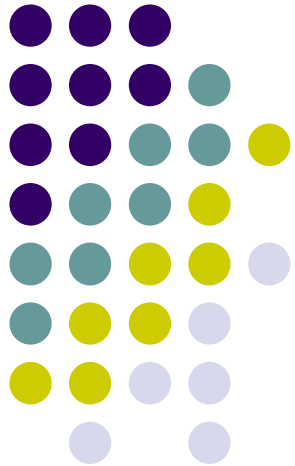
Chap.8
Ultra-trace Analysis



Introduction

- The reason to measure low concentration

  1) Biomagnification
  2) Many of compounds of concern ; high toxicity,
     can be used as an indication of environmental contamination

- Target compounds
  ; PCDDs, PCDFs and PCBs etc

- Analytical methods

  -Factors affecting detection sensitivity ;
  1.increase the chromatographic resolution of the column
  2. Increase pretreatment to increase the removal of hidrance
  3. Change detector

◆ Poison of Dioxin

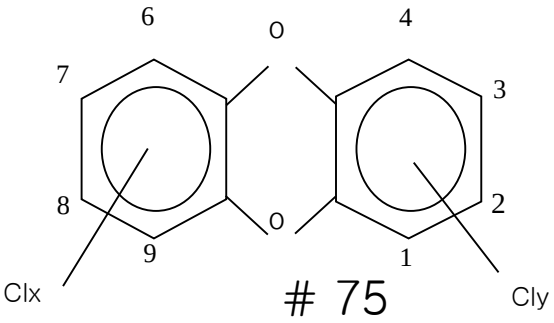
Ukrainian president

Victor, Yushchenko

Before After

Ukrainian presidential candidate Viktor Yushchenko had blood levels of dioxin 6000 times higher than normal.

Physicochemical Properties of dioxin



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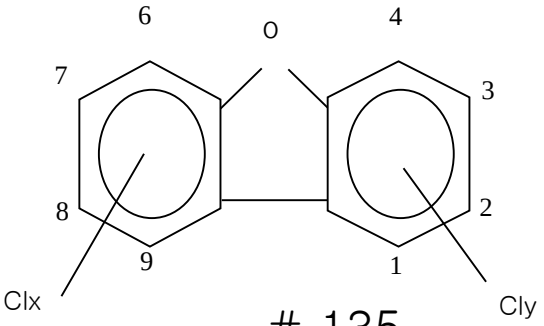


135

- PCDD/Fs (polychlorinated dibenzo-p-dioxins and furans)

- total 210 isomer (17 toxic compounds)
- Very low water solubility (0.07 - 400 ng//)
- Very low vapor pressure

- Strong binding affinity to organic material

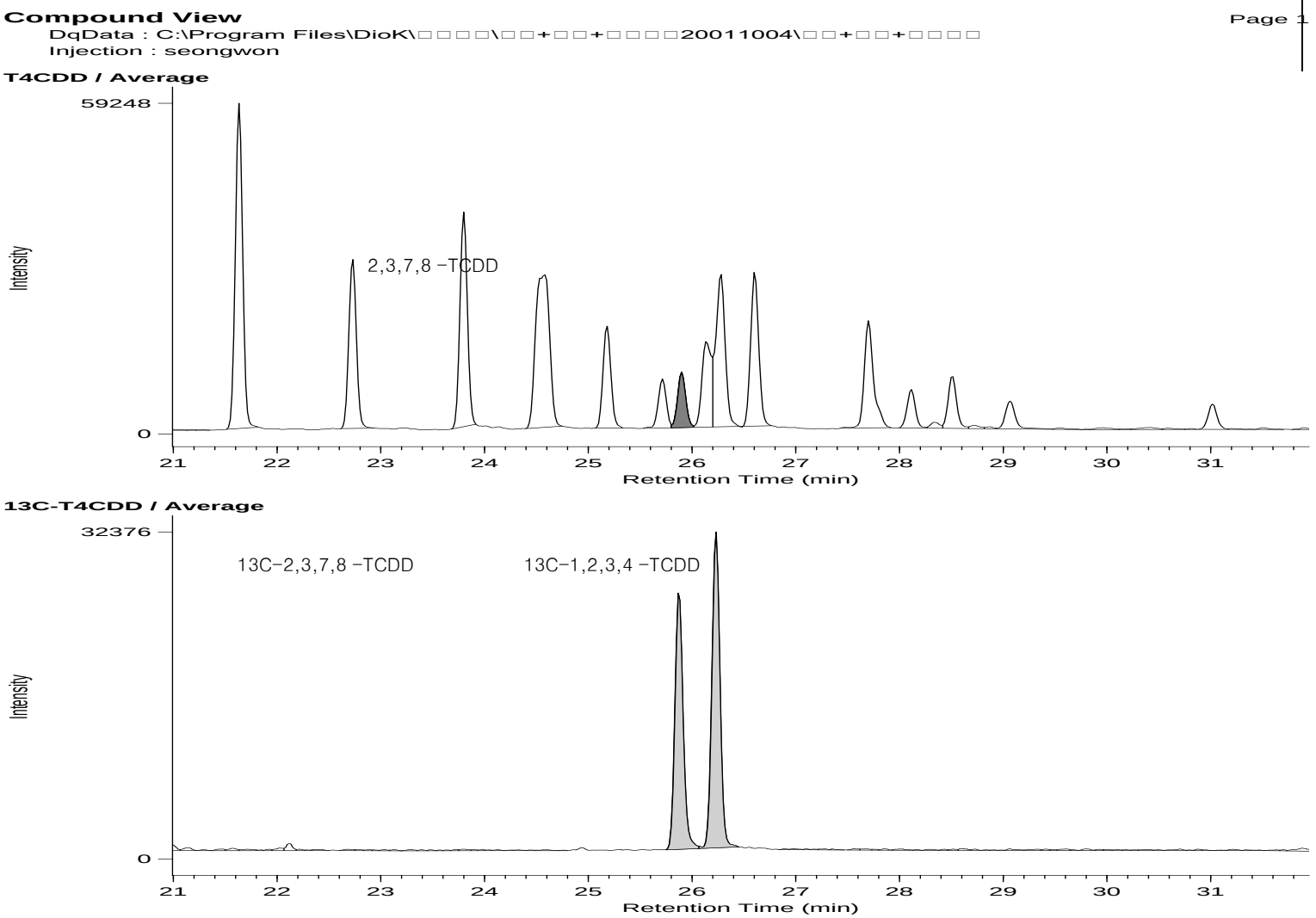
- Sources ; combustion and by-products of chemical products

PCDDs/Fs TEF (toxic equivalent factor) values

Homologue	Isomer	I-TEF	WHO
TCDD	2,3,7,8-TCDD	1	1
PeCDD	1,2,3,7,8-PCDD	0.5	1
HxCDD	1,2,3,6,7,8-HxCDD	0.1	0.1
	1,2,3,4,7,8-HxCDD	0.1	0.1
	1,2,3,7,8,9-HxCDD	0.1	0.1
HpCDD	1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	OCDD	0.001	0.0001
TCDF	2,3,7,8-TCDF	0.1	0.1
PeCDF	1,2,3,7,8-PCDF	0.05	0.05
	2,3,4,7,8-PeCDF	0.5	0.5
HxCDF	1,2,3,4,7,8-HxCDF	0.1	0.1
	1,2,3,6,7,8-HXCDF	0.1	0.1
	2,3,4,6,7,8-HXCDF	0.1	0.1
	1,2,3,7,8,9-HXCDF	0.1	0.1
HpCDF	1,2,3,4,6,7,8-HpCDF	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	OCDF	0.001	0.0001

- TEQ = Σ (conc $\times$ TEF) - 2,3,7,8 - TCDD based
  ex) 0.3 ng-TEQ/m^3, 20 ng/m^3

TCDD Chromatogram



Flow Chart of analysis

Extraction (13C internal std)

↓

Clean up

↓

Multi silica

↓

Florisil, Alumina, carbon etc

↓

concentration

↓

Instrumental Analysis

-To remove DDT, pesticides and PCBs etc, second column is required because of their similar chemical structures (neutral, non-polar, high MM)

Pretreatment for PCDD/F analysis

Pretreatment	
Extraction	**Soxhlet ; reference extraction method** **Liquid-liquid extraction** **Accelerated solvent extraction (ASE) ; fast, high cost** **Ultrasonic extraction ; easy to use, large volume of solvent**
Acid treatment GPC	**To remove lipids and oxidizable compounds**
Clean-up	**Silica ; To remove polar compounds** **Alumina ; To separate PCBs and Dioxin** **Carbon ; To separate PCBs, and** polychlorinated diphenyl ethers **etc** **Cupper ; To remove sulfur**

• External standard method ;

–make an calibration curve with known amount of analyte and compare the peak area (height) with peak area(height) obtained by making an injection of the sample quantitated.

–Can't consider matrix effect, can't get recovery information

– Injection volume precision is critical. Needs a uniform matrix

• Internal standard method ;

– Add a known amount of standard similar to the analyte of interest to the sample (use isotope ex; ^{13}C standard)

– the most accurate type. Difficult to select the internal standard.
– injection volume precision not critical
– can get recovery of internal standard

Mass spectrometry

-Resolution ; ion separation power of mass spectrometer

R =M/ΔM

M : mass of an ion ΔM; difference of two separated ion

Dioxin mass range ; 300 ~ 600

300/0.1 = 3000

low resolution ~ 1000 (can tell the difference unit 1)

High resolution > 10,000

Mass spectrometry ;

- An analytical chemistry technique that helps identify the amount and type of chemicals present in a sample by measuring the mass to charge ratio (by Wikipedia)

Sample

Ion source: makes ions

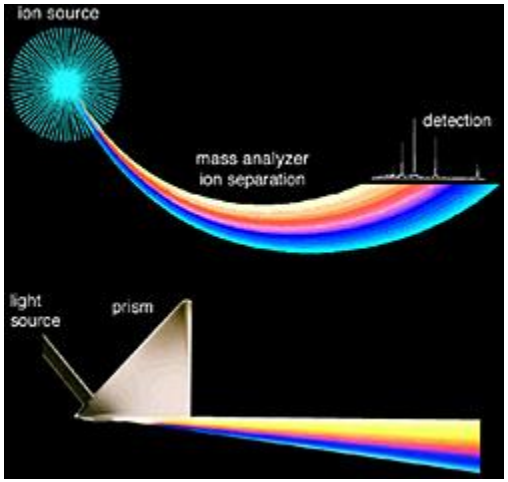
- MALDI
- ESI
- FAB
- EI
- CI

Mass analyzer: separates ions

- Time of flight (TOF)
- Quadrupole
- Ion Trap
- Magnetic Sector
- FTMS

Detector

Mass spectrum: presents information



http://masspec.scripps.edu/mshistory/whatisms_details.php#Basics

Electron ionization, EI

1. Electrons produced from a heated filament are accelerated though an electric field at 70eV to form an electron beam

2. sample is thermally desorbed

3. electrons transfer some of their kinetic energy to the molecule M. (ionization)
M + e-(70eV) → M+ + 2e-

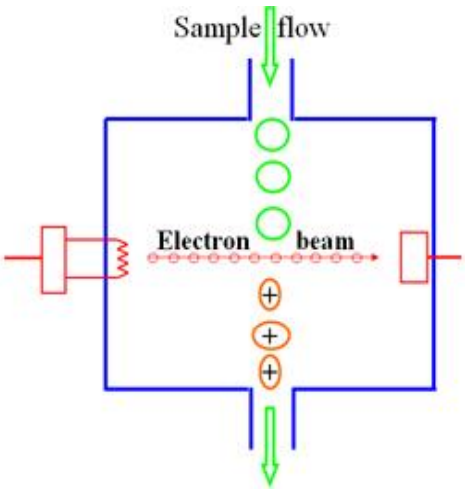
4. M+ → molecular ion + fragment ion + neutral fragments

hard ionization, bombard with highly energetic electrons, fragmentation

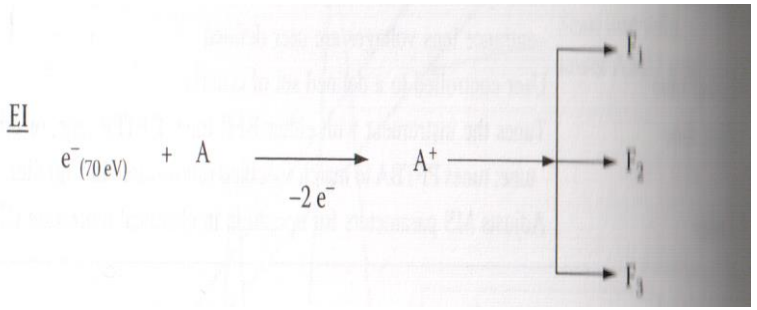
-advantage : use of fragmentation pattern as a fingerprint with databases to identify unknowns. Structural information obtained from fragmentation pattern.

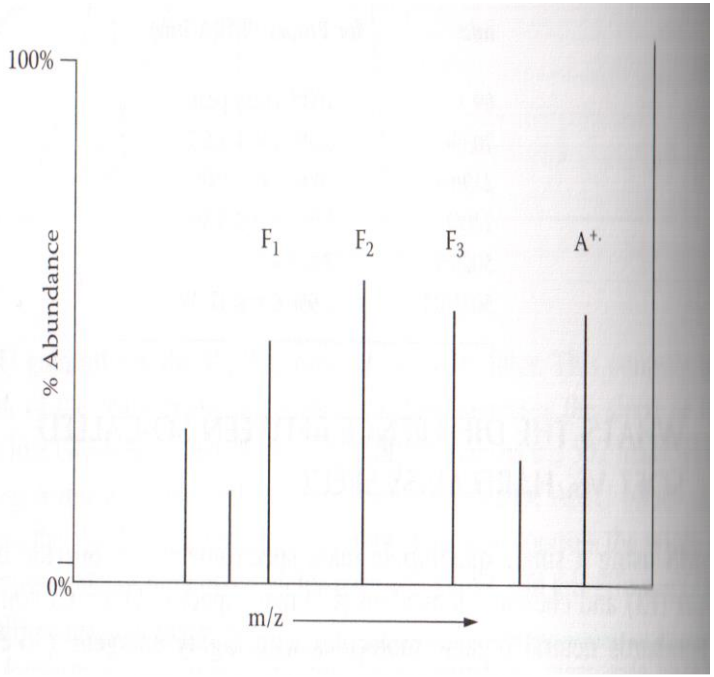
-disadvantage : possible decomposition, too much fragmentation, often resulting in no observable molecular ion

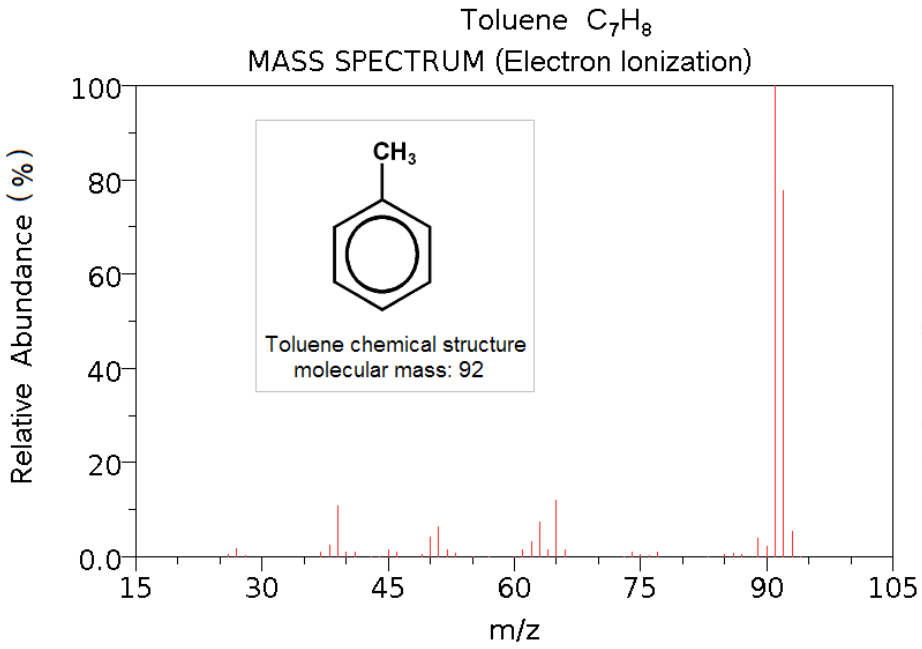
EI (Electron impact)



http://departments.agri.huji.ac.il/zabam/Polaris-Q.html





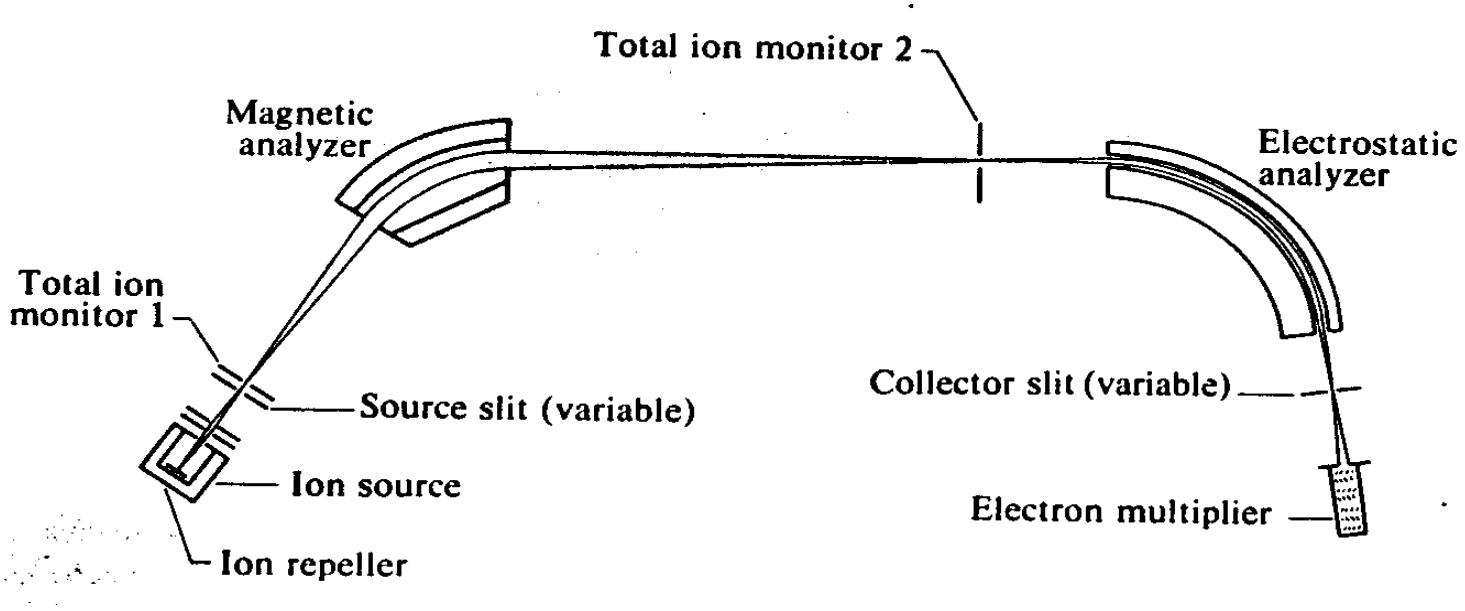


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

• Double Sector mass spectrometer

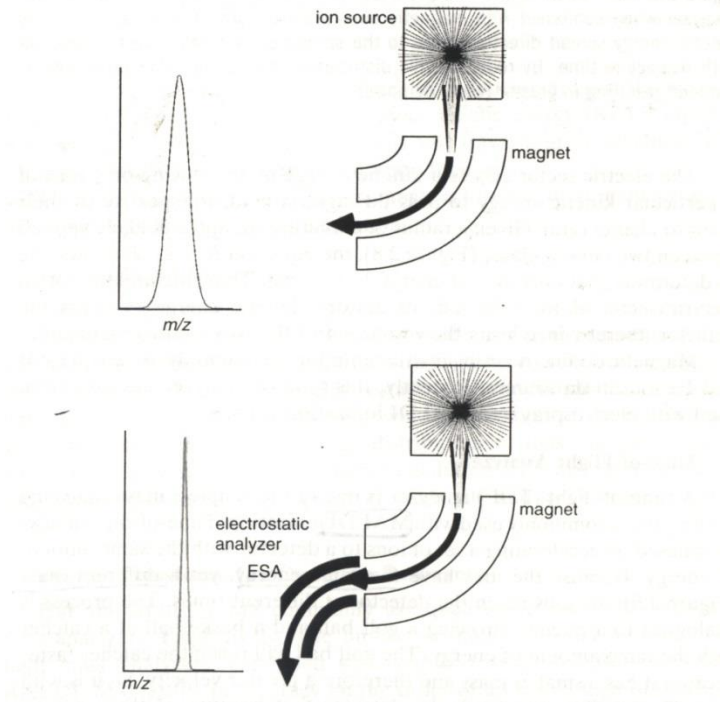
- Ionization (Electron impact (EI)) under high vacuum ⟶

Production of molecules fragment ⟶ Produced ions are focused into a beam and accelerated ⟶ Separated with mass to charge in magnetic and electrostatic field

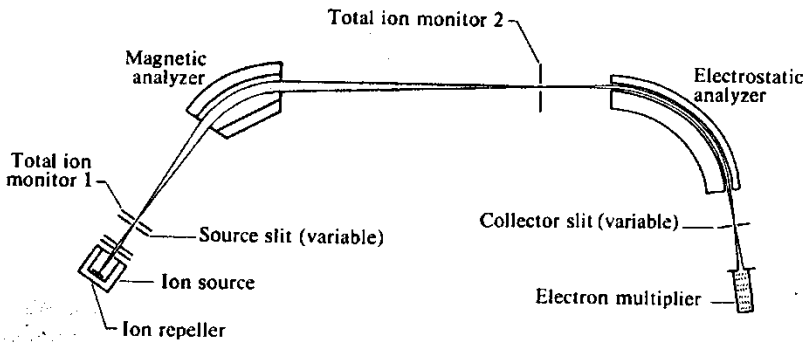


Double Sector mass spectrometer

HRGC/HRMS



gure 2.7 Illustration of the improved resolution obtained with a two-sector double-



- Magnetic sector

$M/z = R^2H^2/2V$

m ; 이온질량

z ; 이온의 전하수

R ; 곡률반경

H ; 자기장 세기

V ; 가속전압

-electric sector ; acts as a kinetic energy filter. (allow only ions of a particular kinetic energy to pass through its field, irrespective of their mass to charge ratio)

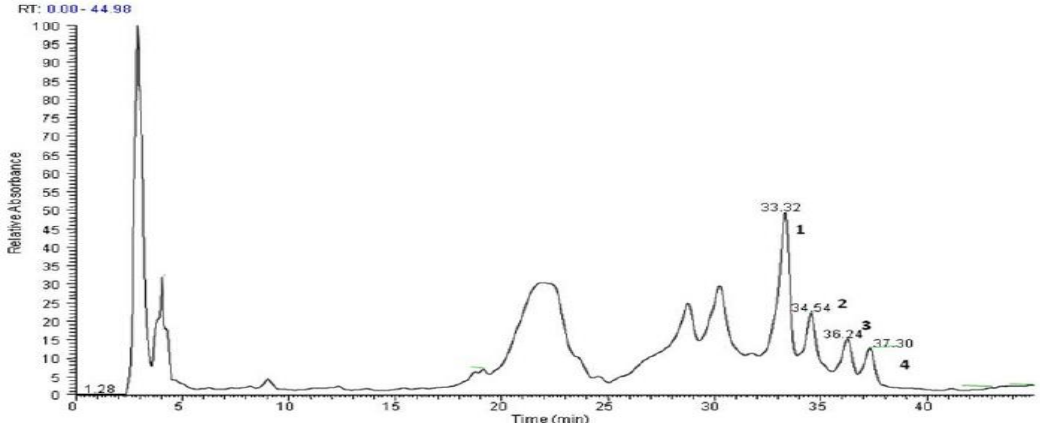
- double focusing
- high resolution

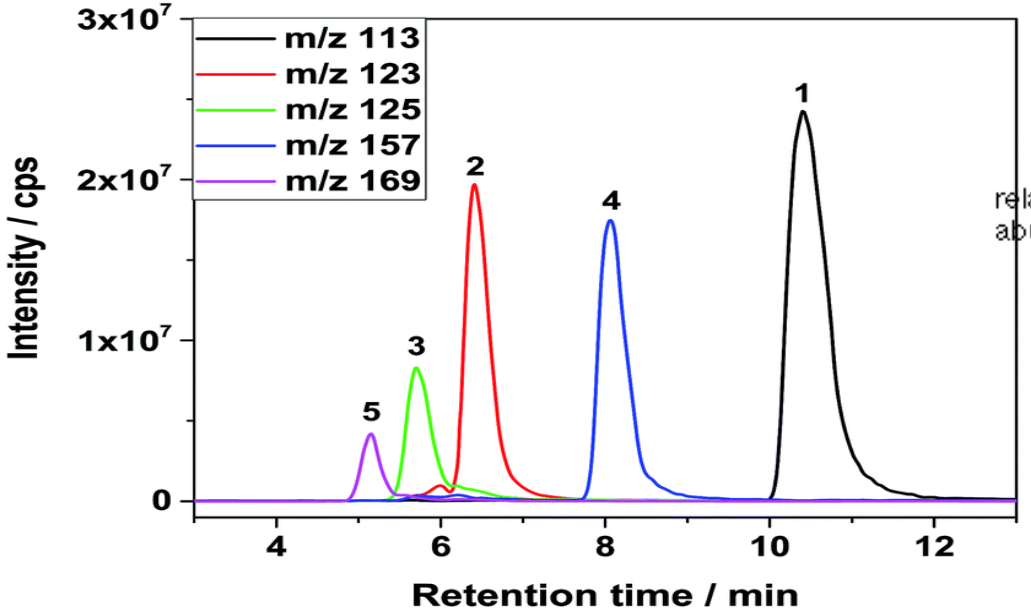
mass spectrum is an intensity vs. *m/z* (mass to charge ratio) plot

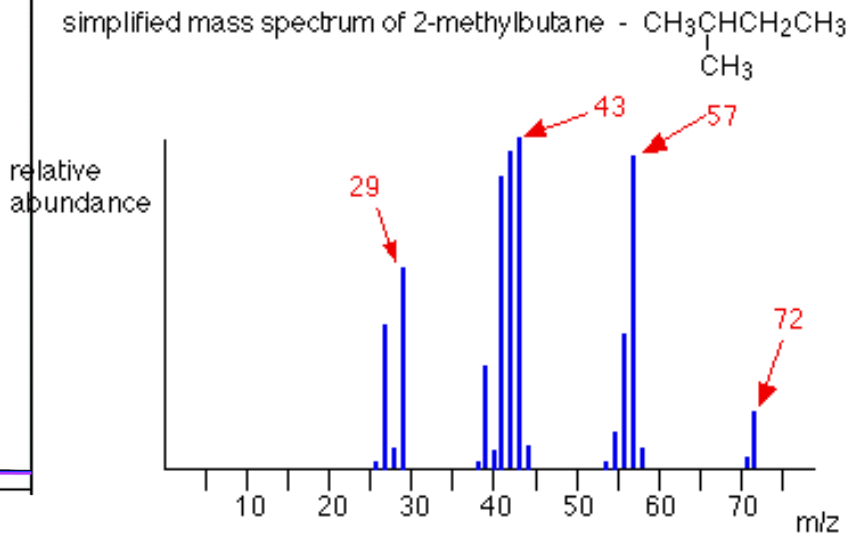
Mass chromatogram ; a representation of mass spectrometry data as a chromatogram, where the x-axis represents time and the y-axis represents signal intensity

The total ion current (TIC) chromatogram represents the summed intensity across the entire range of masses being detected at every point in the analysis

-by the wikipedia


RT: 0.00 - 44.98
Relative Abundance
Time (min)
1.28
33.32
1
34.54
2
36.24
3
37.30
4


m/z 113
m/z 123
m/z 125
m/z 157
m/z 169
Intensity / cps
Retention time / min
1
2
3
4
5


simplified mass spectrum of 2-methylbutane - CH3CHCH2CH3
CH3
relative abundance
m/z
29
43
57
72

• mass analysis

-SIM ; selected ion monitoring, increase sensitivity in comparison with total ion current detection

-Scan ; can obtain the mass spectrum over the required mass range

- Isotope ratio ; measure the ratio of ^{35}Cl and ^{37}Cl (3:1)

Selected ion detection at two or more m/z values

ex) TCDD	m/z	ratio
$^{12}C_{12}{}^{1}H_4{}^{16}O_2{}^{35}Cl_4$	= 320	77
$^{12}C_{12}{}^{1}H_4{}^{16}O_2{}^{35}Cl_3{}^{37}Cl$	= 322	100

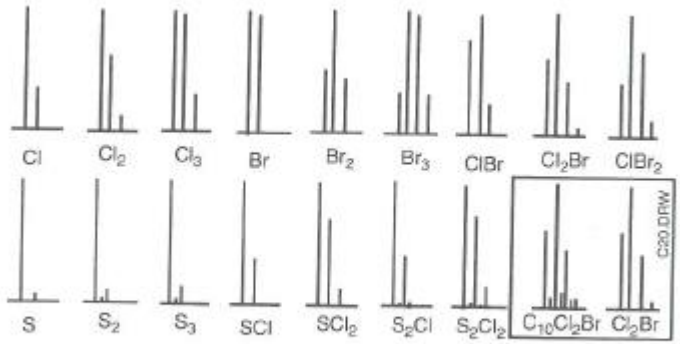


Figure 5.3
Useful isotope combinations in mass spectrometry. Isotopes of other