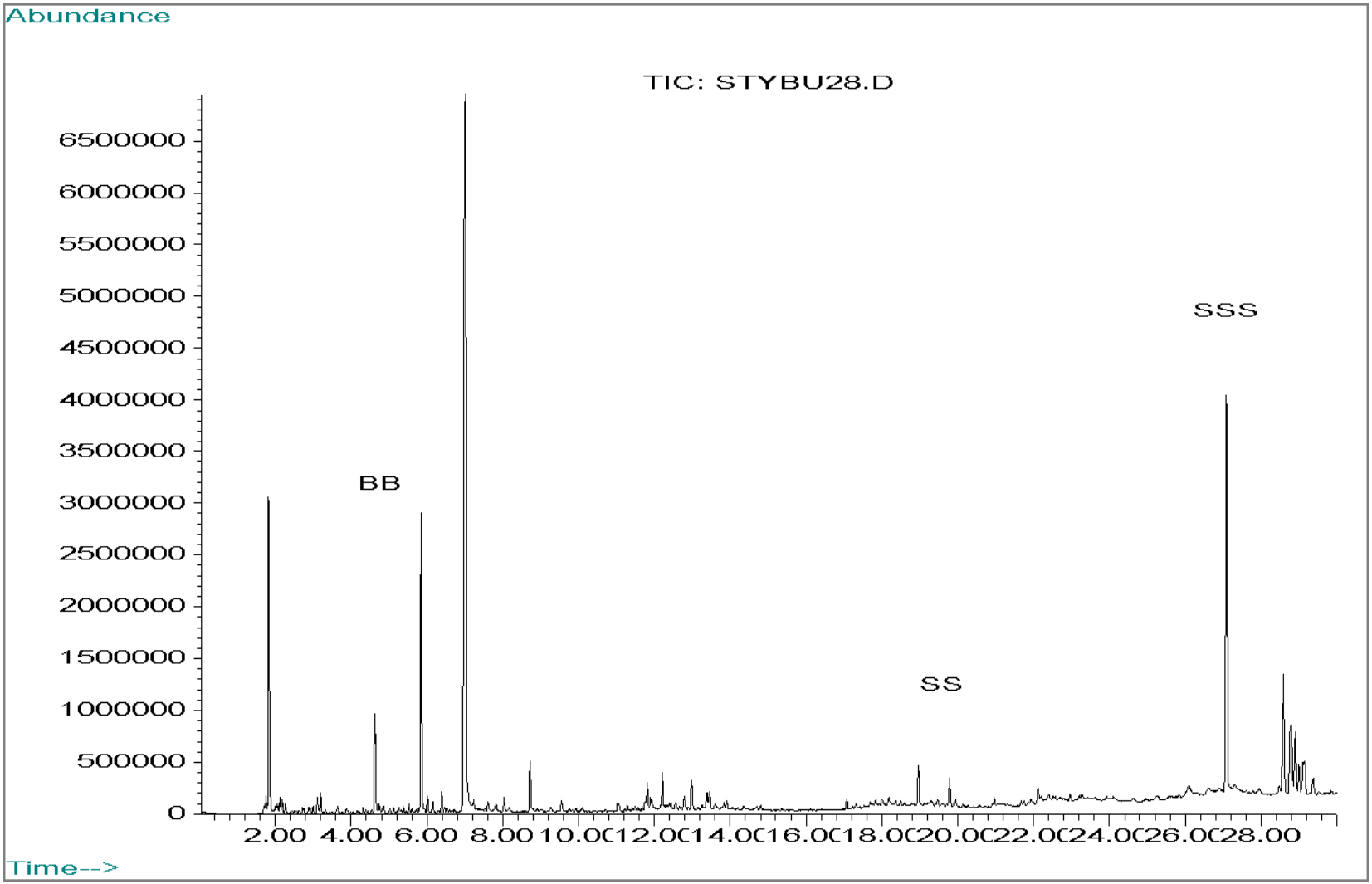


Table 1 Peak Identification

Peak	Compound
1	benzene
2	toluene
3	3-methylthiophene
4	ethylbenzene
5	2,5-dimethylthiophene
6	thiophenol or 1-ethylthiole
7	benzocyclobutane
8	m-xylene
9	2,3-diH-Indene
10	propylbenzene
11	2-(isopropyl)thiophene
12	1-ethenyl-2-methylbenzene
13	4-[methylthio]phenol
14	1-ethynyl-3-methylbenzene or 1,2-propadienylbenzene
15	1-methyl-1-H-Indene
16	[1-methylene-2-propenyl]benzene
17	1-cyclobutenylbenzene
18	azulene or naphthalene
19	benzo[b]thiophene
20	1,4-diH-1,4-methanapthalene
21	1-ethenylindene or 1-methylnaphthalene
22	biphenyl
23	2,4-dimethylquinoline

Polymer- Styrene/Butadiene Copolymer (28% Styrene)



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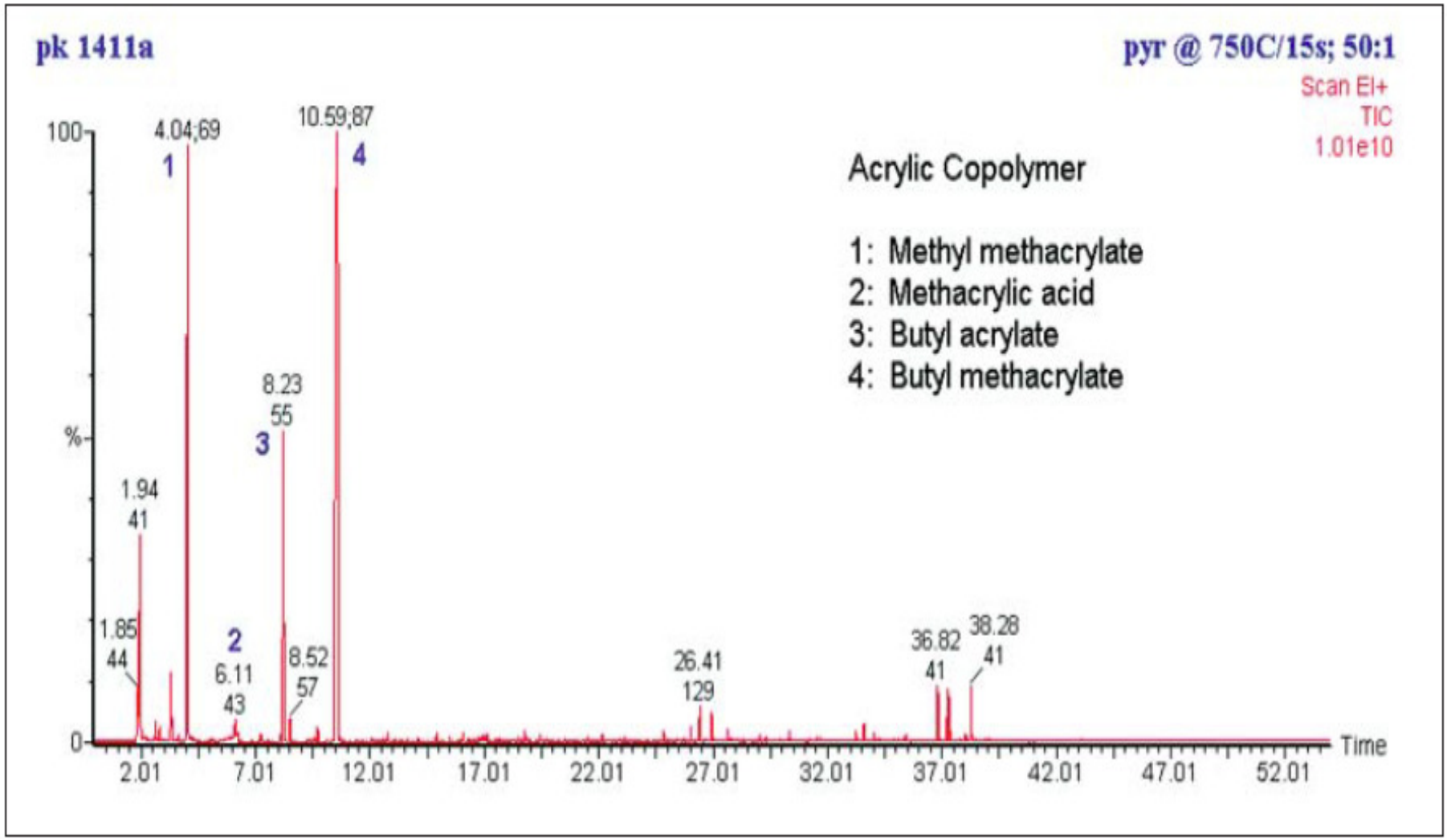
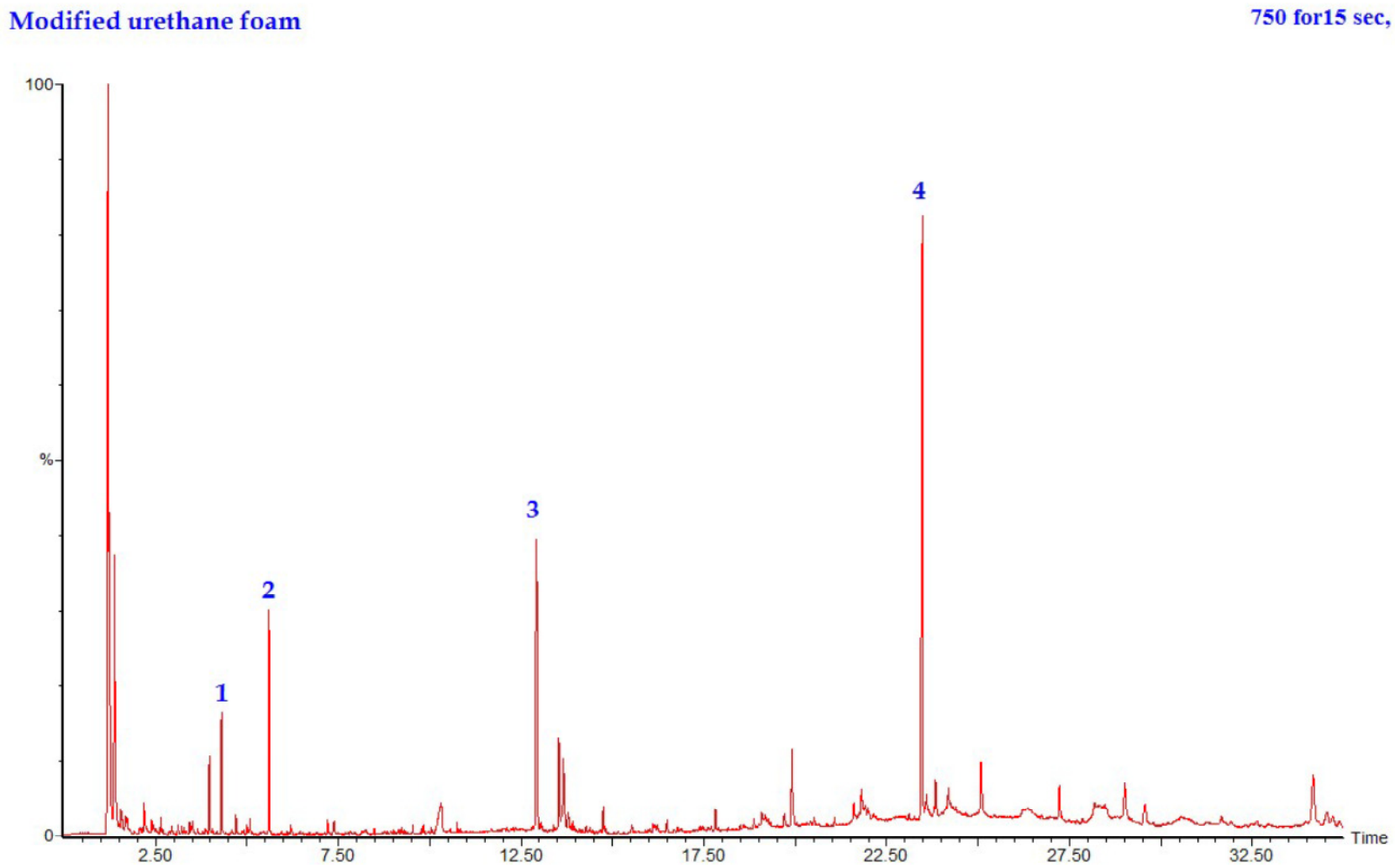
Polymer- Acrylic polymer



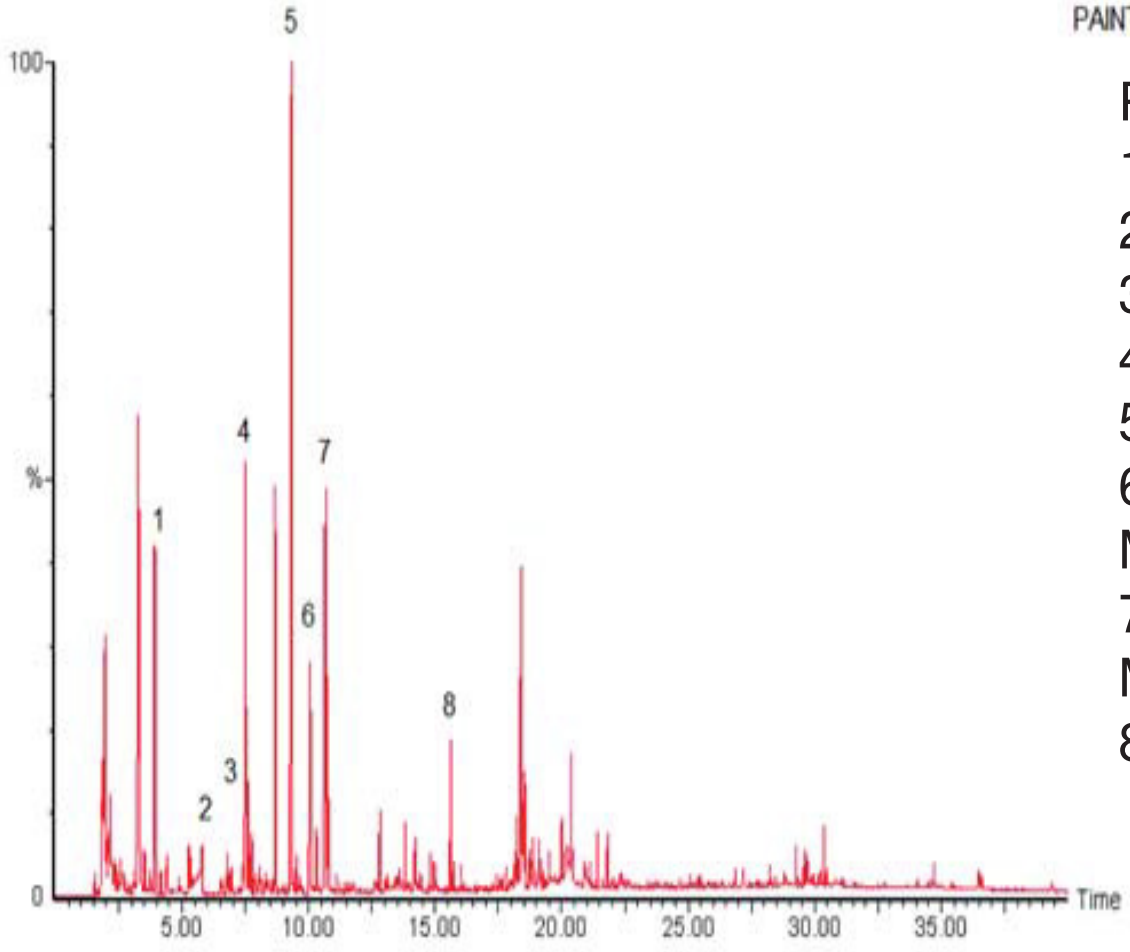
Total ion chromatogram resulting from pyrolyzing the copolymer at 750 °C for 5 seconds.

Polymer-Polyurethan polymer



Pyrogram of a modified foam rubber. Peak 1) 1-(1-methylethoxy)- 2-Propanone, 2) Styrene, 3) Toluene diisocyanate (TDI), 4) Tris-(1,3-dichloroisopropyl) phosphate.

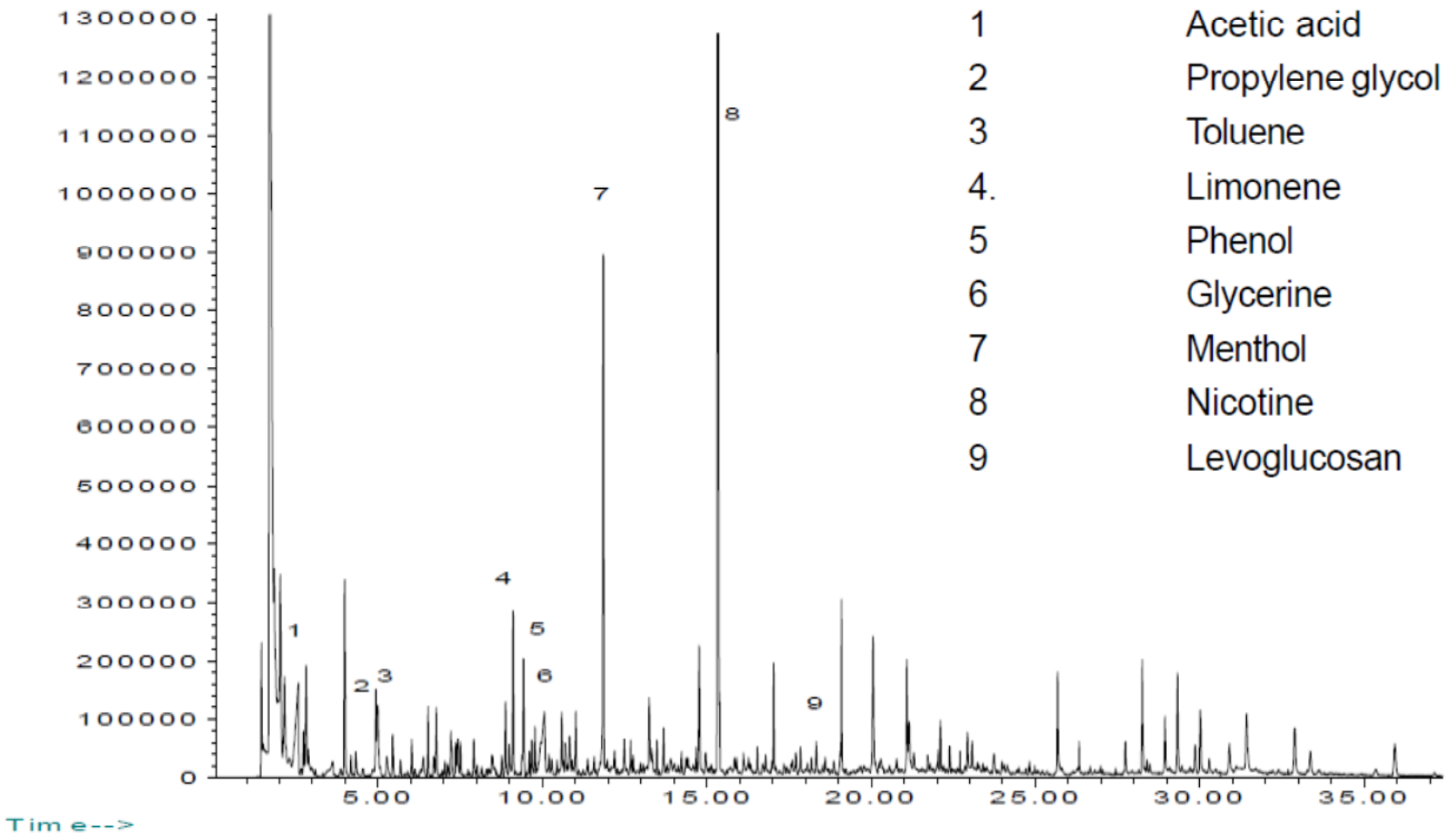
Automobile paint



Peak Identifications.
1 Methyl Methacrylate
2 Methacrylic Acid
3 Styrene
4 Butyl Acrylate
5 Butyl Methacrylate
6 Hydroxyethyl Methacrylate
7 Hydroxypropyl Methacrylate
8 Octyl Methacrylate

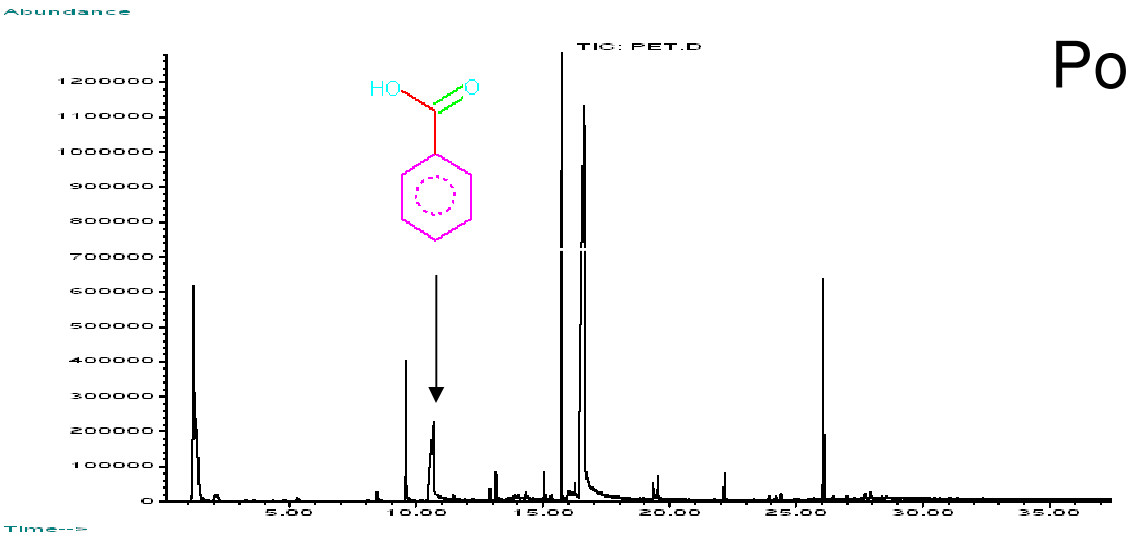
Total Ion Chromatogram resulting from the pyrolysis of a paint sample at 750 ° C for 15 seconds

Food- Tobacco with Menthol

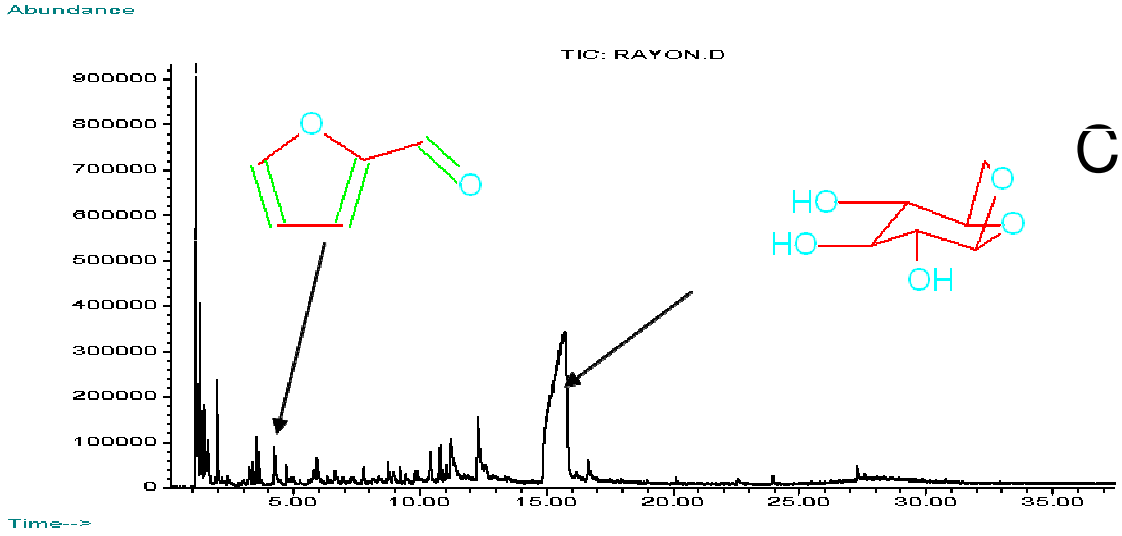


Peak number	Compound
1	Acetic acid
2	Propylene glycol
3	Toluene
4.	Limonene
5	Phenol
6	Glycerine
7	Menthol
8	Nicotine
9	Levoglucosan

Fiber Analysis



Polyester(PET)



Cotton

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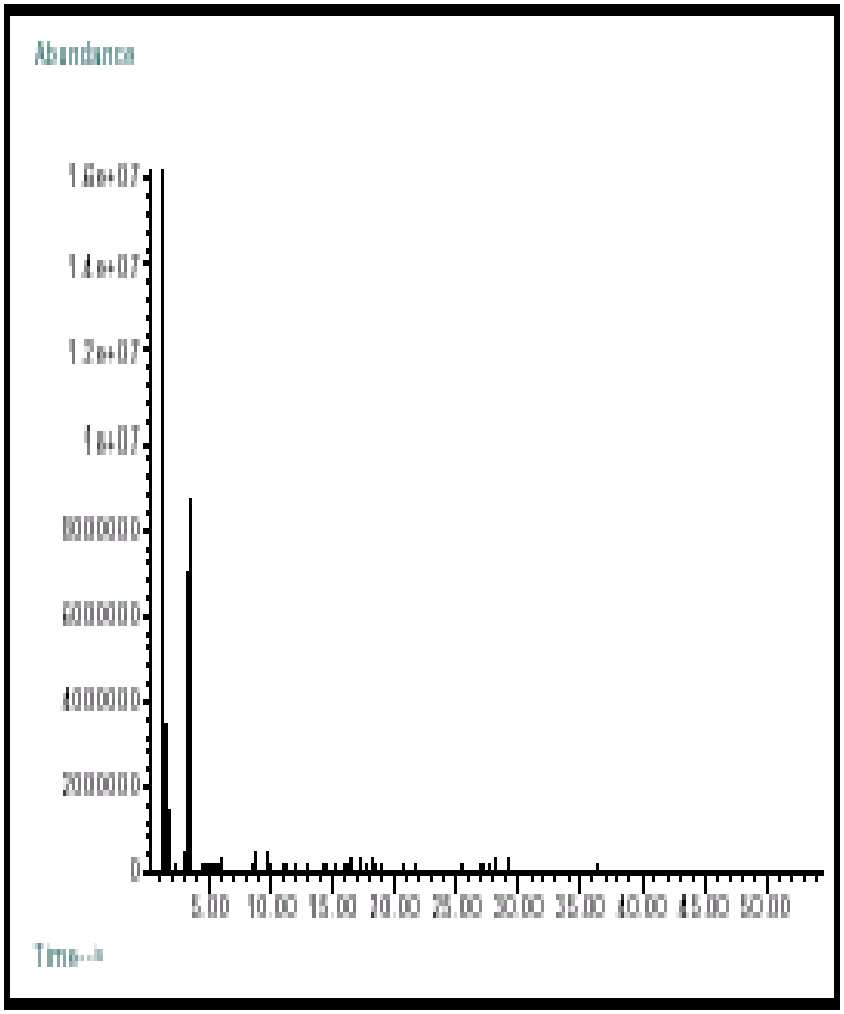
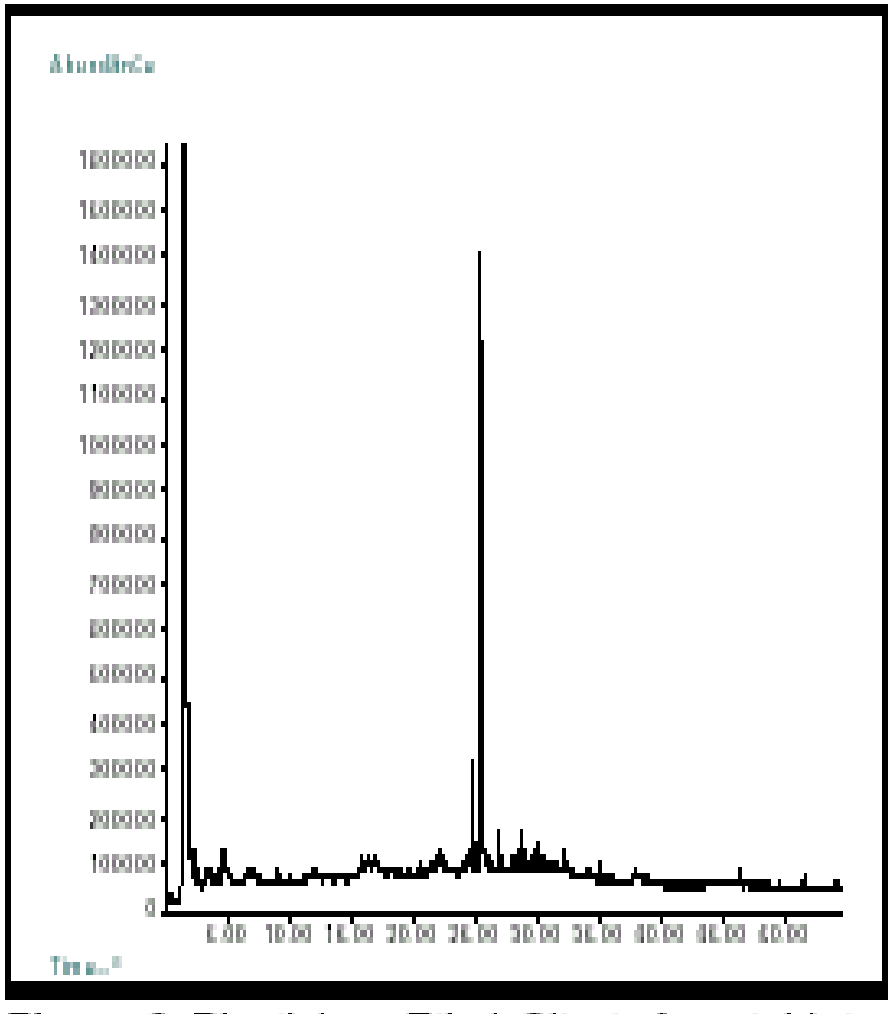
Pharma- Tablet coating

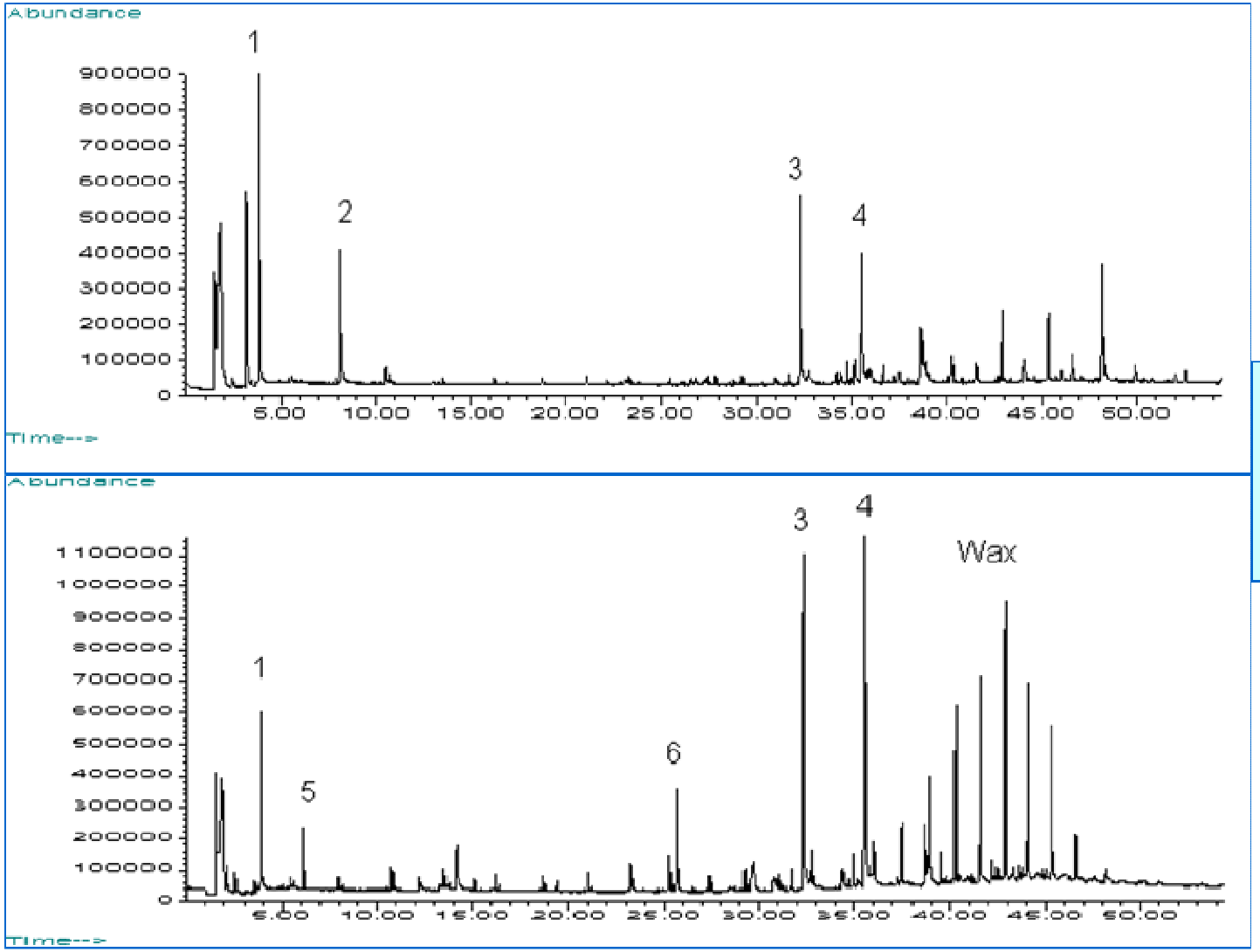


MMA from tablet



Plasticizer Ethyl Citrate from tablet

Consumer Products- **MASCARAS**



1. Methyl Methacrylate
2. Butyl Acrylate
3. Palmitic Acid
4. Stearic Acid
5. Cyclosiloxane
6. IDI

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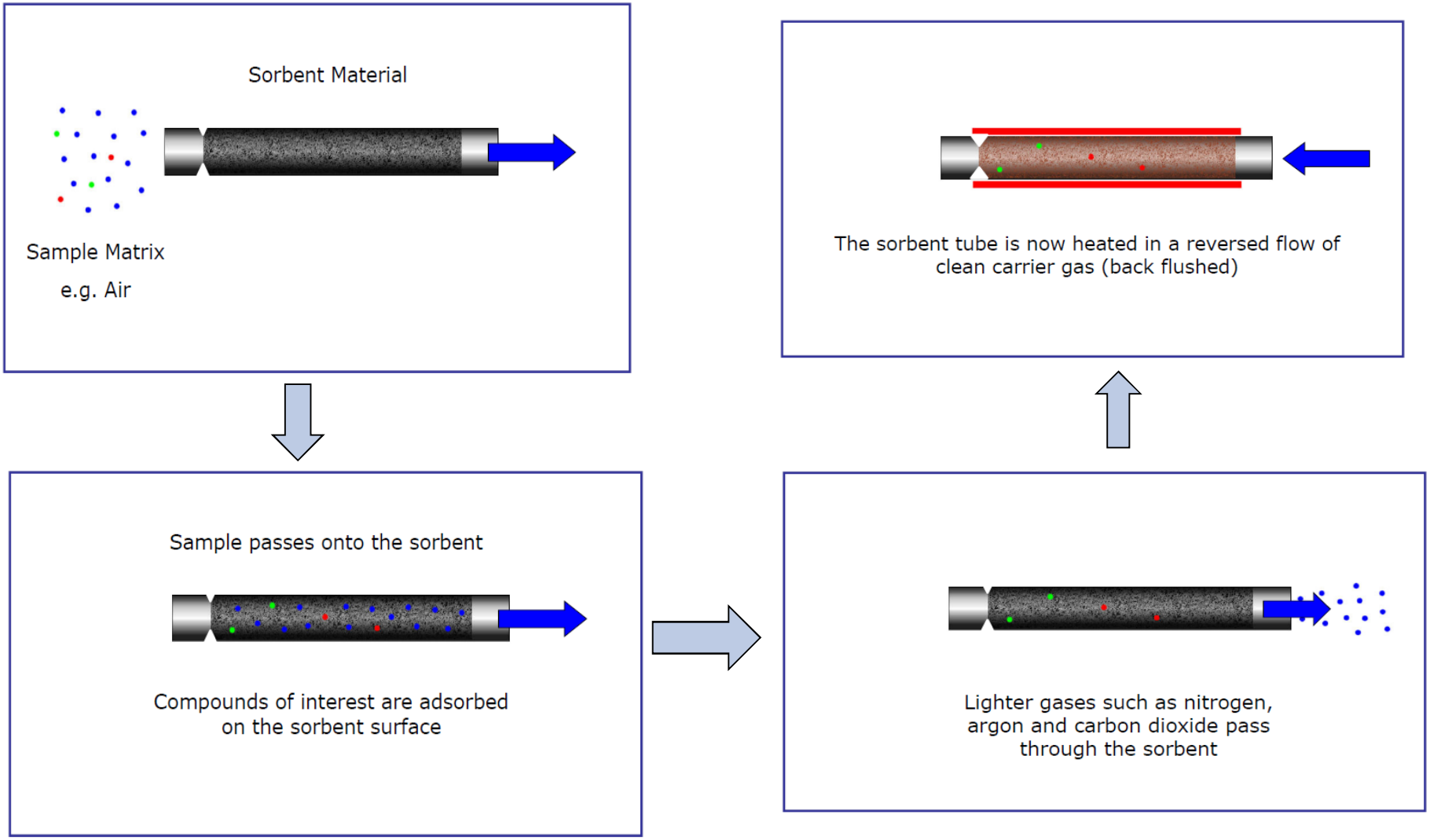
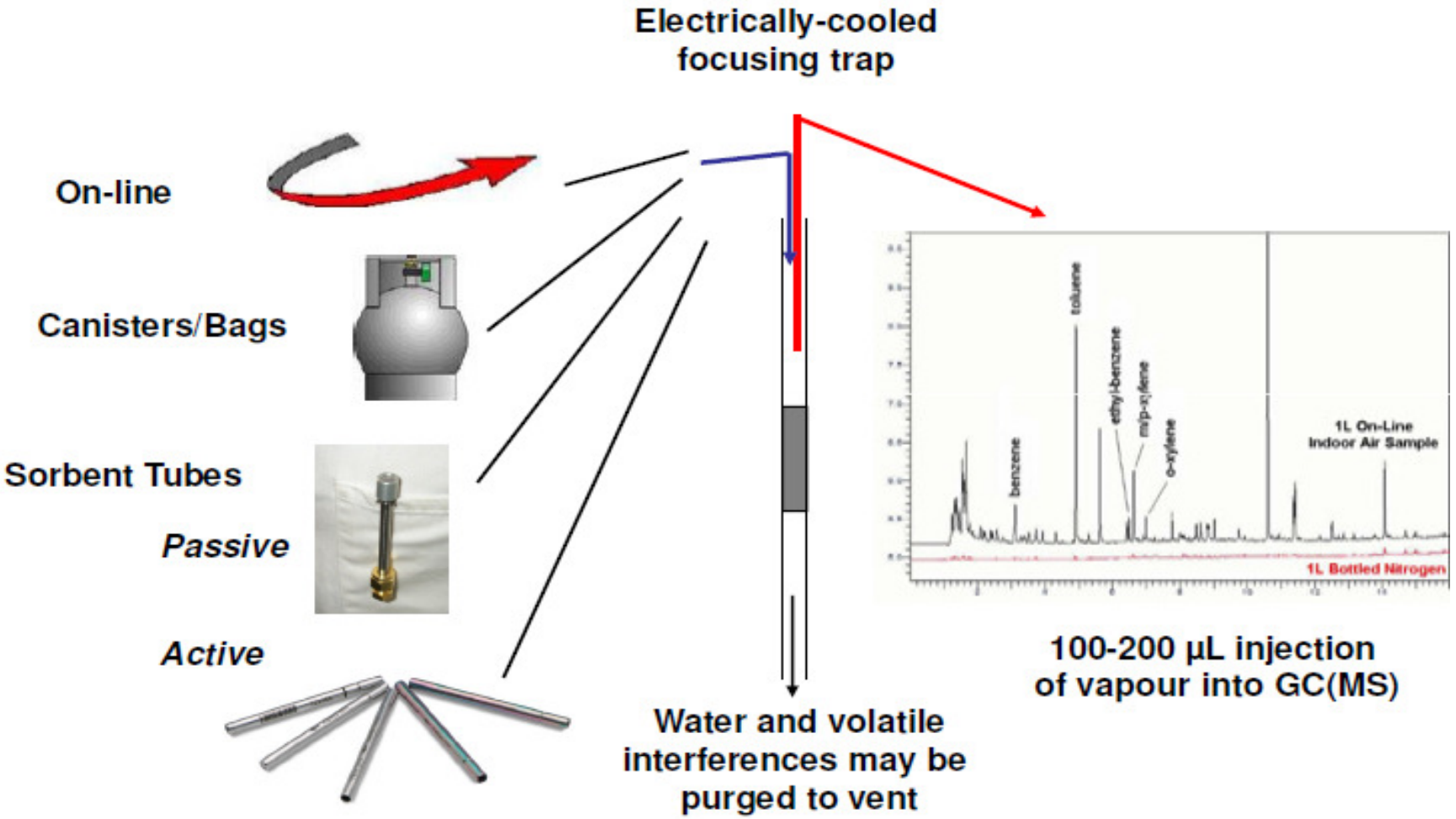
Automated Thermal Desorption (ATD) by Markes International

Thermal Desorption



Automated Thermal Desorption (ATD)



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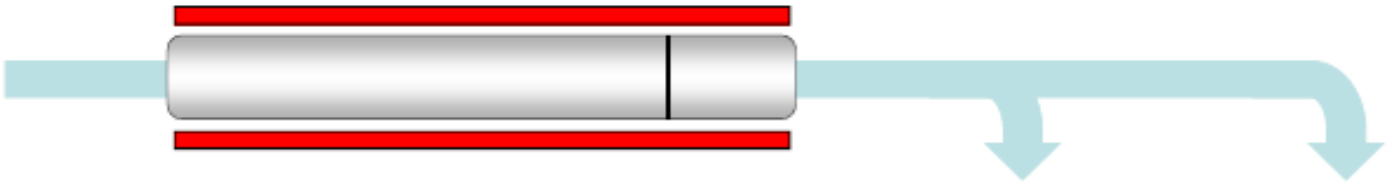
Automated Thermal Desorption (ATD)

- Primary Desorption

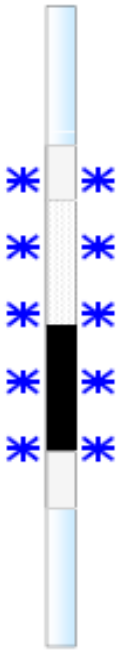


1. TUBE: Complete (representative) desorption of all target analytes from the sorbent tube

i.e. Everything desorbed from the Tube

2. TRAP: Complete (representative) retention of all target analytes for the duration of primary desorption

i.e. Everything retained on the Trap

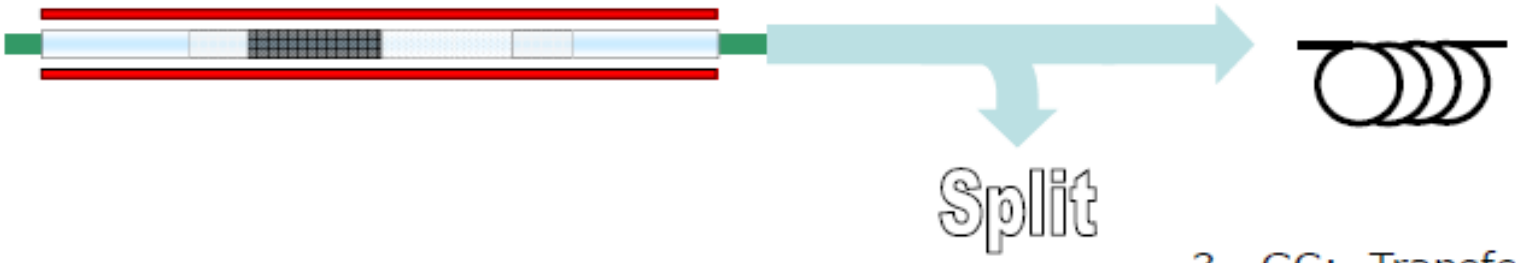


Split

3. SPLIT: Optional (quantitative) split of portion of sample and / or selective elimination of unwanted volatiles

Automated Thermal Desorption (ATD)

- Secondary Desorption



1. TRAP: Complete desorption of all target analytes from the trap

   i.e. Everything desorbed from the trap

2. SPLIT: Optional (quantitative) split of portion of sample

3. GC: Transfer of all analytes (or a representative portion of them) to the analytical system in a narrow band of vapour

   i.e. Injection onto column in a narrow band of vapour

Application areas

- Environmental and workplace air monitoring (Occupational Health & Safety at workplace)

  EPA methods (clean air act) e.g. TO-14 (canister), TO-15 () & TO-17 (tubes)

  ISO- 16017-2; ASTM D6196-03; MDHS 80 (UK HSE)

  Ozone precursor (PAMS)

- Forensic analysis

  Arson residue analysis- Gasoline vapours

- **Materials and materials emissions testing**

  VDA- 278 (VOC and FOG emissions by Thermal Desorption GCM)

  ISO-22219-4(2013)- emission of VOCs for vehicle interior parts & material

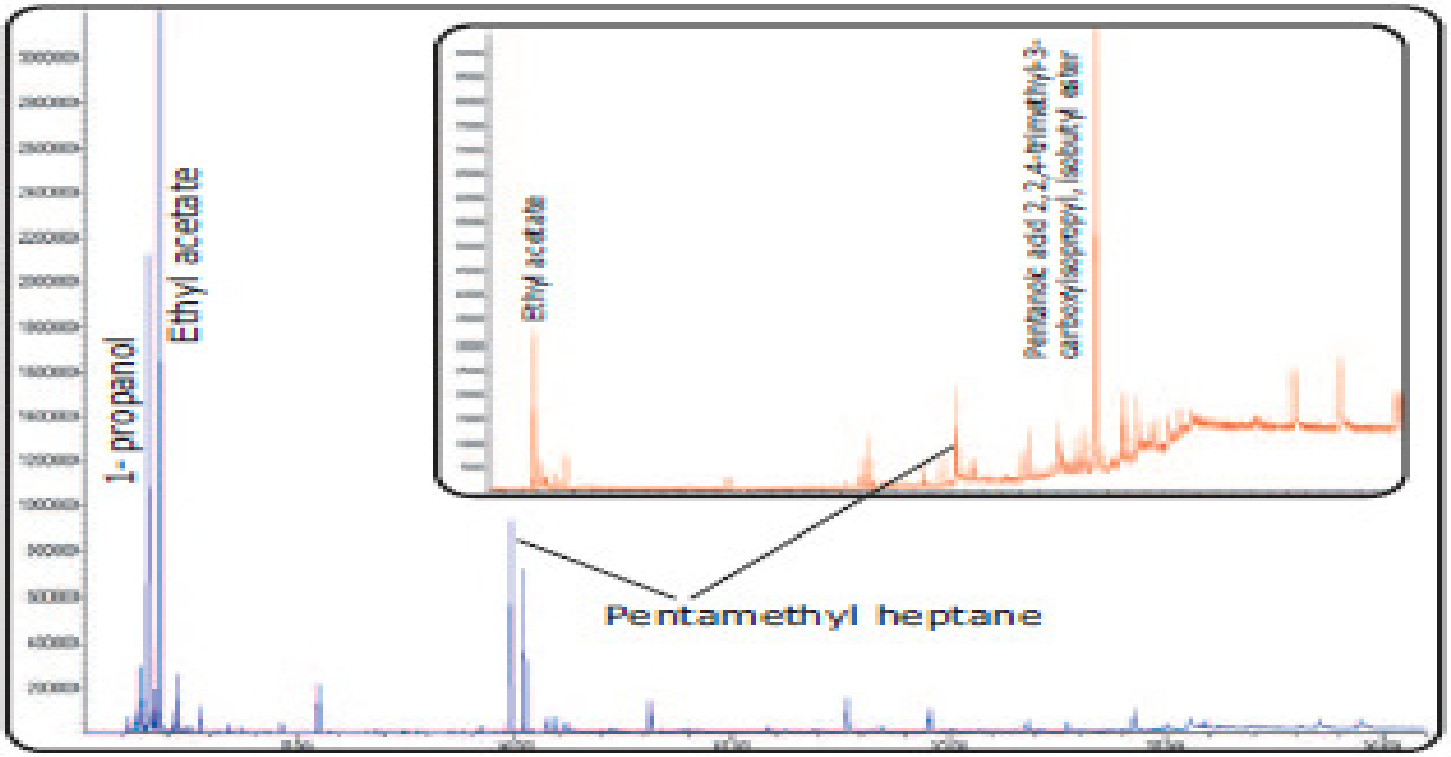
- Automobile industry

  VOCs in vehicle exhaust

- Food, flavour and fragrance profiling

VOCs in Food Packaging

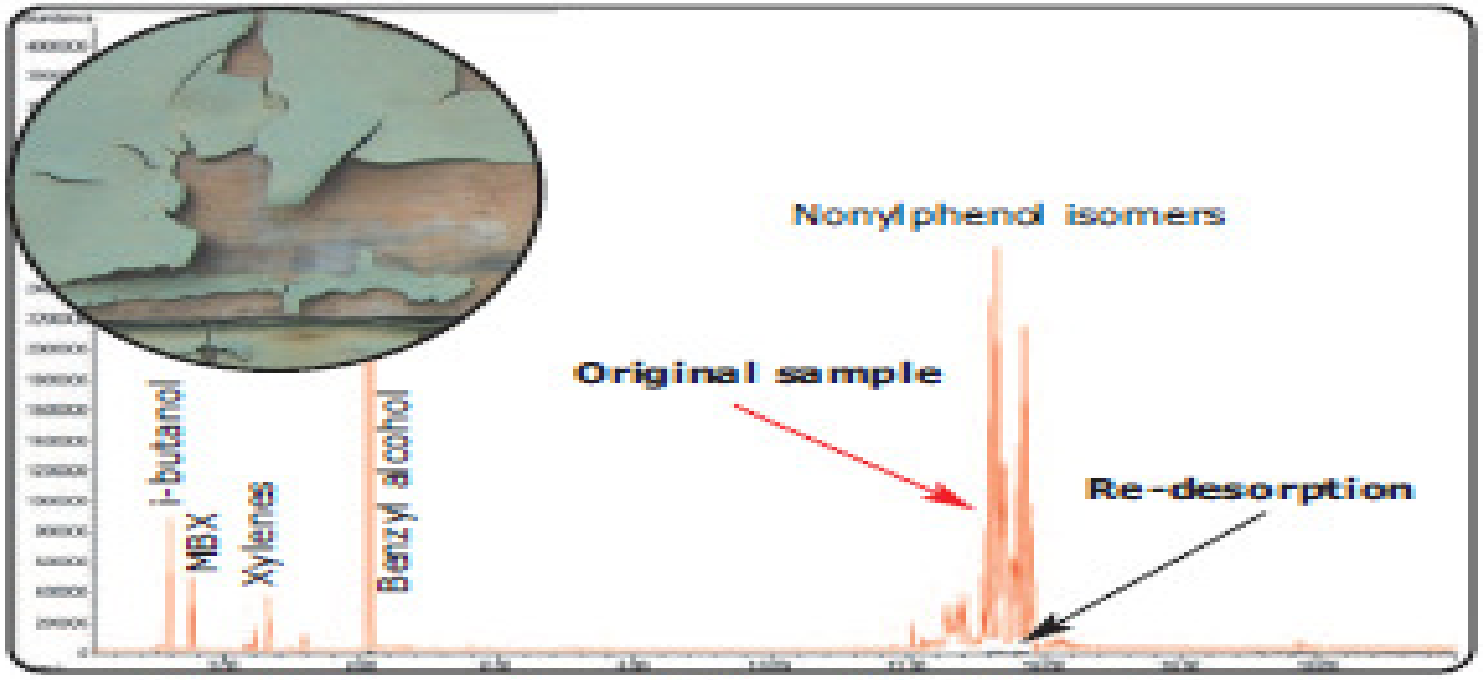
Direct desorption of packaging



Direct desorption of "energy food bar" wrapper (insert) and headspace (HS) analysis of same

Indoor Quality monitoring

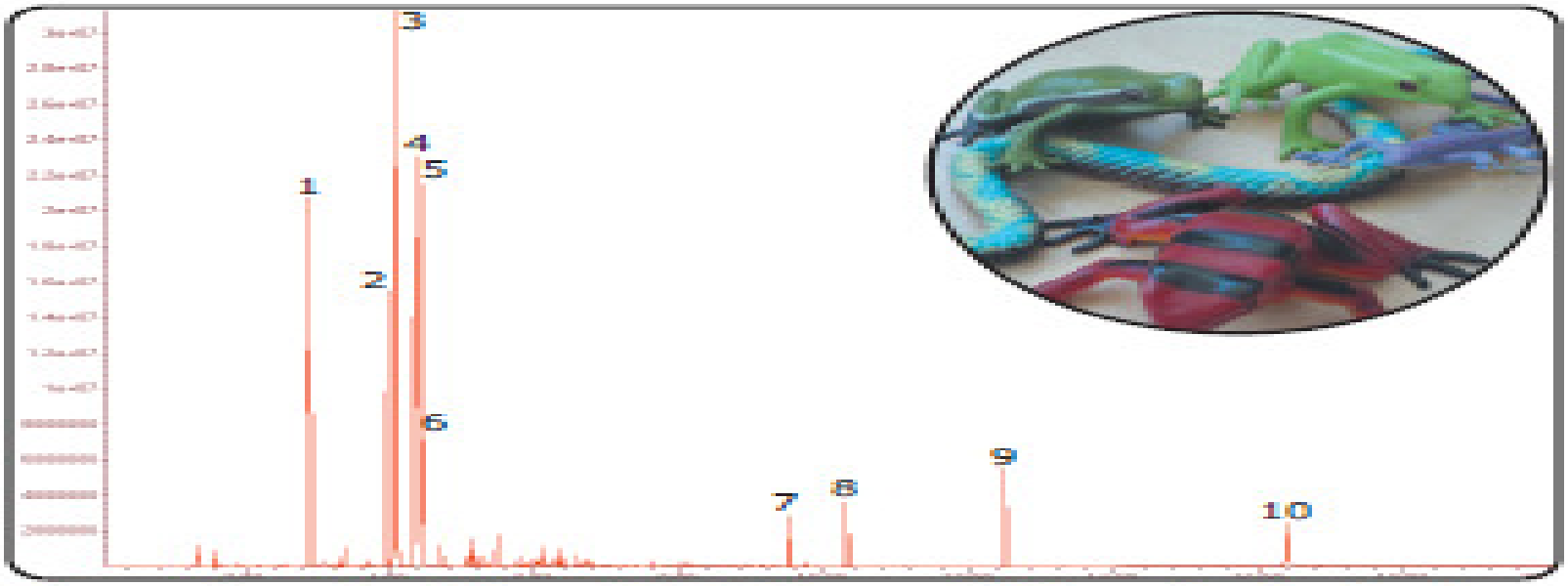
Paint flakes – exhaustive extraction for "content testing"



Direct desorption of dry paint flakes. Repeat desorption shows complete extraction

Emission from children toys

Emissions from childrens' plastic toys using the µ-CTE

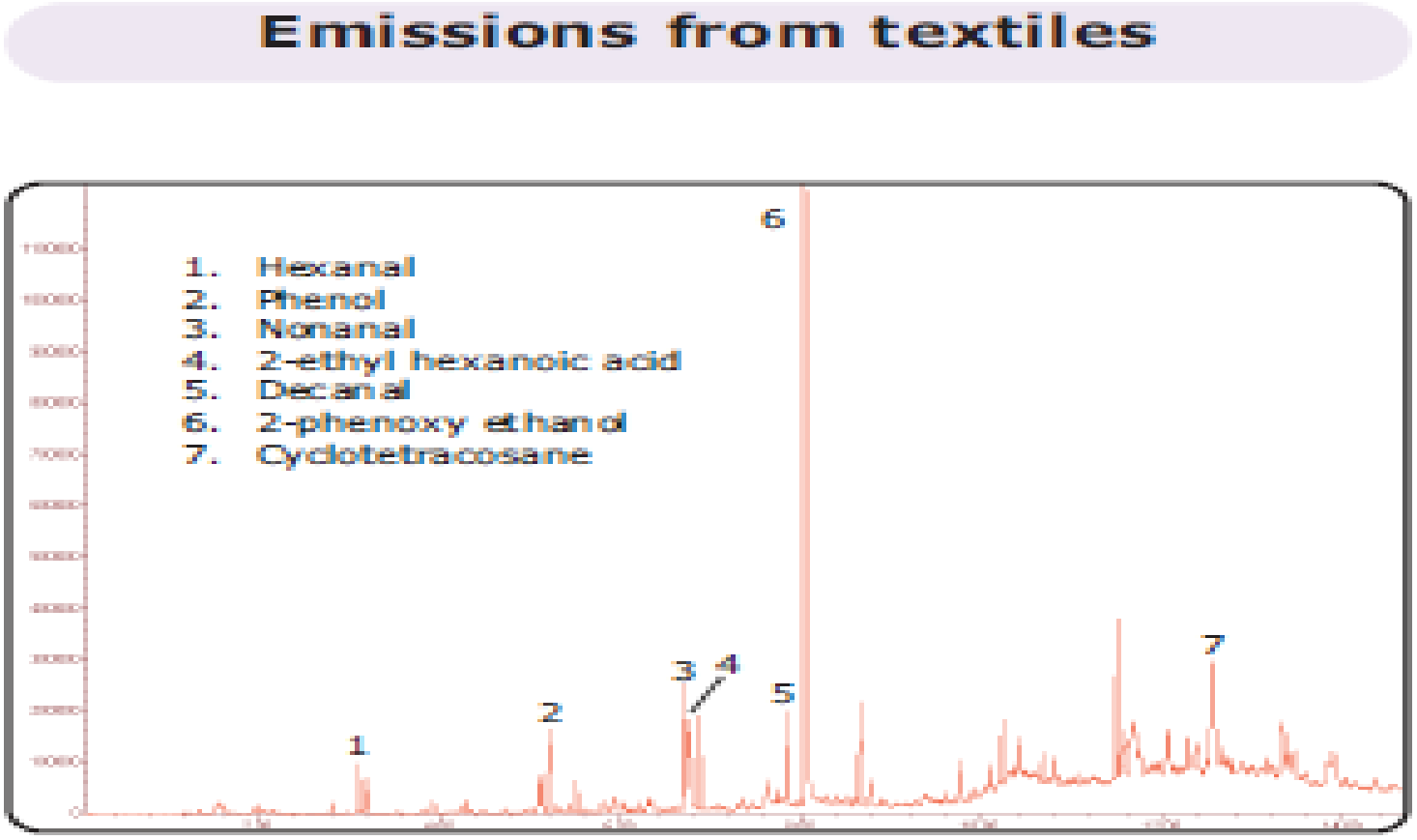


Thermal extraction of VOC from childrens' plastic toys

Analytes:

1. Toluene
2. Ethyl benzene
3. p-xylene
4. o-xylene
5. Cyclohexanone
6. 2-butoxy ethanol
7. Tricyclodecane
8. Diethyl phthalate
9. Dibutyl phthalate
10. Dioctyl phthalate

Emission from textile



Low temperature emissions from nylon sampled using the µ-CTE and analysed using TD-GC-MS

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