Lecture in the course Environmental Chemistry

at University of Trieste

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Transformation and degradation of pollutants in the environment

CHALLENGES AND SOLUTIONS

2

Mass-balance of pollutant

$$I = E_w + E_a + E_s + W + P + dS + D \qquad (2.1)$$

where

I = input (amount produced, purchased, etc.)
E_w = amount discharged with wastewater
E_a = amount emitted into the air
E_s = amount released to the soil
W = amount in outgoing waste
P = amount in outgoing product
dS = difference in amount in storage at start and end of period
D = amount degraded (thermally, biologically and chemically).

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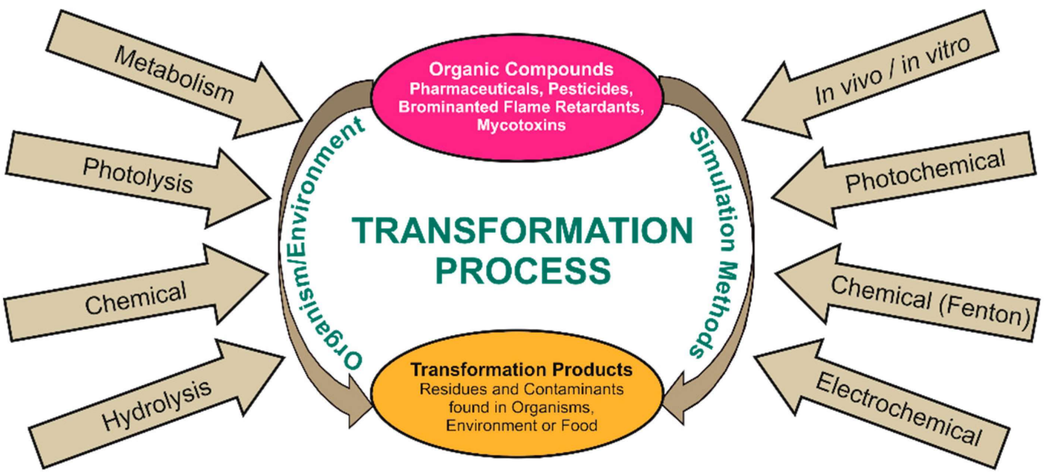

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Transformation/degradation as unwanted processes

1//Determination of lower amount of analyte

2//Measurement of analyte only

3//Different chemical and other (e. g. toxicity) properties of transformation/degradation products

Transformation/degradation as initiated processes

1//Degradation of toxic or health hazardous compounds

2//Different aproaches

Electrochemical

Photo

Biological

Identification of transformation/degradation products

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Transformation/ degradation products

Usually there is no standards

Compared to the parent compound
- Different chemical structure
- Lower concentration
- Higher toxicity, more persistent

Transformation products are not included in routine monitoring (e. g. environmental)

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Transformation/ degradation studies

Parent compound

Prediction of potential transformation/degradation products

Factors influencing transformation/degradation

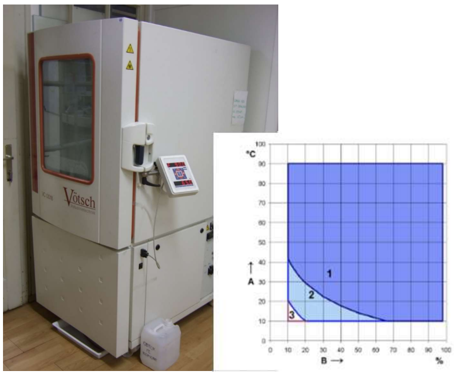
Light (UV)

Temperature

Humidity

Acidic/basic conditions

Oxidative conditions



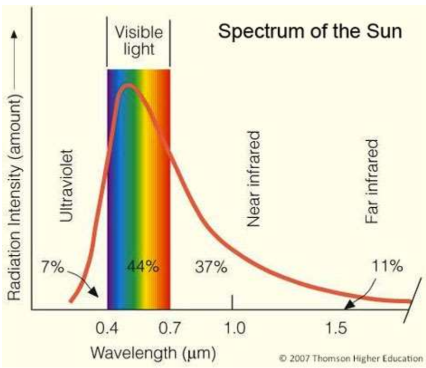
Climatic Chamber (T, RH)

Xenon Weathering Chamber

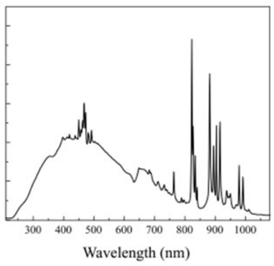
Full daylight spectrum

Outdoors conditions

Window glass filter



Spectrum of xenon lamp



SUNTEST CPS+

Screening and identification

//Screening of transformation/degradation products

LC/MS; CG/MS

LC/MS/MS; GC/MS/MS

//Identification of transformation/degradation products

HRMS

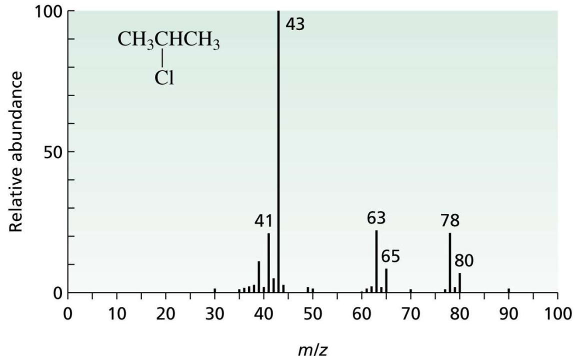
NMR

Identification of unknown compounds

Mass spectrum

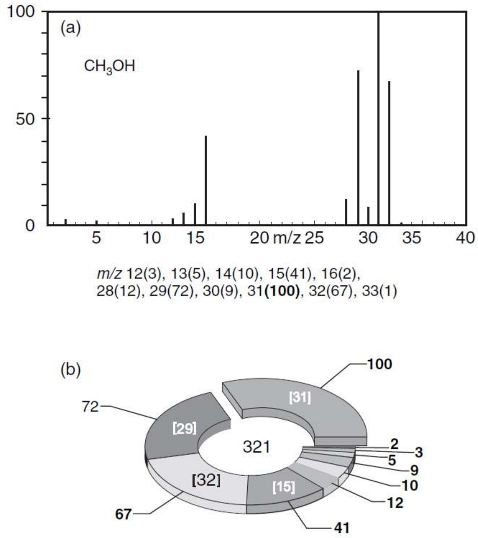
Relative abundance of individual *m/z*

m/z=mass/charge ratio

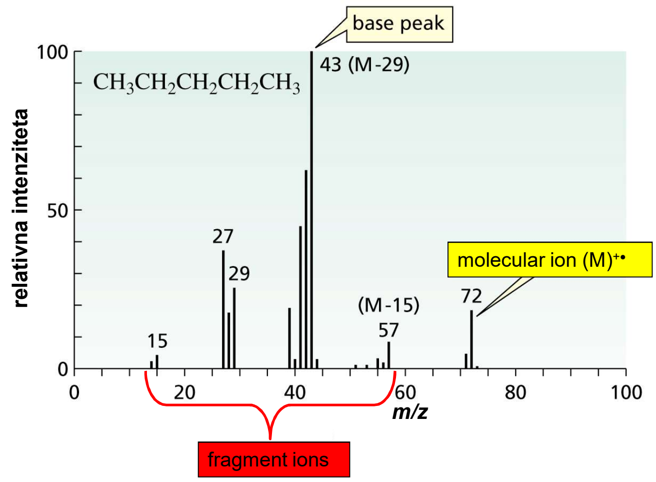


Mass spectrum

ions	m/z
$CH_3OH^{+\cdot}$	32
$H_2C{=}OH^+$	31
$HC{\equiv}O^+$	29
H_3C^+	15



Ions in mass spectrum



m/z	Relative abundance
73	0.52
72	18.56
71	4.32
57	11.20
43	100.00
42	55.27
41	37.93
39	12.44
29	26.65
28	17.75
27	31.22
15	4.22
14	2.56

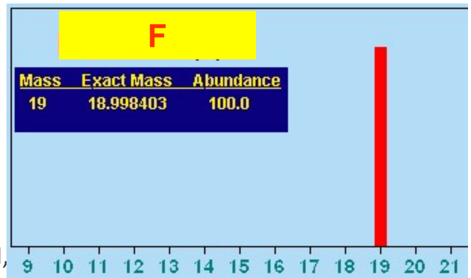
Only positive charged species in mass spectrum

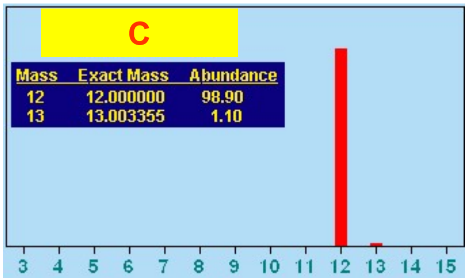
Isotope ratio

one isotope

two isotopes

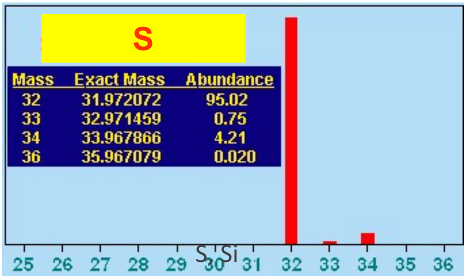
F, P, I,





Isotope ratio

more isotopes



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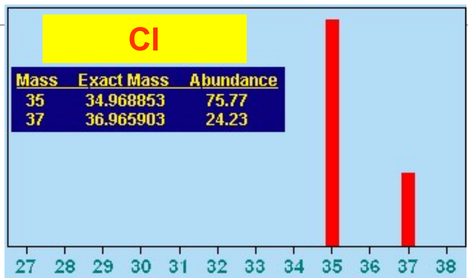
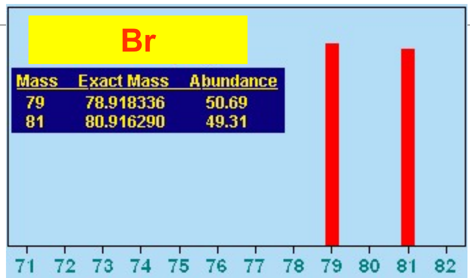
Multi-elements molecules with intensive isotopes, e.g. Cl in Br





Calculation of isotope ratios with binomial approach

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Binomial approach

$$(a+b)^n \times (c+d)^m$$

a = relative intensity of the light isotope of the first element

b = relative intensity of the heavier isotope of the first element

n = number of atoms of the first element in the molecule

c = relative intensity of the light isotope of the second element

d = relative intensity of the heavier isotope of the second element

m = number of atoms of the second element in the molecule

$$(a+b)^2 = a^2 + 2ab + b^2$$

$$(a+b)^3 = a^3 + 3a^2b + 3ab^2 + b^3$$

$$(a+b)^4 = a^4 + 4a^3b + 6a^2b^2 + 4ab^3 + b^4$$

$2 \times Cl$

$a^2 + 2ab + b^2$

ISOTOPES {35, 37} — {3, 1} INTENSITY

$3^2 : 2 \cdot 3 \cdot 1 : 1^2$

$9 : 6 : 1$

2 x Br

ISOTOPES { 79, 81 }   { 1, 1 } INTENSITY

$a^2 + 2ab + b^2$

$1^2 : 2 \cdot 1 \cdot 1 : 1^2$

$1 : 2 : 1$

3 x Br

$a^3 + 3a^2b + 3ab^2 + b^3$

79, 81 } ISOTOPES   1, 1 } INTENSITY

$1^3 : 3 \cdot 1^2 \cdot 1 : 3 \cdot 1 \cdot 1^2 : 1^3$

$1 : 3 : 3 : 1$

3 × Cl

$$a^3 + 3a^2b + 3ab^2 + b^3$$

35, 37 } ISOTOPES

3, 1 } INTENSITY

$$3^3 : 3 \cdot 3^2 \cdot 1 : 3 \cdot 3 \cdot 1^2 : 1^3$$

$$27 : 27 : 9 : 1$$

ISOTOPES

Cl
35
37

Br
79
81

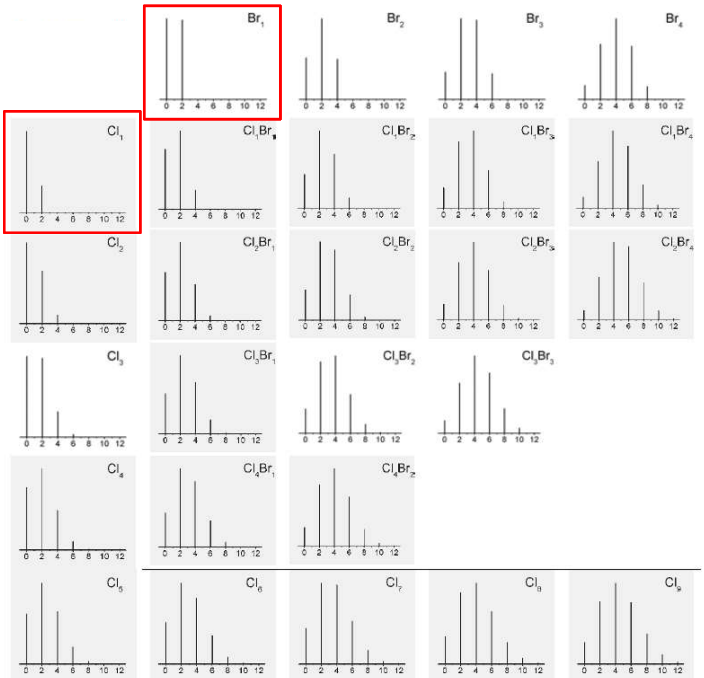
1 × Cl   1 × Br

$$(a+b)^n \times (c+d)^m$$

$$(\underset{M}{3} + \underset{M+2}{1})^1 \times (\underset{M}{1} + \underset{M+2}{1})^1$$

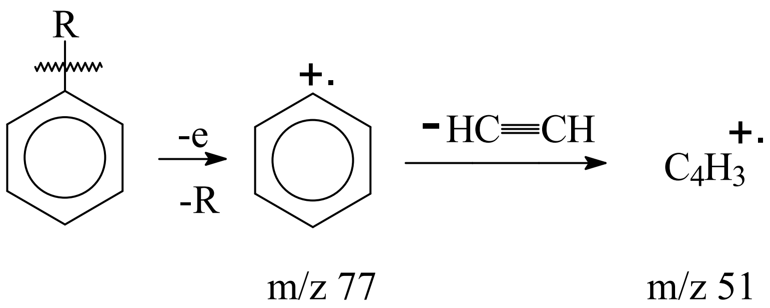
$3 \cdot 1$	$3 \cdot 1$	$1 \cdot 1$	$1 \cdot 1$
M	M+2	M+2	M+4

$$3 : 4 : 1$$

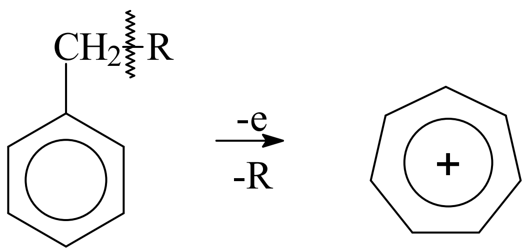


Fragmentation

characteristic fragments of compounds with a benzene ring

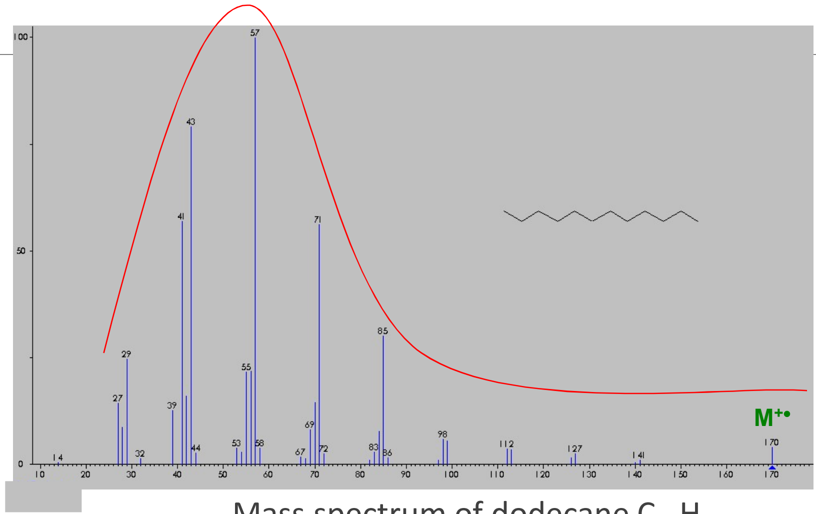


characteristic fragments of compounds with a benzene ring



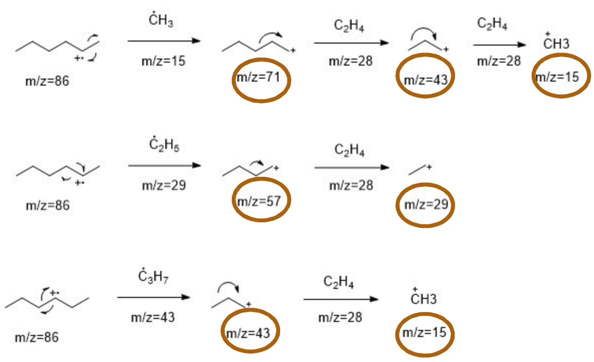
Tropylium ion
m/z=91

Hydrocarbons: characteristic fragments



Mass spectrum of dodecane $C_{12}H_{26}$

The possible mechanisms for EI ionization spectra of hexane



Hydrocarbons: characteristic fragments

low intensity $M^{+\bullet}$

Series 1: odd ions $C_nH_{2n+1}^+$

14n+1 CH_3^+ (15), $CH_3CH_2^+$ (29),…,$CH_3(CH_2)_9^+$ (141),…

the most intensive ions:

m/z 43 $CH_3CH_2CH_2^+$

m/z 57 $CH_3CH_2CH_2CH_2^+$

m/z 71 $CH_3CH_2CH_2CH_2CH_2^+$,

elimination of $H_2C{=}CH_2$ is favourised over $-CH_2$ elimination

Series 2: $C_nH_{2n}^+$ ions

14n RH elimination from $M^{+\bullet}$

Series 3: $C_nH_{2n-1}^+$ ions

14n-1 H_2 elimination from series 1

intensities: series 1>series 2 and series 3

Alcohols: characteristic fragments

ALIPHATIC AND CYCLIC ALIPHATIC ALCOHOLS

1) Low intensity $M^{+\bullet}$

2) **elimination of largest possible radical**, bound to α-C atom relative to OH group is favored (larger radicals are more stable)

$R{-}CH_2{-}O^{+\bullet}H \longrightarrow R^+ + CH_2{=}O^{\bullet}H$ **Base peak**

3) **water elimination** involves transfer of H from 3rd or 4th from C atom relative to OH group via six- or five-membered ring as an intermediate

AROMATIC ALCOHOLS

1) Higher $M^{+\bullet}$ intensity than for aliphatic alcohols

2) Elimination of -CO group from $(M\text{-}H)^+$ or M^+ ions

Nitrogen rule

Compounds without or with even numbers of N atoms (0, 2, 4,…)

have an even molar mass and

fragments with odd mass

Compounds with odd numbers of N atoms (1, 3, 5,…)

have an odd molar mass

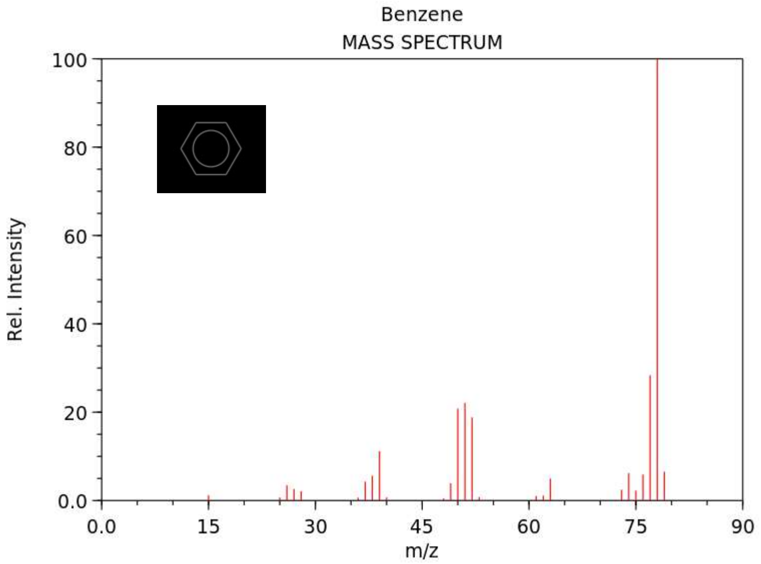
$M^{+\cdot}$ Stability

Depends on excess energy during ionisation

Charge localization:

- Heteroatoms N, O, S
- π bonds
- Quaternary C atoms

Mass spectra interpretation



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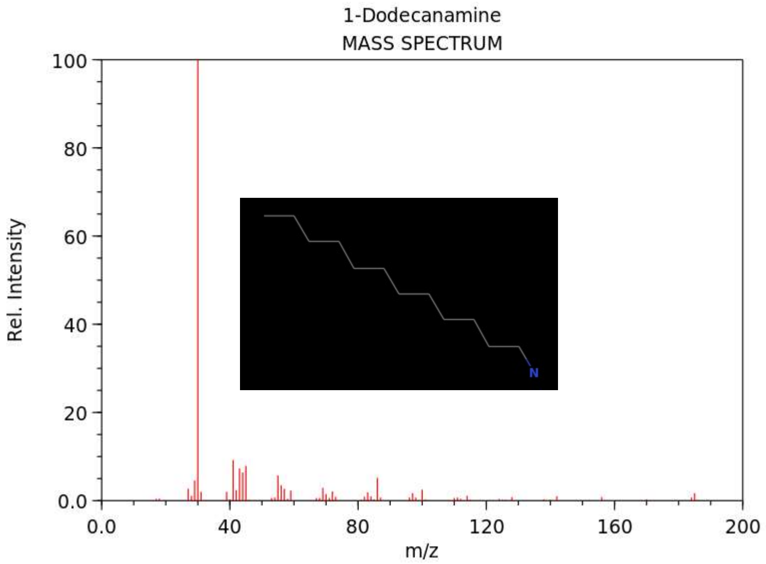
NIST Chemistry WebBook (https://webbook.nist.gov/chemistry)



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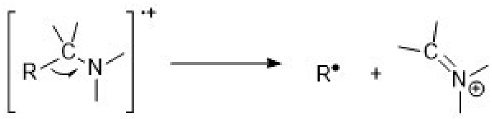
1-Dodecanamine

2

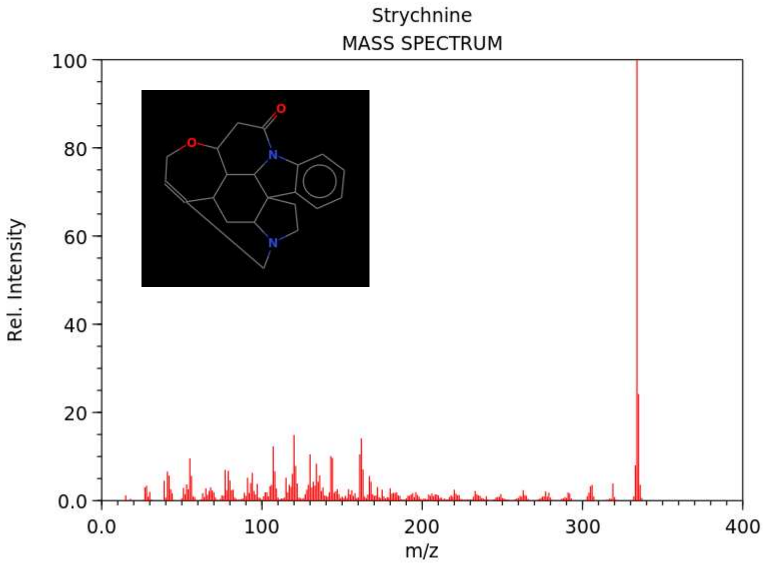


Alpha cleavage of amines

m/z=30

39

3



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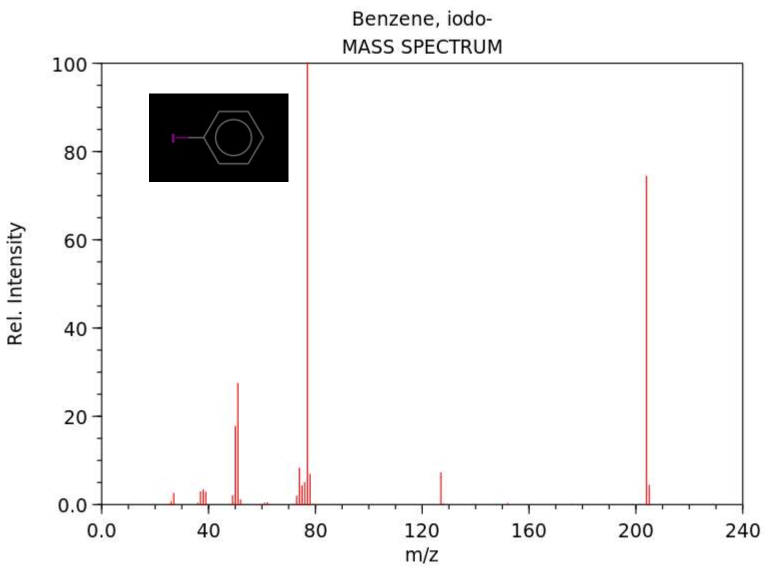

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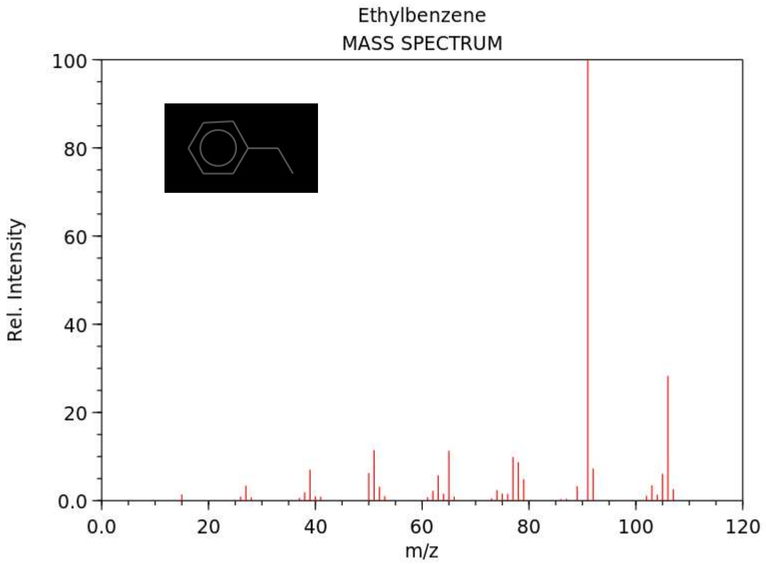

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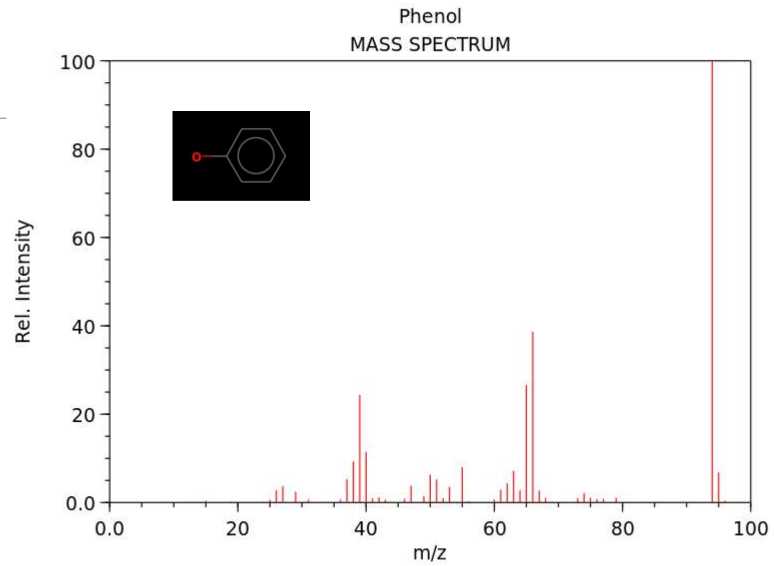

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Phenol

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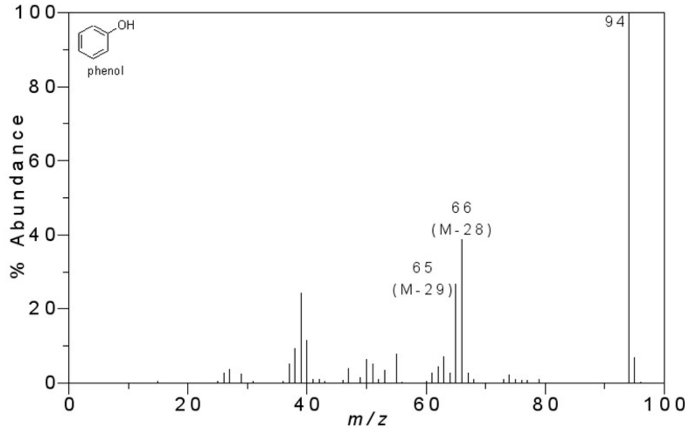
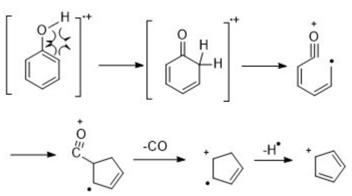
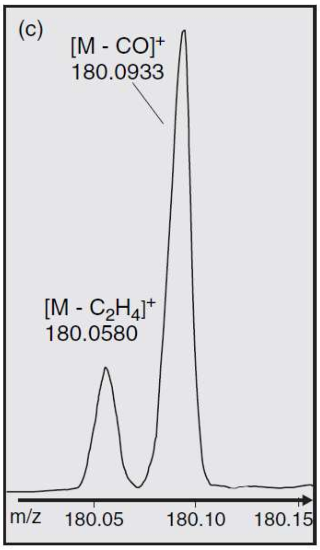




Strong molecular ion peak

Elimination of CO (M – 28)
and formyl radical HCO· (M – 29)

Similar ions



Mass spectrometer enables:

Identification of compounds

mass spectrum: typical fragments

library

Quantitative determination of compounds

TIC and SIM chromatograms

Mass spectra libraries

Different spectra collections (100 000 compounds) :

Wiley, NIST, Drug Library,…

spectra under agreed conditions

(e.g. electron ionisation with 70 eV energy electrons)

Quantitative analysis

All formed ions are measured (also background)

- Total Ion Chromatogram, TIC

Only selected ions (*m/z* values) are measured (avoiding interferences)

- Selected Ion Monitoring, SIM

Signal to Noise ratio, S/N ratio

Investigated cases

Case 1: Emerging contaminants

Diverse group of predominantly anthropogenic pollutants

which are present in the environment

in the concentrations that can cause known or suspected adverse

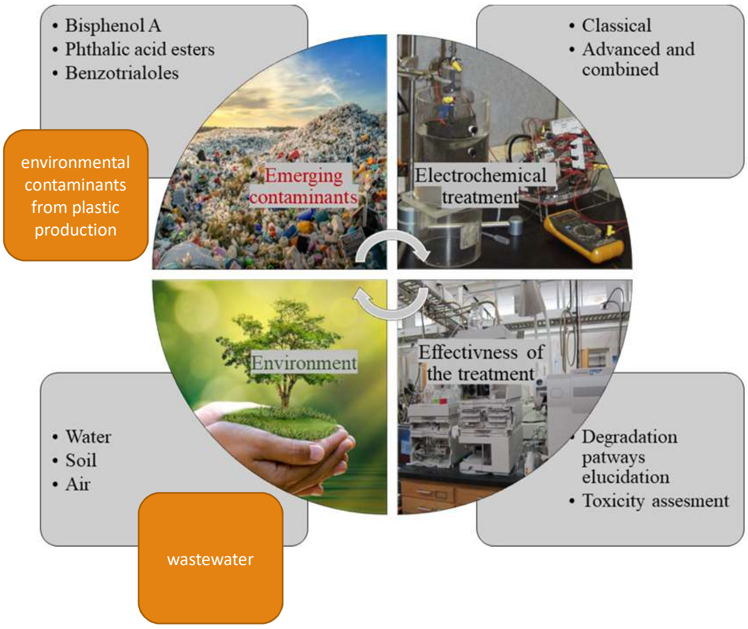
environmental and health effects.

Lack of legislative regulation and

monitoring programs or

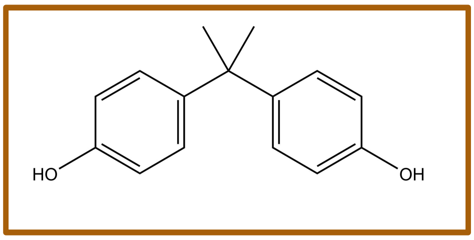
risk assessment studies.

Case 1: Emerging contaminants



Case 1: Emerging contaminants

Bisphenol A



Bisphenol A

starting chemical in the industry of plastic materials (polycarbonates, epoxy resins)

production 7.4 million tons by the end of 2023

additive in powder paints and thermal paper (present in recycled paper)

emerging environmental contaminant (previously food contaminant)

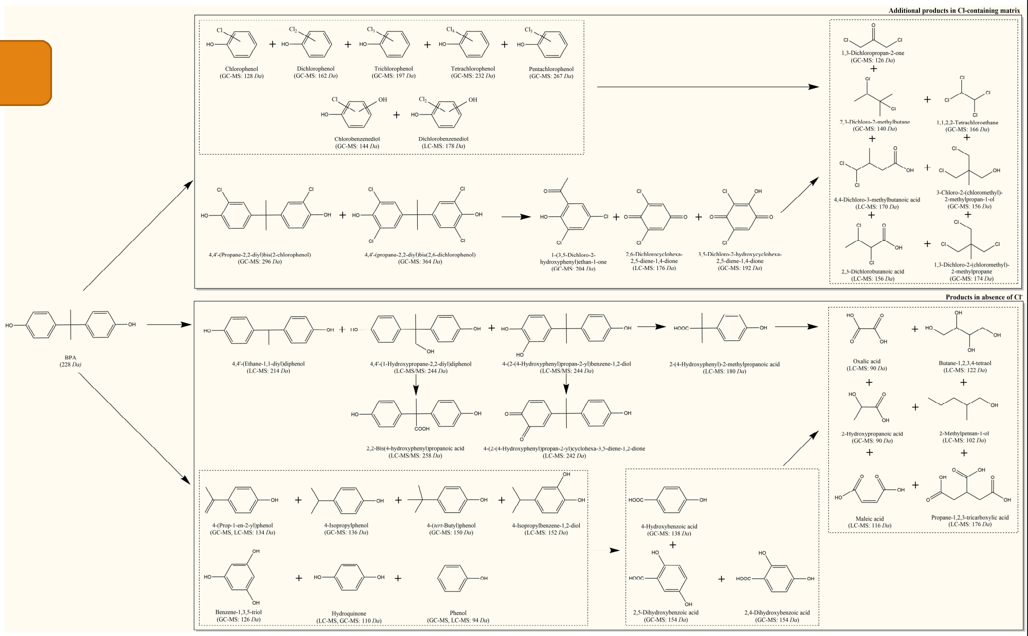
Case 1: Emerging contaminants

Bisphenol A

Replacement for Bisphenol A

https://youtu.be/OEzNjSOwF04

Bisphenol A



Case 1: Emerging contaminants

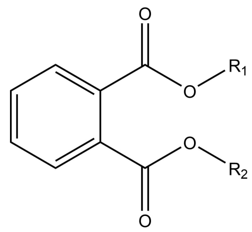
Phtalic acid esters

R1 and R2…….alkyl substituents

5.4 million tons in 2014

Di-(2-ethylhexyl) phthalate (DEHP) ≈50%

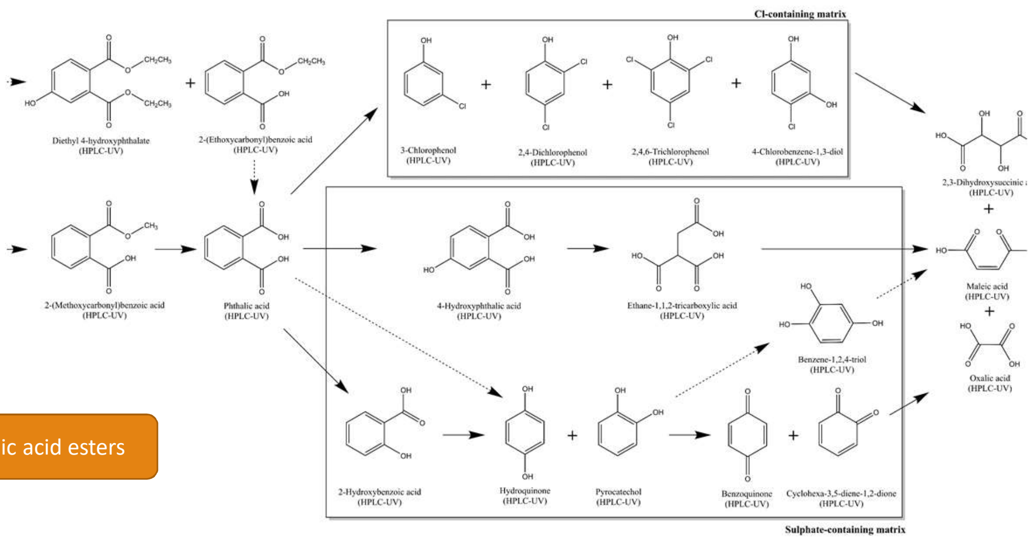
diisononyl phthalate (DINP) ≈25%



Phthalic acid esters

plasticizers for polyvinylchloride (PVC), polyvinylacetate, polyurethane

in personal care products, coatings (pharmaceuticals), dyes , insecticides

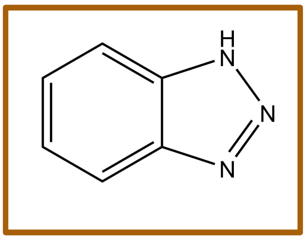


Phtalic acid esters

Case 1: Emerging contaminants

Benzotriazoles

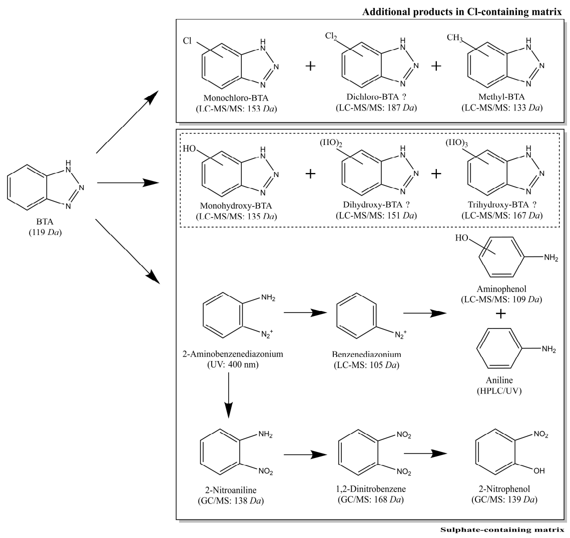
Benzotriazoles



Polar as anticorosive agent (aluminium, copper, iron), household dishwasher detergents, de-icing liquids for aircrafts, cooling systems

Non-polar as UV stabilizers in plastics, cosmetics, textiles, dyes,…

Benzotriazoles



Case 1: Emerging contaminants

environmental contaminants from plastic production

wastewater

- Transformation products
- Due to electrochemical treatment
- Due to UV light
- Due to reactions with other compounds (coexisting chemical species)
  - e. g. halogenated transformation products

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Case 1: Emerging contaminants

environmental contaminants from plastic production

wastewater

Removal of contaminants from environment

- Adsorbtion to different solids (activated carbon, glay minerals,…)
- Membrane processes (i.e. micro-, nano-, or ultra-filtration, reverse and forward osmosis)
- Biological treatment (aerobic and anaerobic microorganisms, enzyme-mediated)
- Advanced oxidation processes
- Photolysis and photocatalysis by UV or visible light in combination with H2O2, O3
- Sonochemically by ultrasound
- Electrochemical treatment

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Case 1: Emerging contaminants

environmental contaminants from plastic production

wastewater

Electrochemical treatments

Electrodeposition

Electrochemical reduction

Electrocoagulation

Electroflotation

Electrodialysis

Electrofiltration

Advanced and combined (electrocoagulation-ozone, electrocoagulation-Fenton, electro-membrane bioreactor)

Case 1: Emerging contaminants

Aspect	Improvement
Effectiveness of electrochemical treatments	
Incomplete mineralisation (coexisting chemical species in samples)	Prolongation of treatment time (high energy requirements). Combination of electrochemical methods with biological and other treatments methods (synergistic effect).
Monitoring of pollutants and transformation products for degradation pathways elucidation	
Monitoring of mineralisation based on total organic carbon (TOC) and chemical oxygen demand (COD).	Non-target analysis of species using LC or GC coupled to high resolution mass spectrometer.
Monitoring of target species with HPLC coupled to UV, diode array detector or low resolution mass spectrometer.	
Toxicity of pollutants	
Transformation products can increase overall toxicity. Toxicity assessment based on various bioassays.	Battery of biotests with organisms from different trophic levels for the evaluation of treatment efficiency. Ecotoxicological assessment. Comprehensive biodegradability study based on non-target chemical analysis of transformation and degradation products.
Electrochemical treatment conditions	
Model system with different electrolytes (NO_3^-, SO_4^{2-}, Cl^-, ClO_4^-, CO_3^{2-}).	Real systems (wastewater or wastewater treatment plant) representing very complex matrix.
Laboratory scale.	Large scale.

Case 2:

Total Petroleum Hydrocarbons (TPH)

Common contaminants in the environment

Mixture of hydrocarbons found in crude oil and petroleum products:

Aliphatic
- gasoline range organics ($>C_6–C_{10}$),
- diesel range organics ($>C_{11}–C_{28}$),
- and oil range organics ($C_{29}–C_{35}$).

Aromatic
- hexane, benzene, toluene, xylenes, and polycyclic aromatic hydrocarbons

  (carbon ranges between $\geq C_5$ and $\leq C_{35}$).

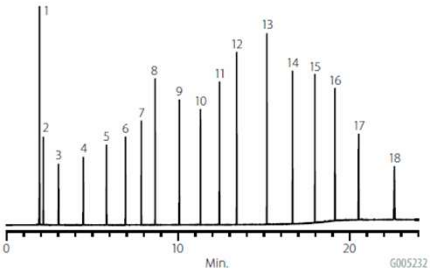
Several houndred compounds

Case 2:

Total Petroleum Hydrocarbons (TPH)

column: SLB-5ms, 30 m x 0.25 mm I.D., 0.25 µm (28471-U)
oven: 45 °C (3 min.), 20 °C/min. to 360 °C (10 min.)
inj.: 275 °C
det.: FID, 365 °C
carrier gas: helium, 1.3 mL/min. constant
injection: 1.0 µL, 100:1 split
liner: 2 mm I.D. straight
sample: 17 analytes, each at 1000 µg/mL in carbon disulfide

1. Carbon disulfide (solvent)
2. Hexane
3. Heptane
4. Octane
5. Nonane
6. Decane
7. Undecane
8. Dodecane
9. Tetradecane
10. Hexadecane
11. Octadecane
12. Eicosane
13. Tetracosane
14. Octacosane
15. Dotriacontane
16. Hexatriacontane
17. Tetracontane
18. Tetratetracontane

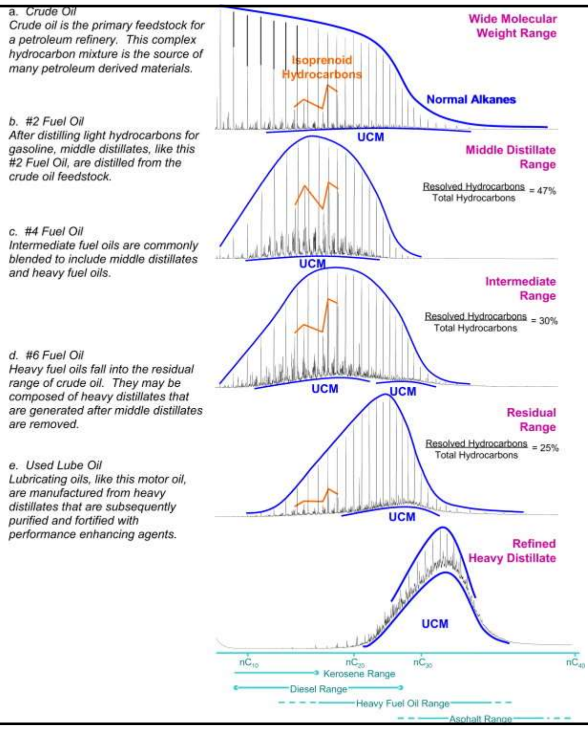


17=$C_{40}H_{82}$
18=$C_{44}H_{90}$

CG-FID or GC-MS

Case 2:

Total Petroleum Hydrocarbons (TPH)



Case 2:

Total Petroleum Hydrocarbons (TPH)

“fingerprinting” analysis as Petroleum Hydrocarbon Identification (PHI)

Identification of individual TPH or the group of TPH

Appropriate sample extraction procedure

Long chromatographic-run time