Persistent organic pollutants - sample analysis

Jana Klánová

klanova@recetox.muni.cz

1. Environmental analytical chemistry

Specific features, general scheme

2. Sampling

Sampling plan, strategy, sampling protocol, sample size and quality, transport, storage

3. Sample preparation

Extraction of solid (Soxhlet, automatic extraction, MAE, ASE, SFE) and liquid (L-L, SPE, SPME, head-space) samples, fractionation and clean-up (column chromatography, gel permeation)

4. Analytical techniques

Chromatographic techniques, principals, instrumentation, HPLC, GC, GC-MS

5. Persistent organic pollutants

Priority pollutants (PCBs, PCDDs/Fs, PAHs, pesticides), emerging pollutants (SCCPs/MCCPs, antibiotics, degradation products)

6. QA/QC

Calibration, limit of detection and quantification, internal and recovery standards, blanks, certified reference materials, interlaboratory calibration tests, method validation and verification, GLP

Environmental science brings together scientists from many fields to perform complex studies of various environmental compartments, processes, and interactions.

They may include:

- **water and food quality monitoring**
- **level of contamination of environmental compartments**
- **ozone depletition as a result of the presence of certain chemicals in the atmosphere**
- **regional contamination studies**
- **evaluation of the impact of local sources of pollution**
- **toxicity of chemical compounds as a function of their chemical structure**
- **impact of chemical substances on living organisms**
- **bioavailability**
- **bioaccumulation**
- **biotic and abiotic transformations**
- **transport of pollutants in the environment**
- **global fate of pollutants**
- **international directives and their impact on the global contamination**
- **remediation actions and their quality control**
- **sustainable development**

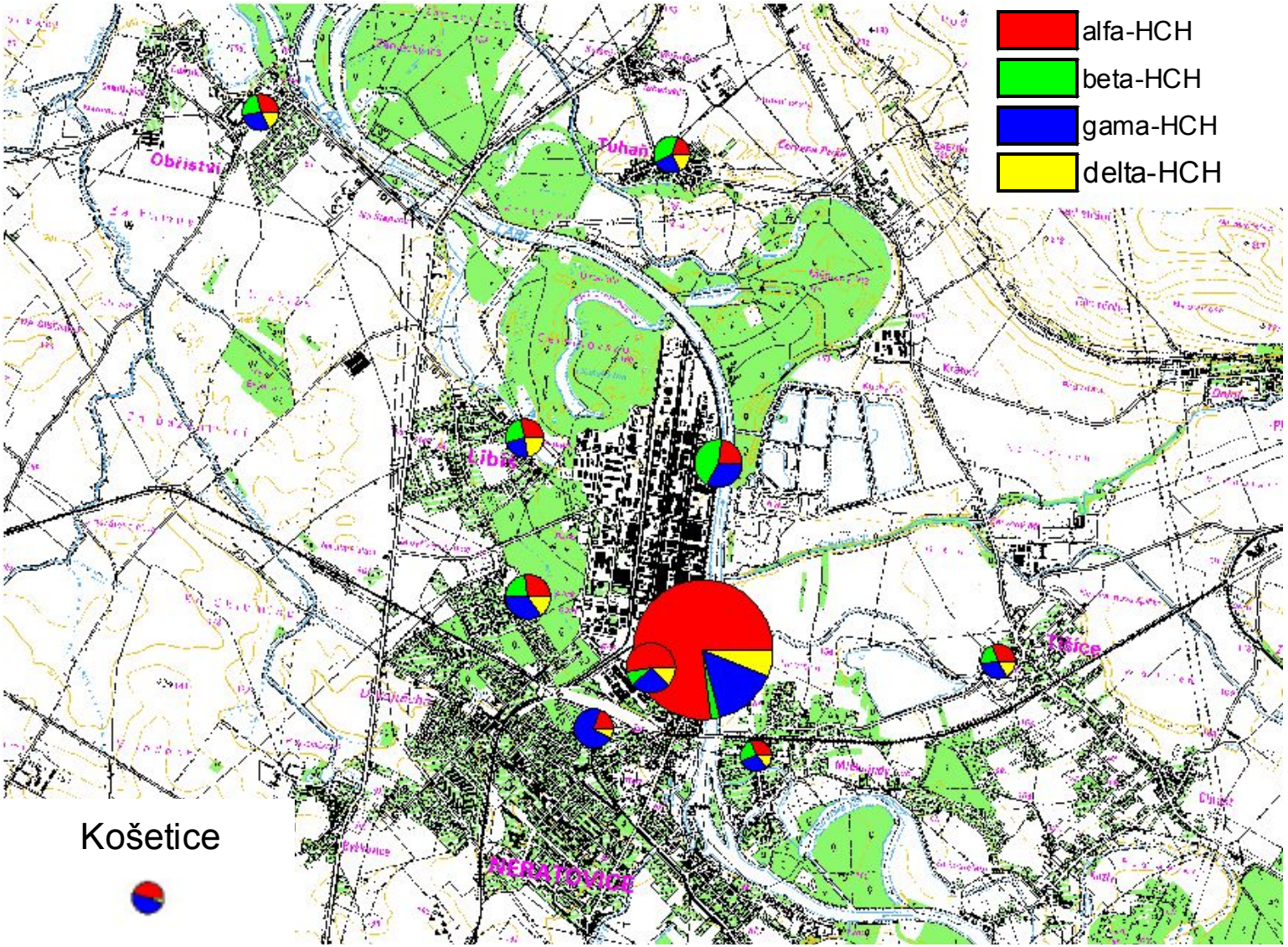
Most of them involve the chemical analysis as one of necessary steps.

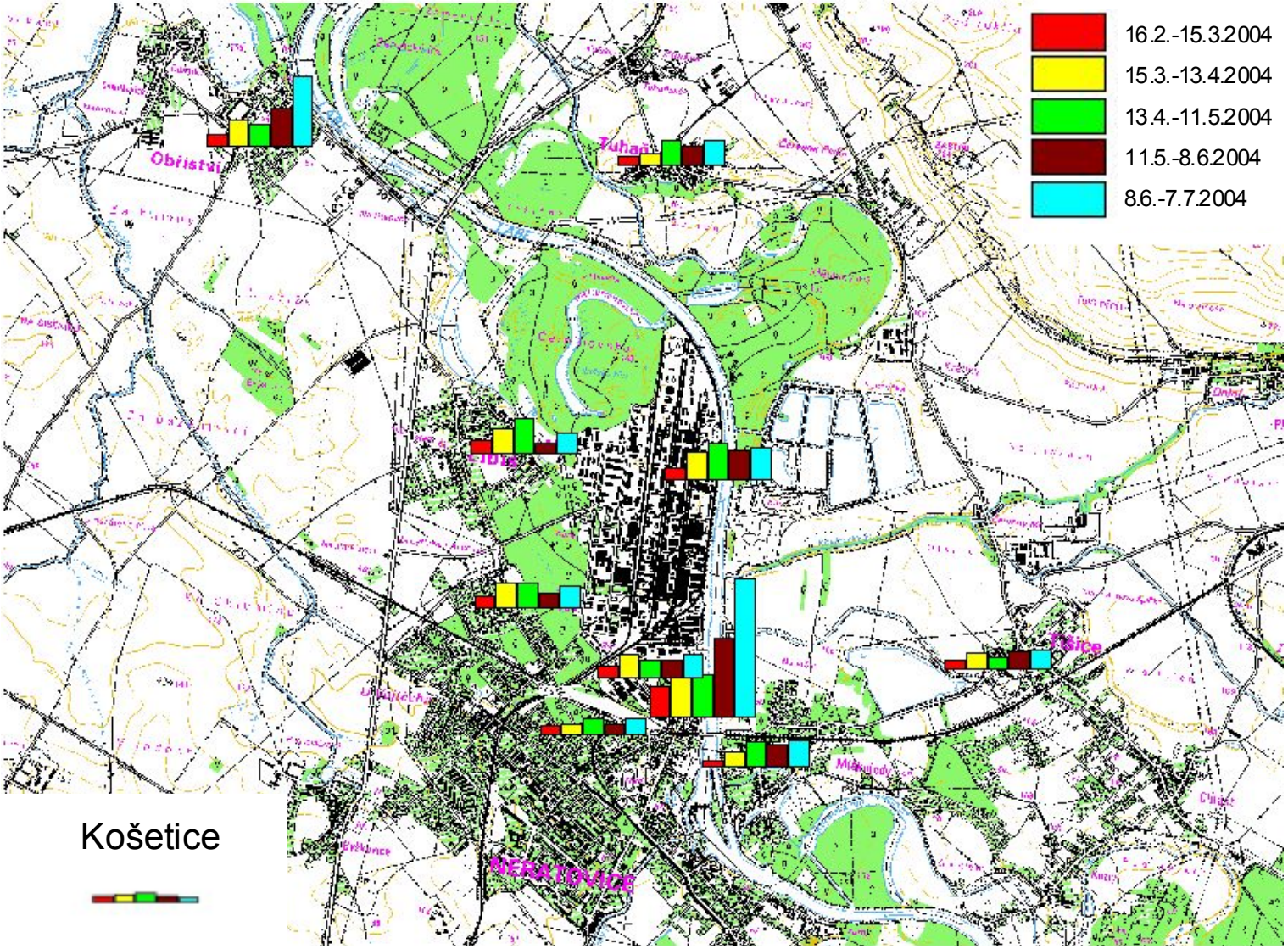
Environmental analytical chemistry chalenges:

- international conventions focus attention on the new groups of pollutants
- old contamination brings the problem of residue analyses
- lowering limits as well as environmental levels require low detection limits
- large-scale monitoring is crutial for the studies of the long-range transport
- development of new sampling techniques is encouraged
- increasing number of samples stresses the need for automatization
- fate studies require understanding of distribution processes and equilibria
- photochemical reaction complicate the sampling and data interpretation
- consideration of both, analytical and toxicological data is important for successful risk assessment
- methods of biochemistry and molecular-biology are often implemented in toxicological studies
- international studies require standardization of all procedures

There are several steps necessary for environmental contamination control:

- problem definition
- screening of the situation, data interpretation
- evaluation of the extent of the problem
- selection of the best procedure to monitor the situation
- evaluation of the present state and future development
- exposure evaluation and risk assessment
- suggestion of correcting measures or remediation activities
- new directives to control the situation
- monitoring designed to evaluate effectiveness of measures


alfa-HCH
beta-HCH
gama-HCH
delta-HCH
Obříství
Tuhaň
Libiš
Tišice
NERATOVICE
Košetice


16.2.-15.3.2004
15.3.-13.4.2004
13.4.-11.5.2004
11.5.-8.6.2004
8.6.-7.7.2004
Obříství
Zuhaj
Libiš
Tišice
Mělnický
NERATOVICE
Košetice

Specific problems of environmental analysis

- low homogenity of samples (soil)
- low stability of samples (biota)
- various matrices (methods for extraction of analytes from matrices)
- wide range of analytes (method development)
- wide range of concentration (robust methods)
- monitoring on the levels close to the detection limits (high deviations)
- risk of secondary contamination
- price of ultra-trace analysis (instrumentation, chemicals, standards)

General scheme of environmental analysis

Sampling
- **homogenization**
- **conservation**
- **transport**
- **storage**

- **Sample preparation**
  - **extraction**
  - **clean-up**
  - **selective elution**
  - **concentration**
  - **derivatization**

- **Sample analysis**
- **Data interpretation**

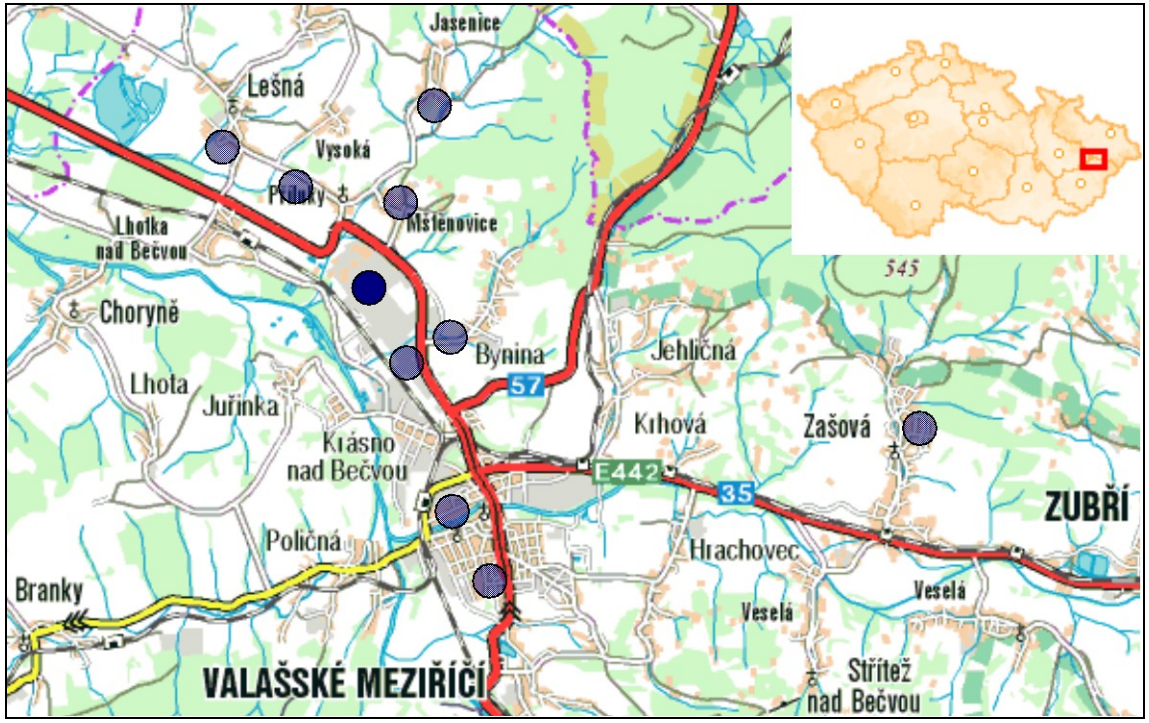
Sampling – documentation required

sampling plan (a goal, selection of sampling sites, analytes, sampling method, number of samples, sampling period and frequency, safety procedures), seeks the balance between the value of data and its price

- **standard operational procedure** for sampling various matrices (sampling devices, steps involved in collecting of representative sample -homogenous, of reasonable size and stability, quality of transport and storage)

-**sampling protocols** (name and number of the sample, sampling site, matrix, date of sampling, local conditions and measurements, methods, sample size, responsible person)

Sampling site 1. DEZA

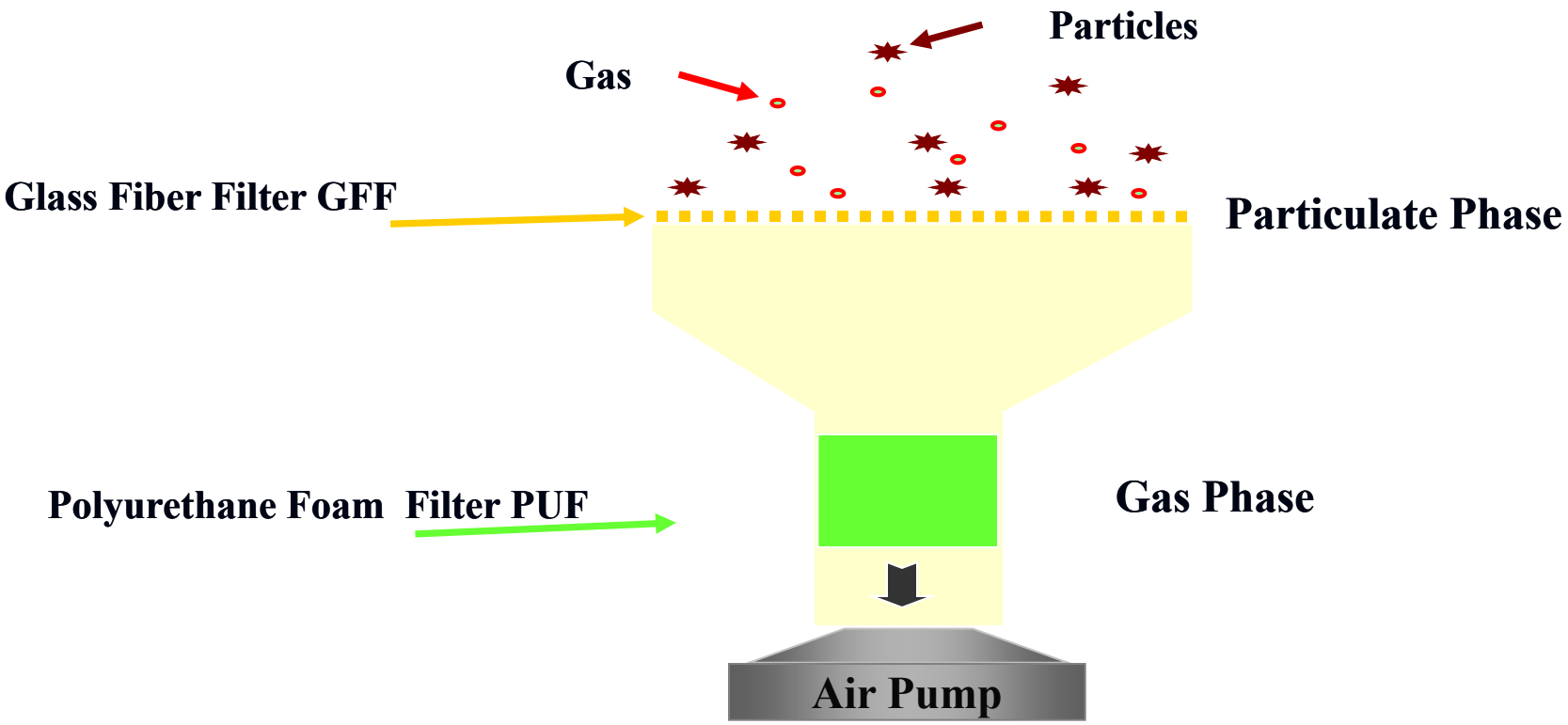


GPS:

49 29’48”
17 57’14”
245 m

Local conditions:

Sampling Techniques



High-Volume sampler

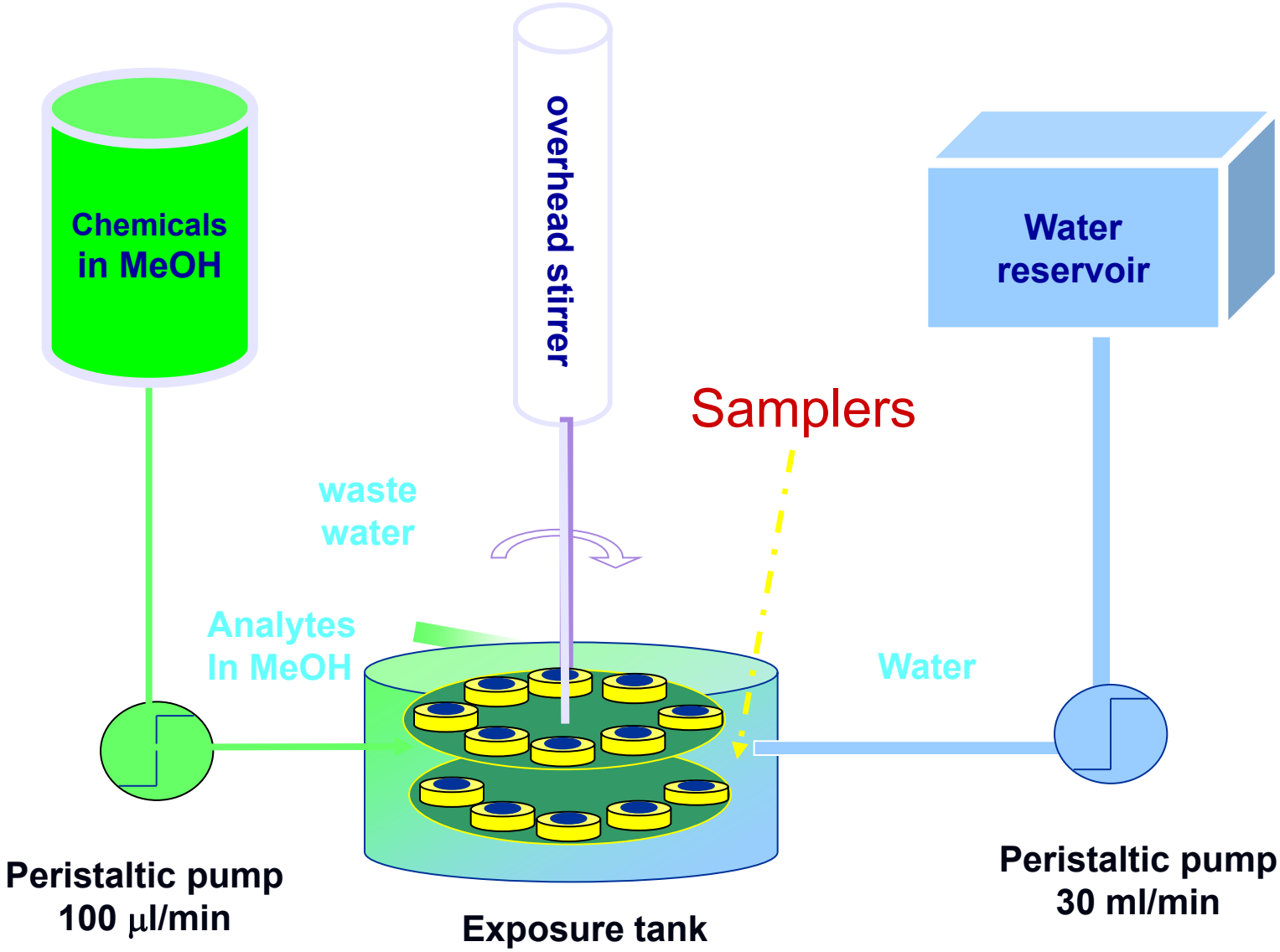
Passive sampling

Can environmental concentrations of pollutants be calculated from the analyte levels accumulated in an integrative passive sampler?

- Calibration conditions should approximate field conditions

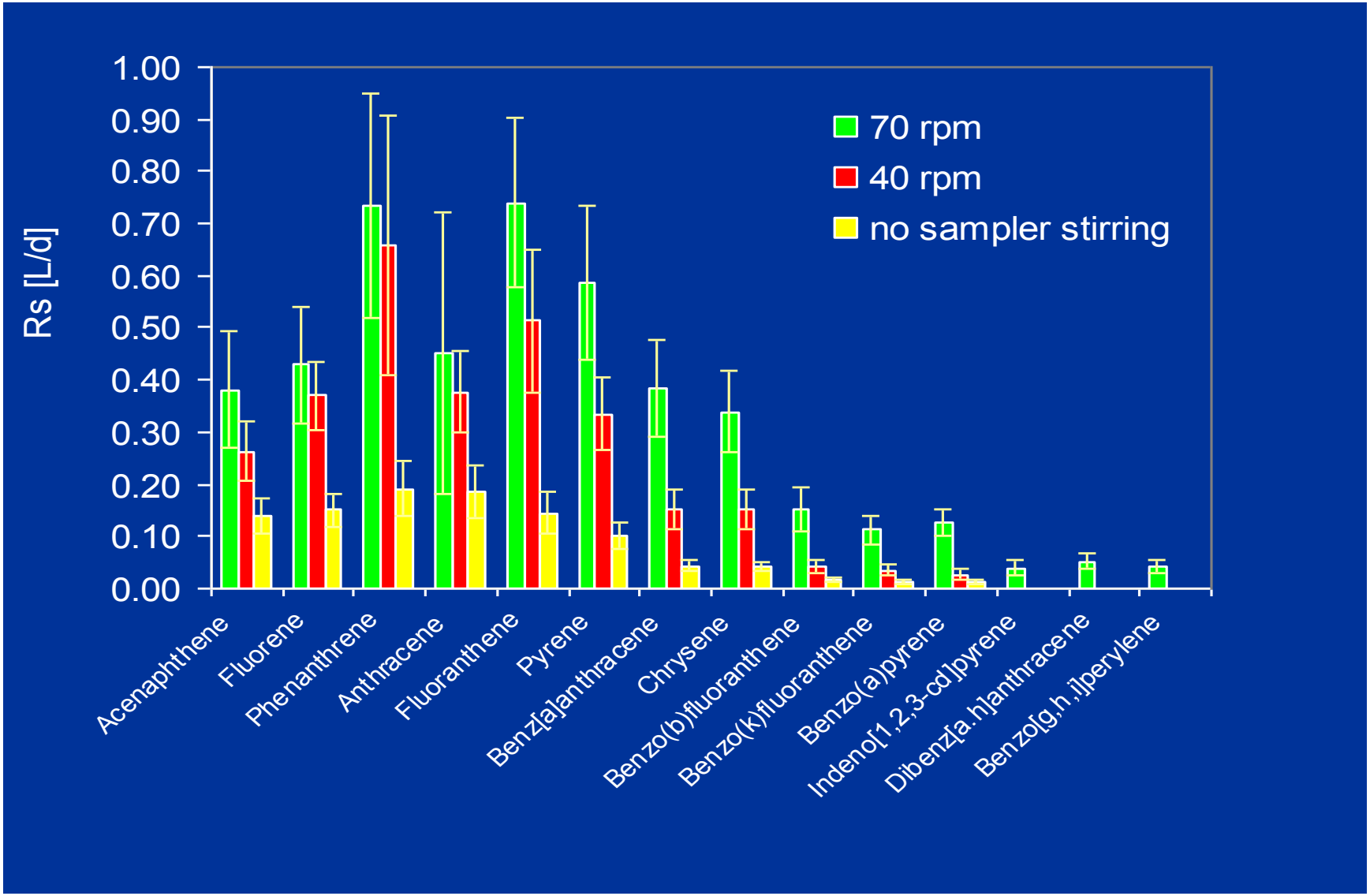
- Performance Reference Compounds

Calibration of a passive sampler in a flow-through system



B. Vrana, R. Greenwood, G. Mills

Sampling rates of PAHs



B. Vrana, R. Greenwood, G. Mills

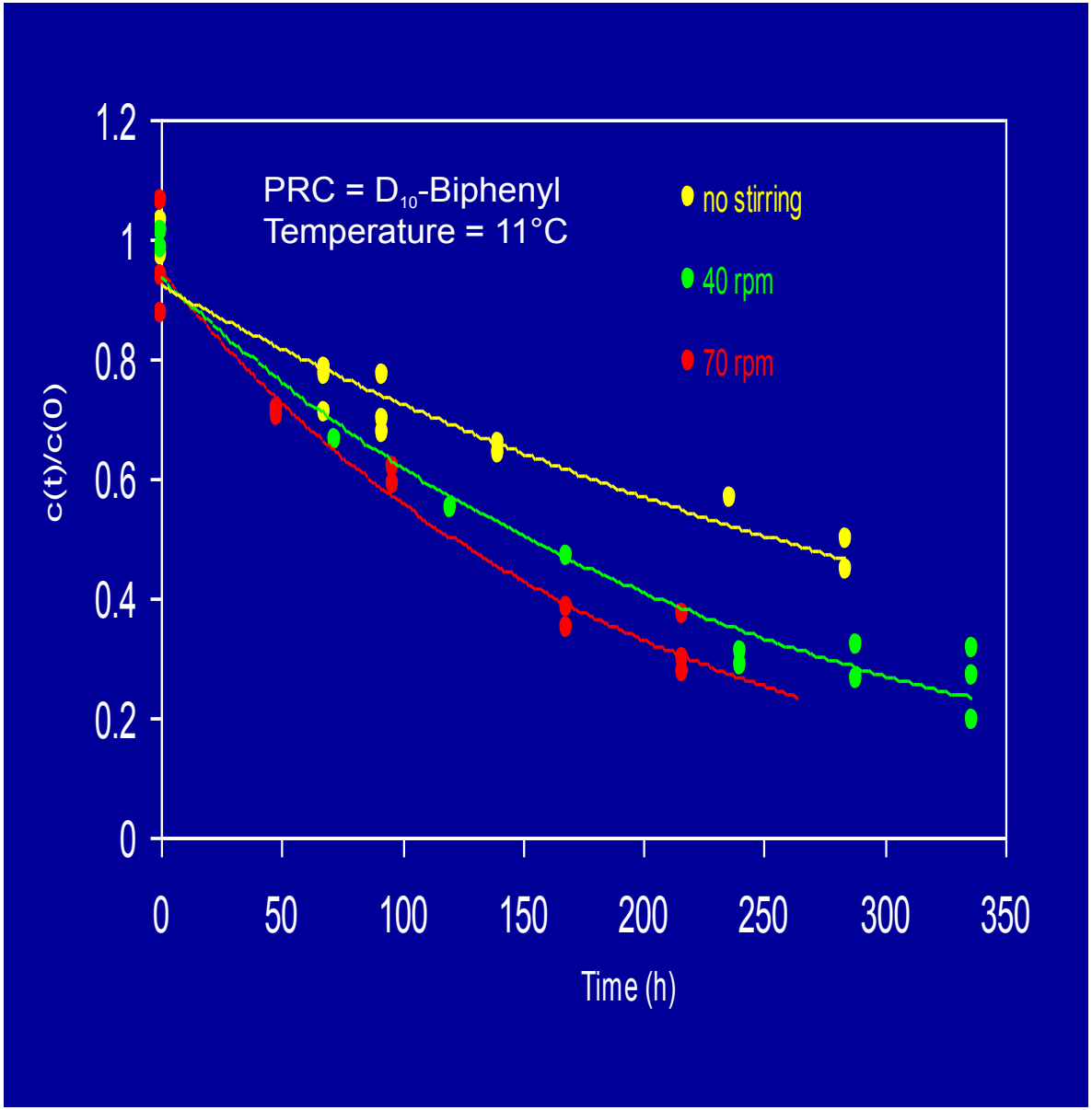
Performance reference compounds

PRCs are non-interfering compounds added to the sampler prior to exposure.

They are used for in situ calibration approach, where the rate
of PRC loss during an exposure is related to the target compound uptake.

This is accomplished by measuring PRC loss rates during calibration studies and field exposures.

Use of performance reference compounds



B. Vrana, R. Greenwood, G. Mills

Preparation of the sample before extraction

Soil samples
- lyofilization or air-drying
- sieving (< 2mm) and homogenization
- appropriate storage (protected from sunlight, heat and humidity)

Sediment samples
- stone and water removal, lyofilization or air-drying
- grating and sieving (<63um), homogenization
- powder copper treatment for sulphur removal

Plant samples
- lyofilization or air-drying
- grating, homogenization

Animal samples
- lyofilization or
- homogenization of a wet sample with sodium sulphate

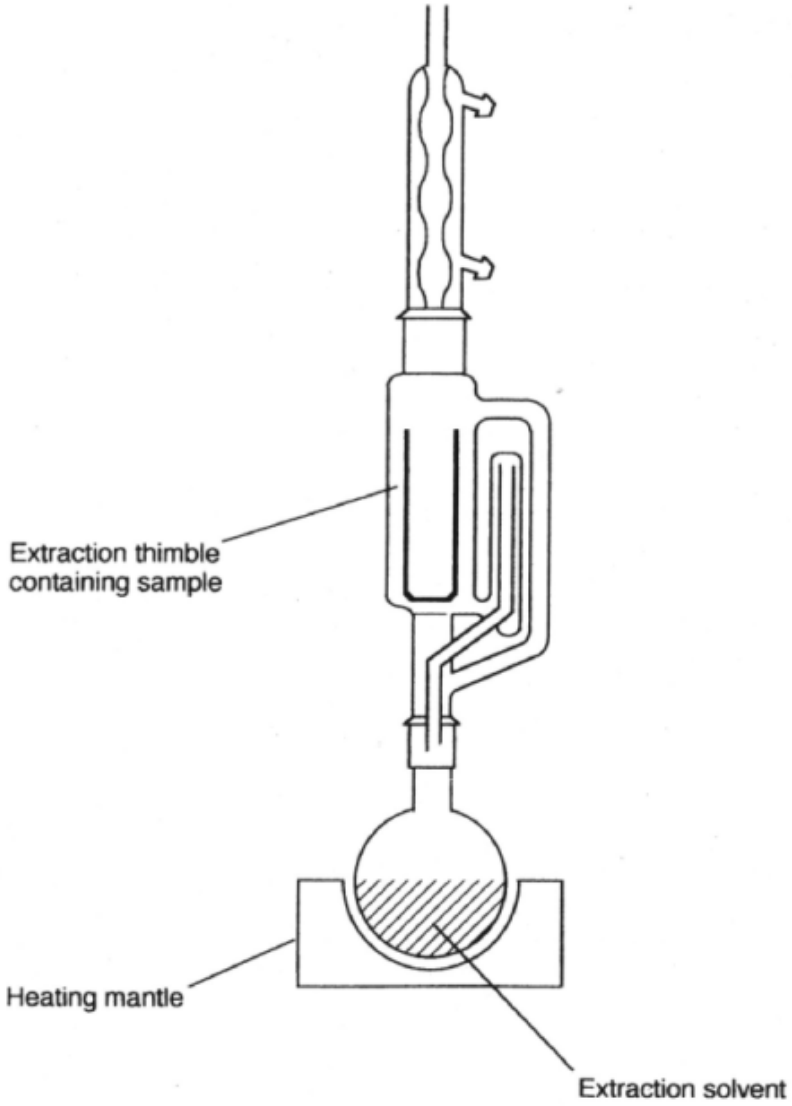
Extraction and clean-up

The goal: transfer of analytes to the chemical phase suitable for analysis, removal of interferences and pre-concentration of the sample.

Extraction techniques:
- solvent extraction (Soxhlet, automatic Soxtec, MAE, ASE, SFE)
- liquid-liquid extraction
- solid phase extraction and microextraction (SPE, SPME)
- semipermeable membrane separation
- head space analysis

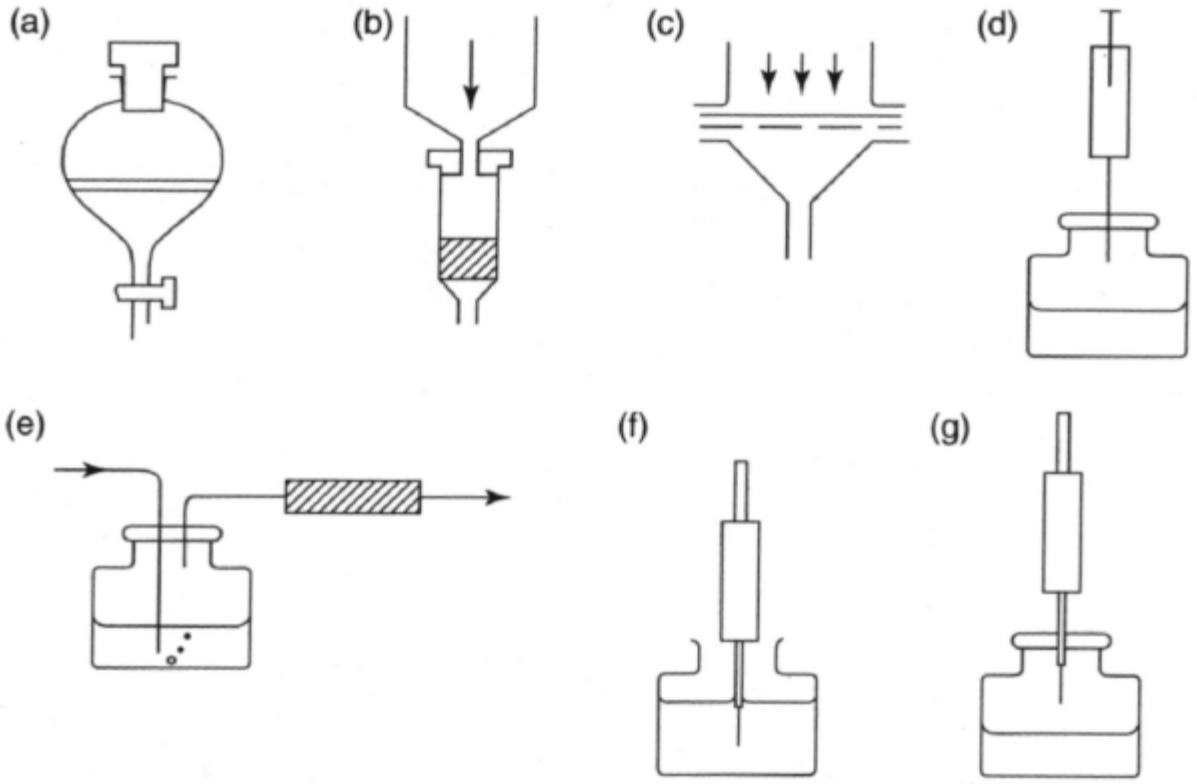
Clean-up techniques
- sulphuric acid treatment
- column liquid chromatography (silica gel, alumina, florisil)
- gel permeation chromatography

Solid sample extraction



Schematic of a Soxhlet extraction system.

Liquid sample extraction



Summary of extraction methods: (a) solvent extraction; (b) solid-phase extraction – cartridge; (c) solid-phase extraction – disc; (d) head-space analysis; (e) purge and trap; (f) solid-phase microextraction – direct; (g) solid-phase microextraction – head-space.

Air samples

- filters from high volume samplers or passive samplers are extracted as solid samples (Soxhlet, MAE, ASE, SFE)

Water samples

direct analysis of the samples with high concentration of pollutants

- head space, SPE, L-L

Soil and sediment samples

Soxhlet, MAE, ASE, SFE

- powder copper treatment for the sulphur removal in sediment samples

Biotic samples

- high molecular compounds removal by gel permeation chromatography and column chromatography

Presence	Availability	Activity
Total mass	Fraction of total mass	Measure that drives diffusion and partitioning
How much is there?	How much is available for ... ?	How high is the diffusive pressure into other media?
Exhaustive Extraction	Depletive Extraction/ Sampling	Equilibrium Sampling Devices

P. Mayer, F. Reichenberg

Supercritical Fluid Extraction (SFE)

High pressure CO_2 (100 to 400 bar, 40 to 150 °C) is pumped through a sample, and extracted analytes are collected in a suitable solvent for GC analysis.

Why to use supercritical carbon dioxide?

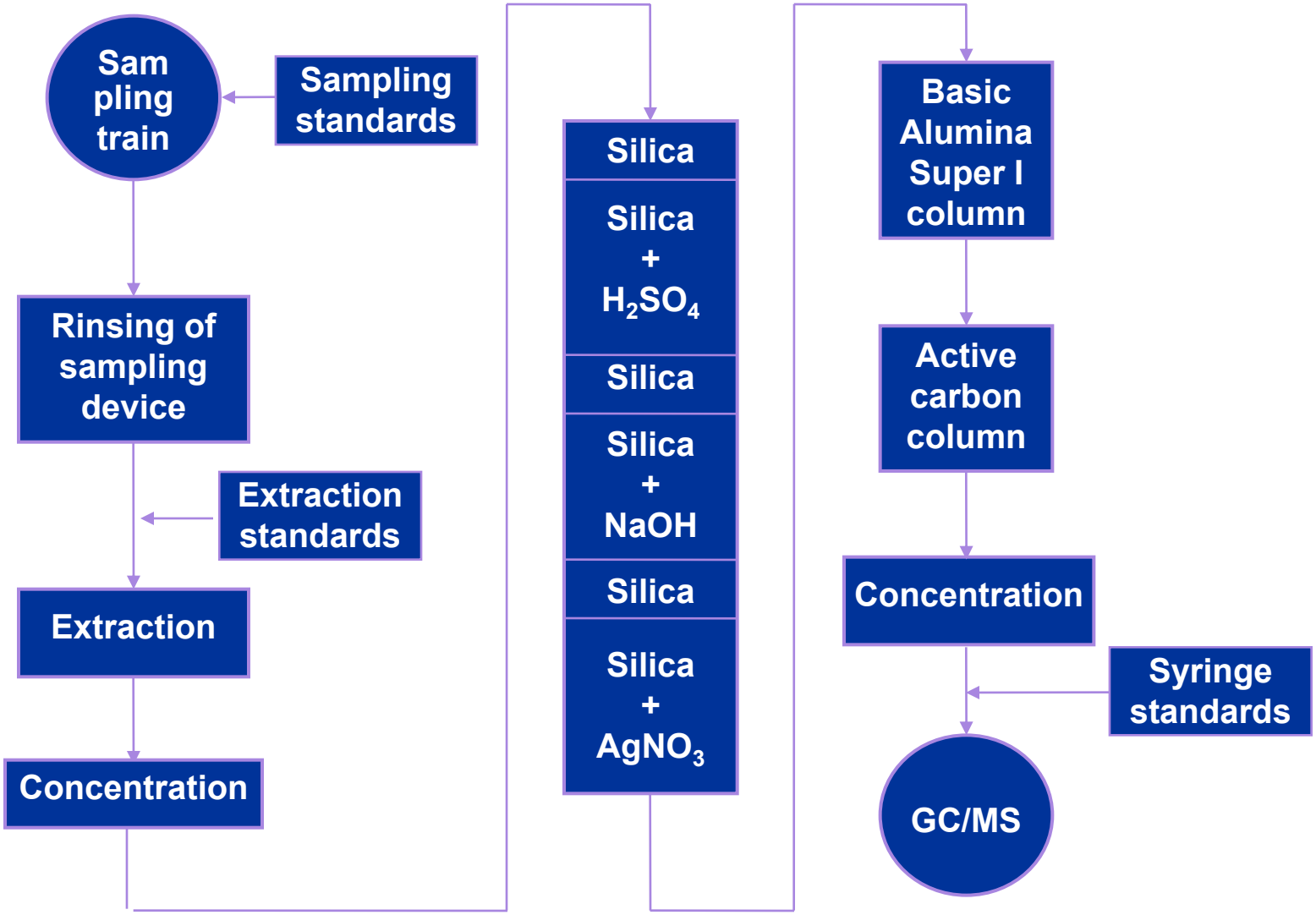
- CO_2 is a lipophilic solvent much like biological lipids in polarity
- PAH solubilities in CO_2 are proportional to those in water, but ca. 10^4 higher
- pressure and temperature gradients enable the extraction of both, non-polar and polar compounds
- mild SFE can be used to predict bioavailability of compounds

Earthworm Mortality Depends on Available PAHs (measured by SFE), not on Total PAH Concentrations

Soil Mortality	Total PAH (ug/g soil)	Available Fraction (SFE)	Available Total PAH (ug/g C)	Mortality %
CG15	1020	0.25	1040	0
OG14	168	0.46	2720	0
CG11	15600	0.06	3280	0
CG12	3790	0.16	7880	0
OG17	17200	0.27	9720	0
OG5	1870	0.41	11100	0
OG10	42100	0.33	16300	0
CG3	4100	0.83	45700	100
OG18	17300	0.74	50100	100

S. B. Hawthorne, C. B. Grabanski, D. J. Miller

Flow chart of a clean-up procedure for stack emission samples

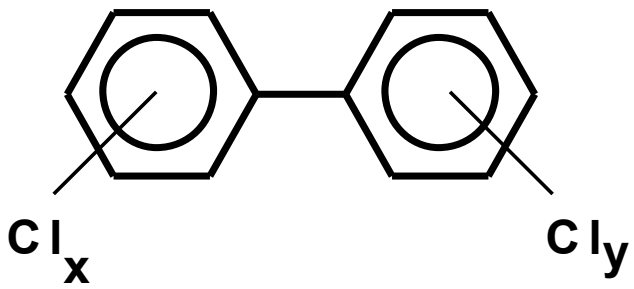


A. Kočan, Slovak Medical University

Priority pollutants

- polychlorinated biphenyls
- polychlorinated dibenzo-*p*-dioxins and furans
- organochlorinated pesticides and their metabolites
- polyaromatic hydrocarbons
    - aromatics and nitro-aromatics
- chlorinated benzenes
- fenol and chlorinated fenols
- halogenated alkans

Polychlorinated biphenyls



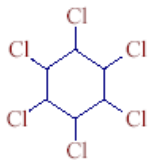
- sulphuric acid treatment
- silica gel column chromatography
- activated carbon for non-ortho PCBs
- GC-ECD, GC-MS, GC- HRMS

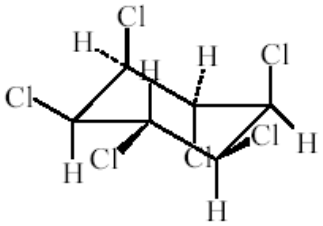
IUPAC numbering and substitution pattern of PCB congeners

No.	Structure	No.	Structure	No.	Structure	No.	Structure
	Monochlorobiphenyls		Tetrachlorobiphenyls		Pentachlorobiphenyls		Hexachlorobiphenyls
1	2	52	2,2′5,5′	105	2,3,3′4,4′	161	2,3,3′4,5′6
2	3	53	2,2′5,6′	106	2,3,3′4,5	162	2,3,3′4′5,5′
3	4	54	2,2′6,6′	107	2,3,3′4′5	163	2,3,3′4′5,6
	Dichlorobiphenyls	55	2,3,3′4	108	2,3,3′4,5′	164	2,3,3′4′5′6
		56	2,3,3′4′	109	2,3,3′4,6	165	2,3,3′5,5′6
4	2,2′	57	2,3,3′5	110	2,3,3′4′6	166	2,3,4,4′5,6
5	2,3	58	2,3,3′5′	111	2,3,3′5,5′	167	2,3′4,4′5,5′
6	2,3′	59	2,3,3′6	112	2,3,3′5,6	168	2,3′4,4′5′6
7	2,4	60	2,3,4,4′	113	2,3,3′5′6	169	3,3′4,4′5,5′
8	2,4′	61	2,3,4,5	114	2,3,4,4′5		Heptachlorobiphenyls
9	2,5	62	2,3,4,6	115	2,3,4,4′6		
10	2,6	63	2,3,4′5	116	2,3,4,5,6	170	2,2′3,3′4,4′5
11	3,3′	64	2,3,4′6	117	2,3,4′5,6	171	2,2′3,3′4,4′6
12	3,4	65	2,3,5,6	118	2,3′4,4′5	172	2,2′3,3′4,5,5′
13	3,4′	66	2,3′4,4′	119	2,3′4,4′6	173	2,2′3,3′4,5,6
14	3,5	67	2,3′4,5	120	2,3′4,5,5′	174	2,2′3,3′4,5,6′
15	4,4′	68	2,3′4,5′	121	2,3′4,5′6	175	2,2′3,3′4,5′6
	Trichlorobiphenyls	69	2,3′4,6	122	2′3,3′4,5	176	2,2′3,3′4,6,6′
		70	2,3′4′5	123	2′3,4,4′5	177	2,2′3,3′4′5,6
16	2,2′3	71	2,3′4′6	124	2′3,4,5,5′	178	2,2′3,3′5,5′6
17	2,2′4	72	2,3′5,5′	125	2′3,4,5,6′	179	2,2′3,3′5,6,6′
18	2,2′5	73	2,3′5′6	126	3,3′4,4′5	180	2,2′3,4,4′5,5′
19	2,2′6	74	2,4,4′5	127	3,3′4,5,5′	181	2,2′3,4,4′5,6
20	2,3,3′	75	2,4,4′6		Hexachlorobiphenyls	182	2,2′3,4,4′5,6′
21	2,3,4	76	2′3,4,5			183	2,2′3,4,4′5′6
22	2,3,4′	77	3,3′4,4′	128	2,2′3,3′4,4′	184	2,2′3,4,4′6,6′
23	2,3,5	78	3,3′4,5	129	2,2′3,3′4,5	185	2,2′3,4,5,5′6
24	2,3,6	79	3,3′4,5′	130	2,2′3,3′4,5′	186	2,2′3,4,5,6,6′
25	2,3′4	80	3,3′5,5′	131	2,2′3,3′4,6	187	2,2′3,4′5,5′6
26	2,3′5	81	3,4,4′5	132	2,2′3,3′4,6′	188	2,2′3,4′5,6,6′
27	2,3′6		Pentachlorobiphenyls	133	2,2′3,3′5,5′	189	2,3,3′4,4′5,5′
28	2,4,4′			134	2,2′3,3′5,6	190	2,3,3′4,4′5,6
29	2,4,5	82	2,2′3,3′4	135	2,2′3,3′5,6′	191	2,3,3′4,4′5′6
30	2,4,6	83	2,2′3,3′5	136	2,2′3,3′6,6′	192	2,3,3′4,5,5′6
31	2,4′5	84	2,2′3,3′6	137	2,2′3,4,4′5	193	2,3,3′4′5,5′6
32	2,4′6	85	2,2′3,4,4′	138	2,2′3,4,4′5′		Octachlorobiphenyls
33	2′3,4	86	2,2′3,4,5	139	2,2′3,4,4′6		
34	2′3,5	87	2,2′3,4,5′	140	2,2′3,4,4′6′	194	2,2′3,3′4,4′5,5′
35	3,3′4	88	2,2′3,4,6	141	2,2′3,4,5,5′	195	2,2′3,3′4,4′5,6
36	3,3′5	89	2,2′3,4,6′	142	2,2′3,4,5,6	196	2,2′3,3′4,4′5,6′
37	3,4,4′	90	2,2′3,4′5	143	2,2′3,4,5,6′	197	2,2′3,3′4,4′6,6′
38	3,4,5′	91	2,2′3,4′6	144	2,2′3,4,5′6	198	2,2′3,3′4,5,5′6
39	3,4′5	92	2,2′3,5,5′	145	2,2′3,4,6,6′	199	2,2′3,3′4,5,6,6′
	Tetrachlorobiphenyls	93	2,2′3,5,6	146	2,2′3,4′5,5′	200	2,2′3,3′4,5′6,6′
		94	2,2′3,5,6′	147	2,2′3,4′5,6	201	2,2′3,3′4,5,5′6′
40	2,2′3,3′	95	2,2′3,5′6	148	2,2′3,4′5,6′	202	2,2′3,3′5,5′6,6′
41	2,2′3,4	96	2,2′3,6,6′	149	2,2′3,4′5′6	203	2,2′3,4,4′5,5′6
42	2,2′3,4′	97	2,2′3′4,5	150	2,2′3,4′6,6′	204	2,2′3,4,4′5,6,6′
43	2,2′3,5	98	2,2′3′4,6	151	2,2′3,5,5′6	205	2,3,3′4,4′5,5′6
44	2,2′3,5′	99	2,2′4,4′5	152	2,2′3,5,6,6′		Nonachlorobiphenyls
45	2,2′3,6	100	2,2′4,4′6	153	2,2′4,4′5,5′		
46	2,2′3,6′	101	2,2′4,5,5′	154	2,2′4,4′5,6′	206	2,2′3,3′4,4′5,5′6
47	2,2′4,4′	102	2,2′4,5,6′	155	2,2′4,4′6,6′	207	2,2′3,3′4,4′5,6,6′
48	2,2′4,5	103	2,2′4,5′6	156	2,3,3′4,4′5	208	2,2′3,3′4,5,5′6,6′
49	2,2′4,5′	104	2,2′4,6,6′	157	2,3,3′4,4′5′		Decachlorobiphenyl
50	2,2′4,6			158	2,3,3′4,4′6		
51	2,2′4,6′			159	2,3,3′4,5,5′	209	2,2′3,3′4,4′5,5′6,6′
				160	2,3,3′4,5,6		

Organochlorinated pesticides

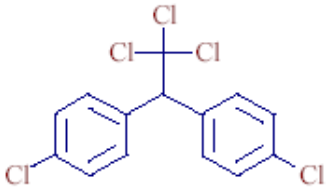
(DDT, HCH, hexachlorobenzene, toxaphene, aldrin, dieldrin, endrin, endosulfane, chlordane)



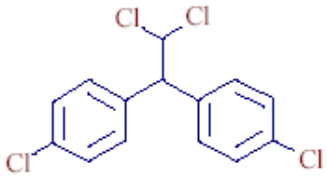


HCH

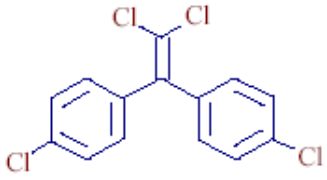
- for HCHs and DDTs analytical procedures similar to PCBs
- GC-ECD, GC-MS, NCI-MS, HRMS



p,p'-DDT



p,p'-DDD

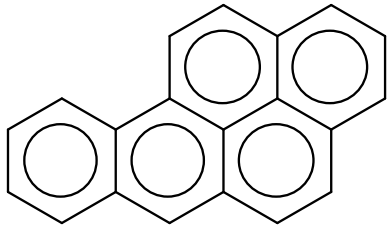


p,p'-DDE

- analytical procedures similar to PCBs for toxaphene,
- sulphuric acid has to be omitted for aldrin or endosulfane
- GC-MS, NCI-MS, HRMS

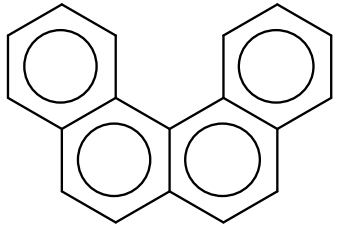
Polychlorinated dibenzodioxins and dibenzofurans

combined modified silica gel clean-up
- fractionation on alumina/florisil column
- non-ortho PCBs separation on activated carbon column
- HRGC-HRMS
- kapilary columns 50-60m (DB-5, DB-17, DB-DIOXIN)
- EI, NCI
- SIM
- MS-MS



Polyaromatic hydrocarbons

- silica gel column chromatography
- GC-MS, FLD-HPLC



Sample analysis

Chromatographic separation (GC, HPLC) is the most common technique for the analysis of environmental samples.
It is a physical method based on the distribution of compounds between two phases (stationary and mobile). Process of continuous sorption and desorption of compounds in contact with the stationary phase is responsible for different migration times and for separation of analytes.

Two dimensional (GC-GC) and two modal (HPLC-GC) chromatography provide even more sofisticated tools for environmental analysis

GC-MS, HPLC-MS and HRMS enable the trace and ultra-trace analysis

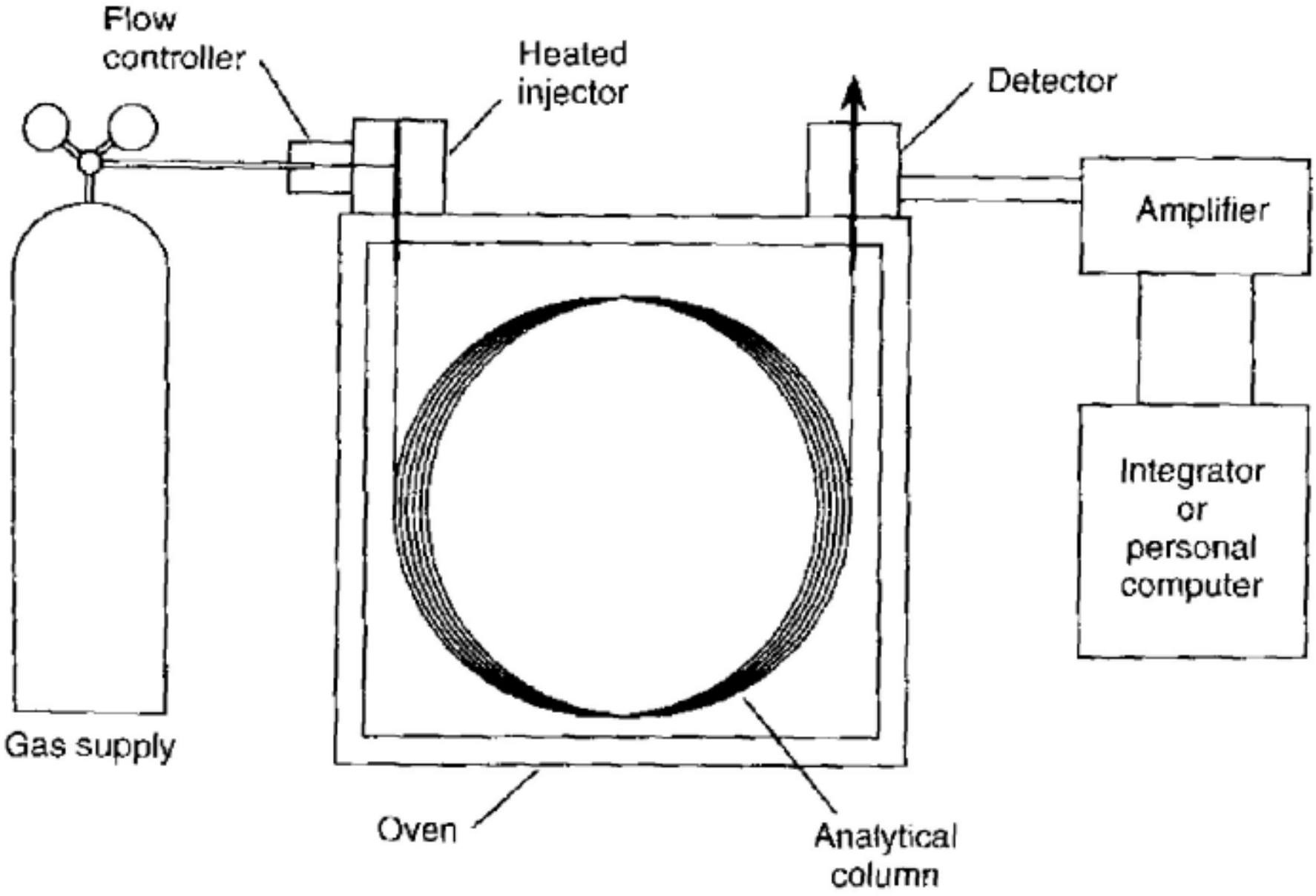


Figure 4.4 Major components of a gas chromatograph.

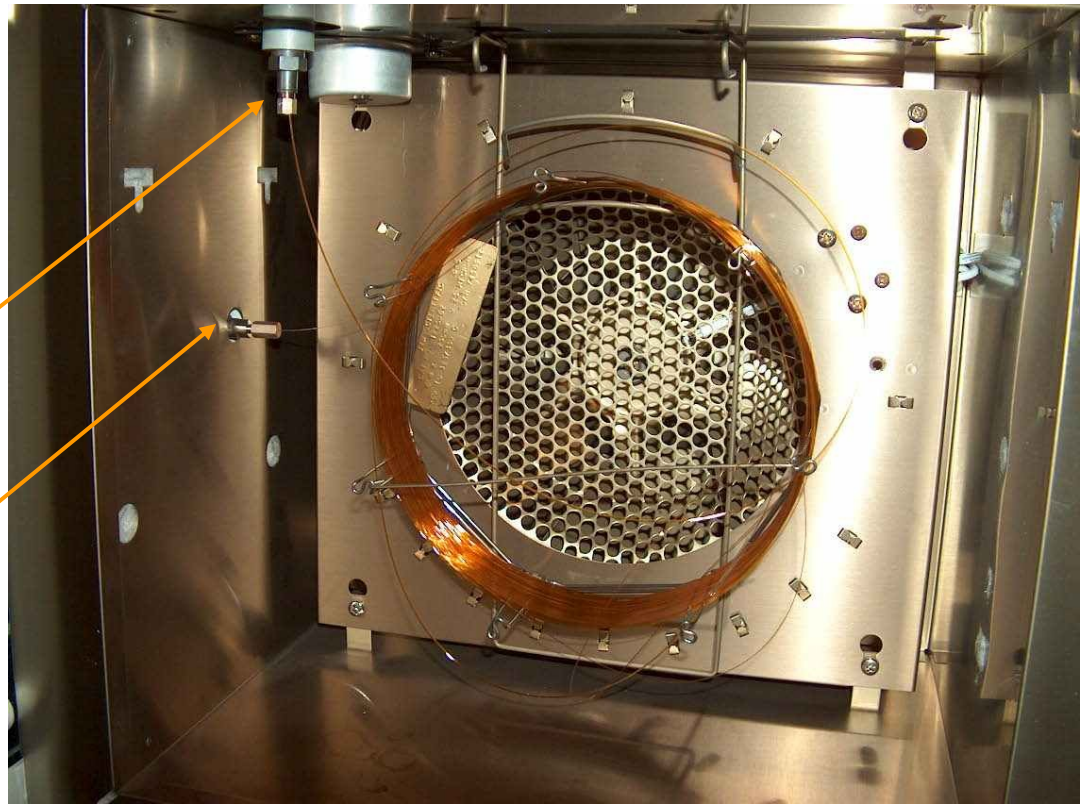
GC separation:

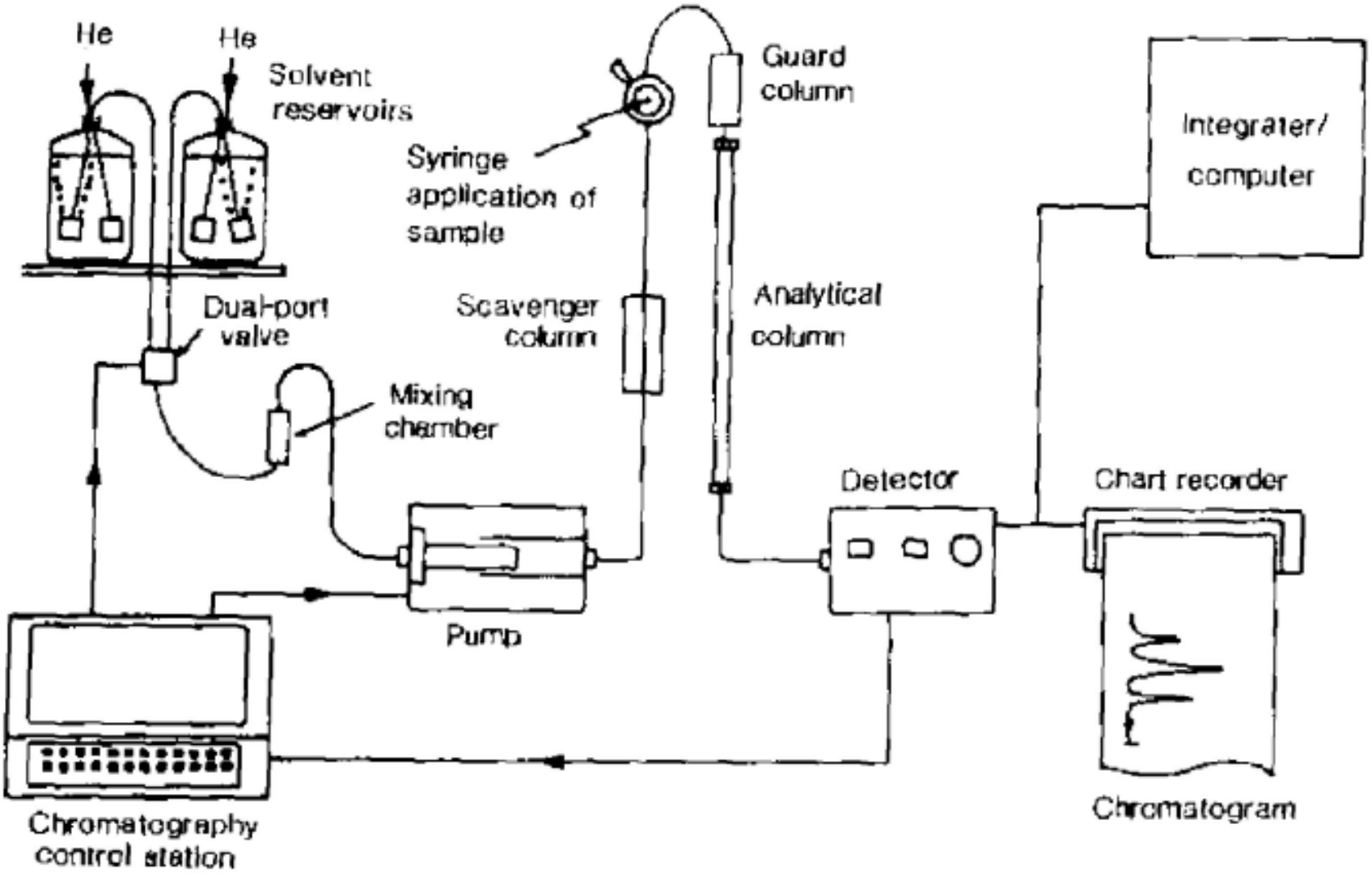
Non-polar stationary phase (e.g. DB-5) – used for the samples of animal origin and higher chlorinated congeners

Polar phase (e.g. SP-2330) – used for environmental samples (good separation but shorter lifetime)

Splitless, on-column or large-volume injection

Direct connection of the column to the ion source





5.7 Schematic diagram of a binary (two-solvent) HPLC system. Source: Fifield, F.W. Kealey, D. (1995) *Principles and Practice of Analytical Chemistry*, 4th edition, Blackie Academic & Professional, Glasgow.

Chromatogram

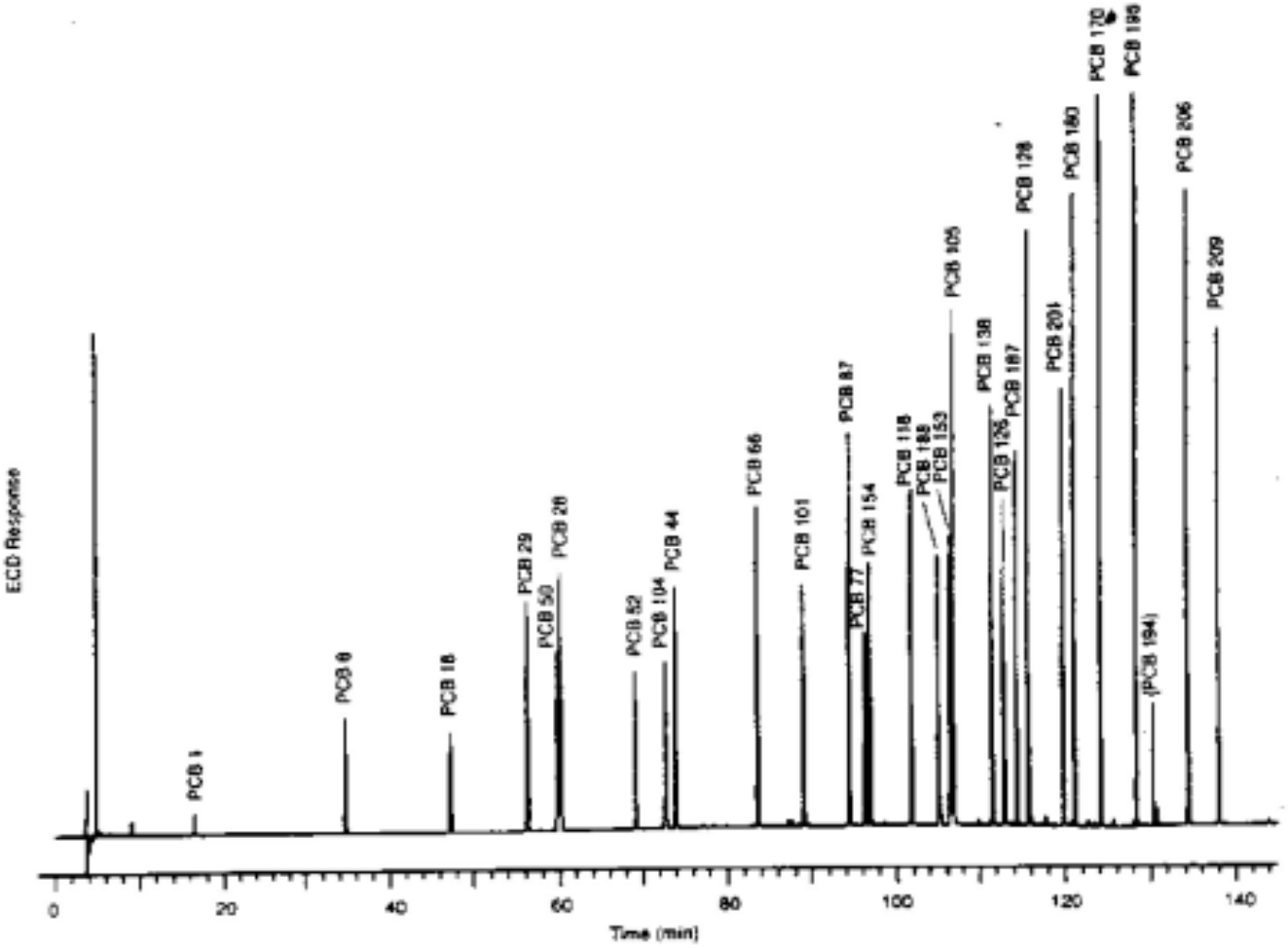
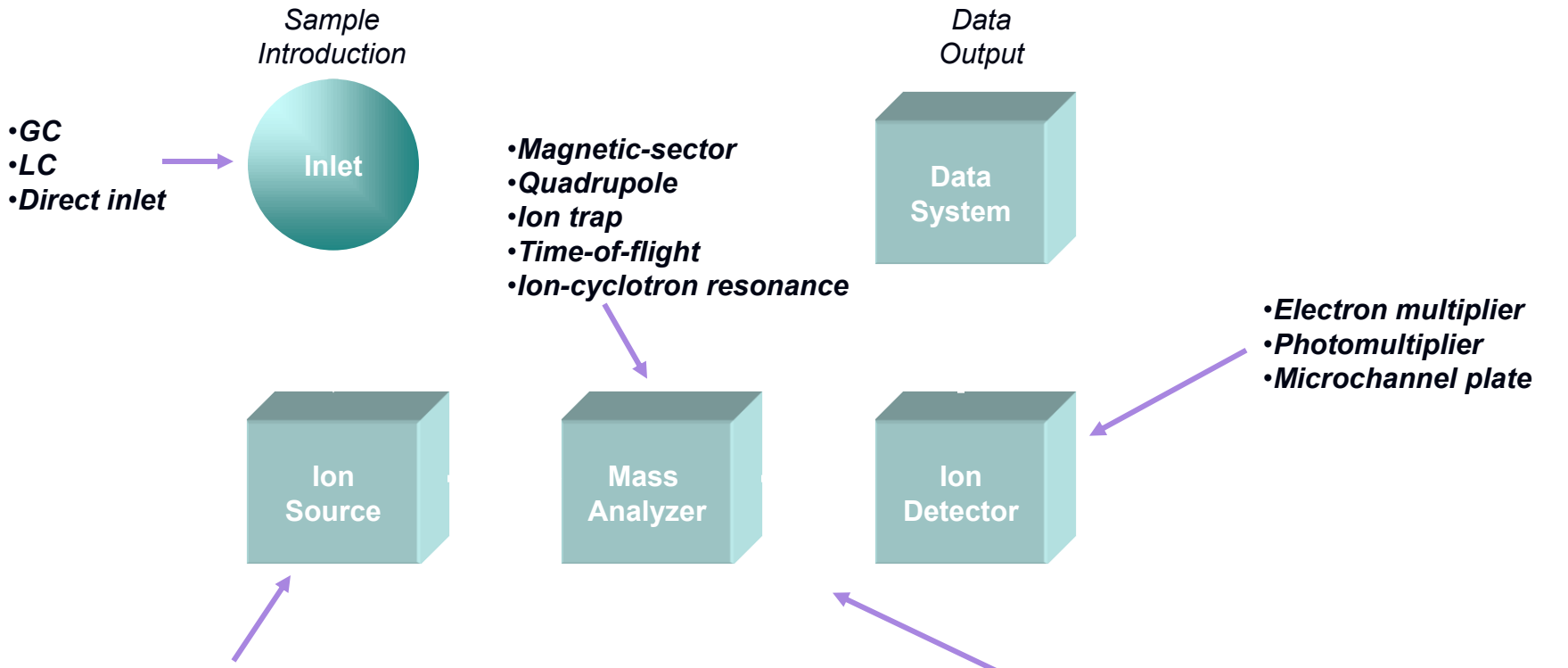


Figure A-1. Chromatogram of NIST SRM 2262 by GC-ECD using a 0.25-mm i.d. x 60-m fused silica capillary column with a 5% phenyl-substituted methylpolysiloxane phase (0.25 µm film thickness) (DB-5, J&W Scientific, Folsom, CA) Temperature Program: 150 °C (40 min) to 220 °C (0 min) at 1 °C/min to 280 °C (25 min) at 3 °C/min.

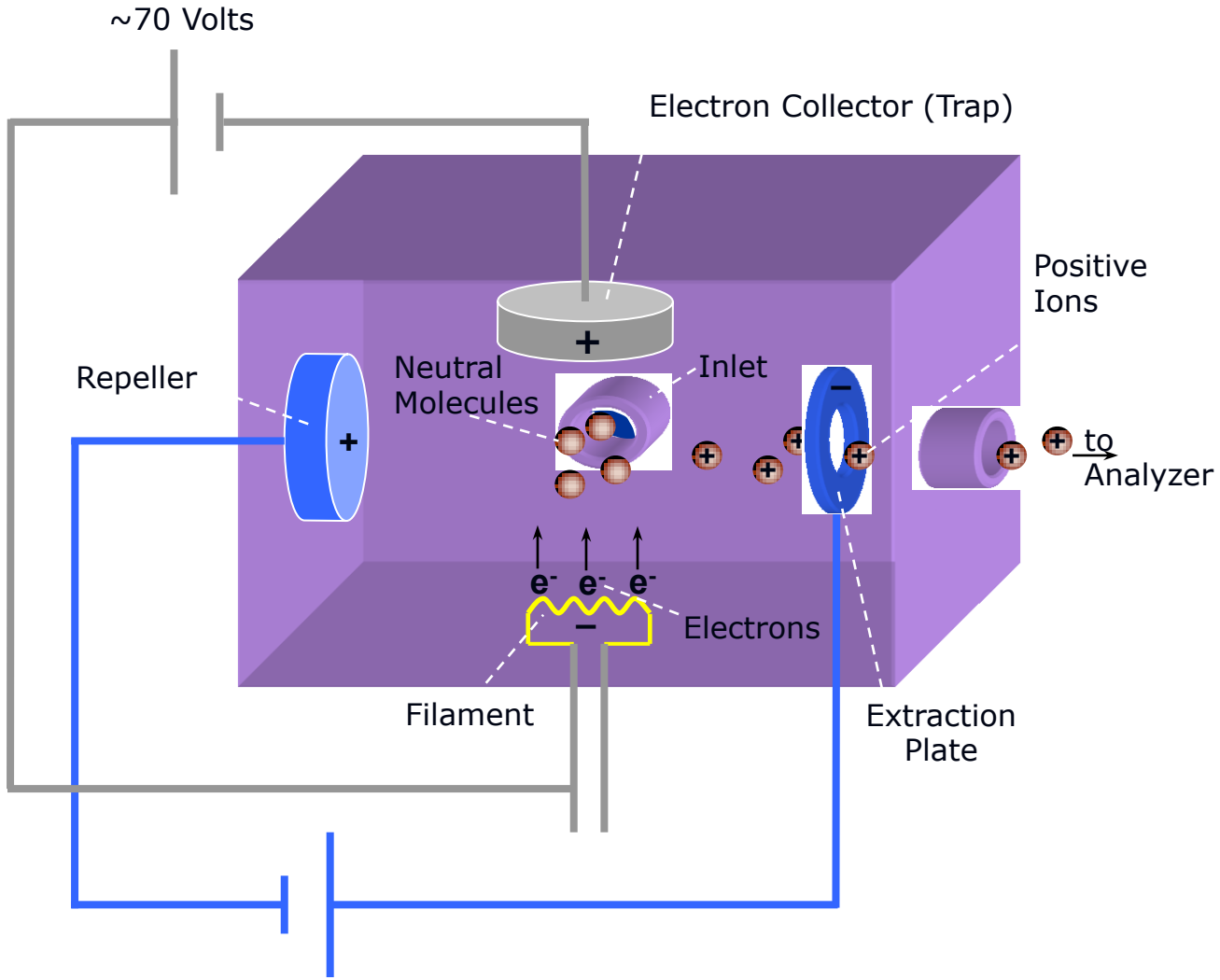
Mass Spectrometer

- **All the MS systems compose of the following parts:**



Electron Impact Ionization Source

10 to 20 eV out of those 70 eV are transferred to the molecules during the ionization process;

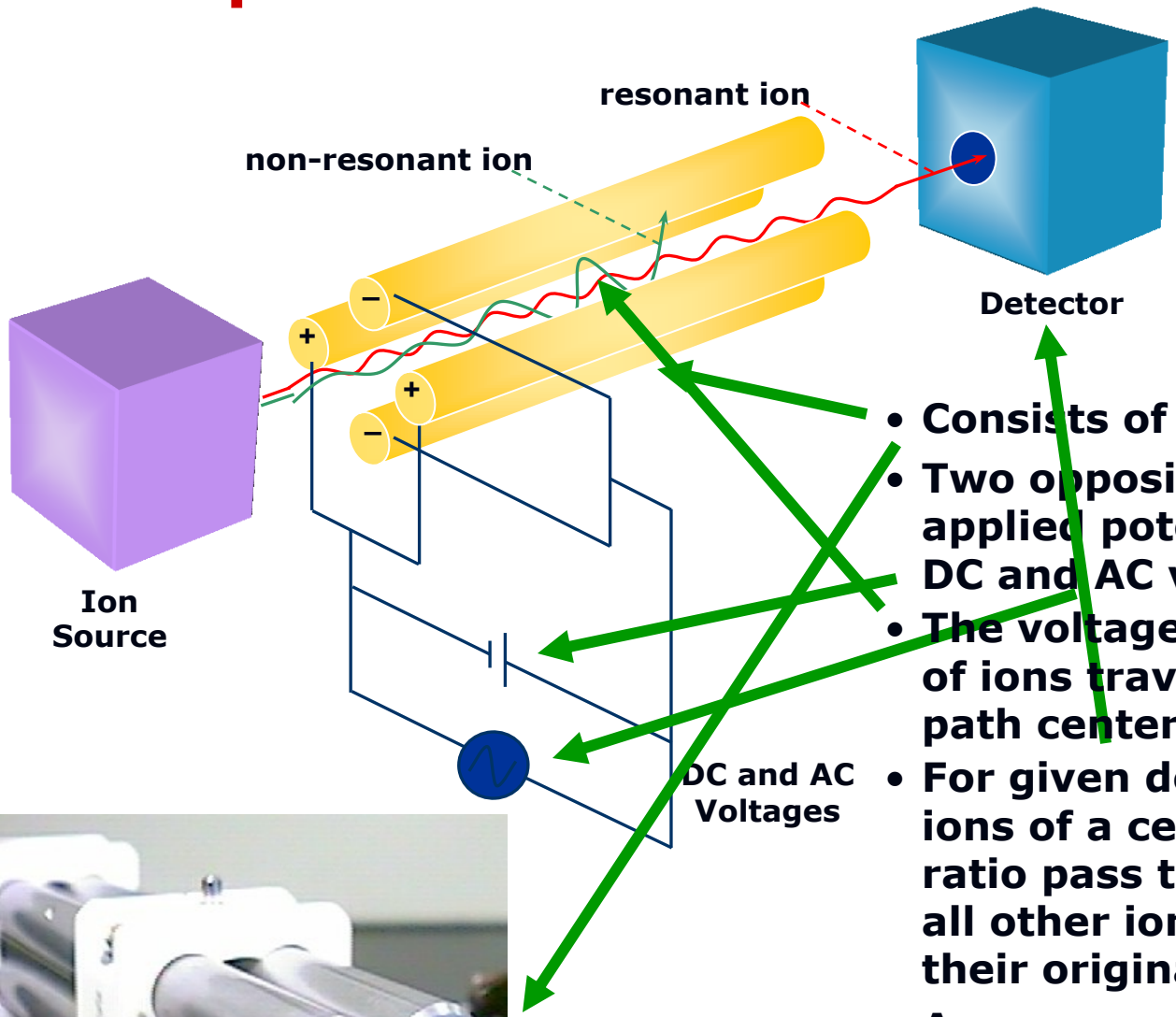


Since ~ 10 eV are enough to ionize most organic molecules the excess energy leads to extensive fragmentation;

Hence EI is classified as a „hard“ ionization technique

The fragmentation gives structural information

Quadrupole Mass Filter

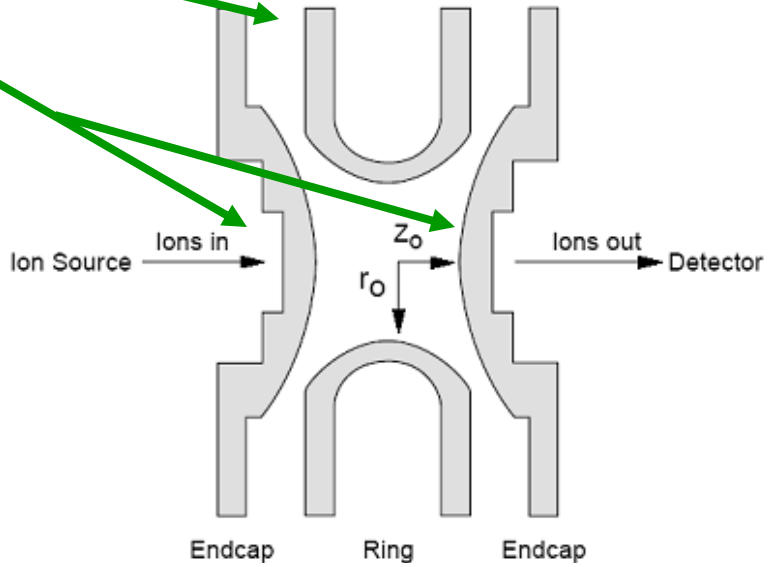


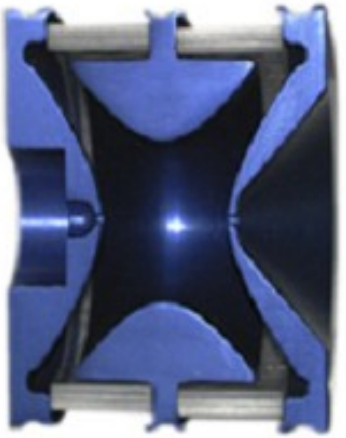
- Consists of 4 parallel metal rods.
- Two opposite rods have an applied potential combined from DC and AC voltages.
- The voltages affect the trajectory of ions traveling down the flight path centered between the rods.
- For given dc and ac voltages, only ions of a certain mass-to-charge ratio pass through the filter and all other ions are thrown out of their original path.
- A mass spectrum is obtained by monitoring the ions passing through the quadrupole filter as the voltages or frequency on the rods are varied.

Ion Trap Mass Spectrometry

Wolfgang Paul
1989 Nobel Price for Physics „for the development of the ion trap technique“

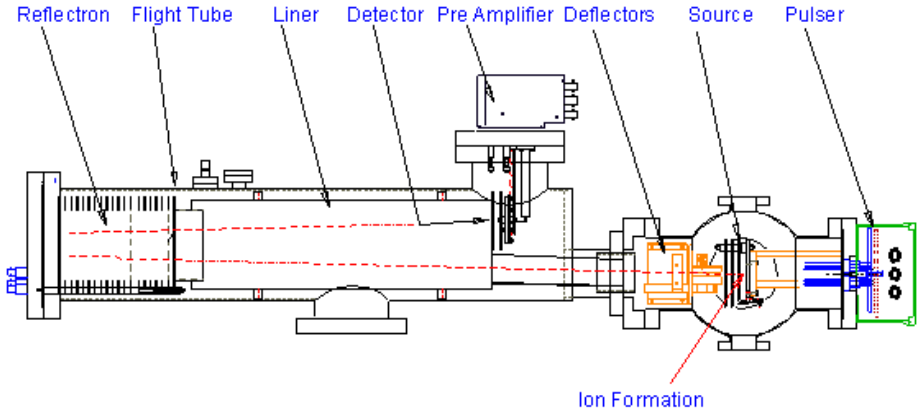
- **The ion-trap analyzer consists of 3 electrodes with hyperbolic surfaces to trap ions in a small volume – the central ring electrode and 2 adjacent endcap electrodes. A mass spectrum is obtained by changing the electrode voltages to eject the ions from the trap.**
- **The advantages of the ion-trap mass spectrometer include compact size, and the ability to trap and accumulate ions to increase the signal-to-noise ratio of a measurement.**
- **This technique can be used easily in the MS/MS (MS^n) mode**

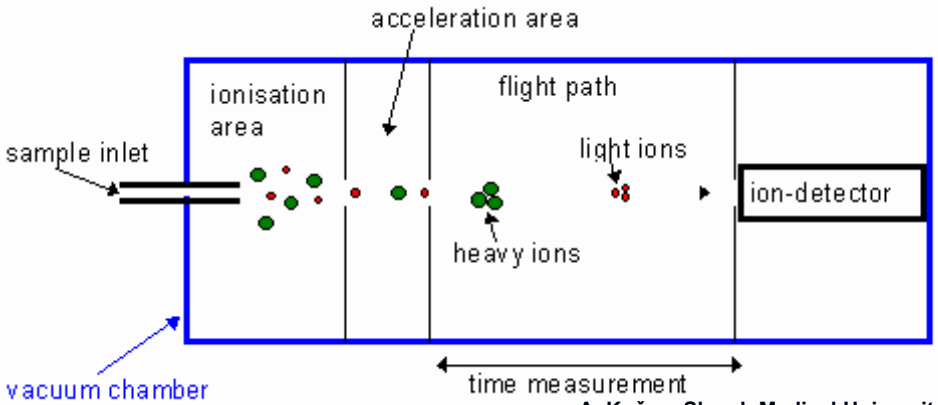




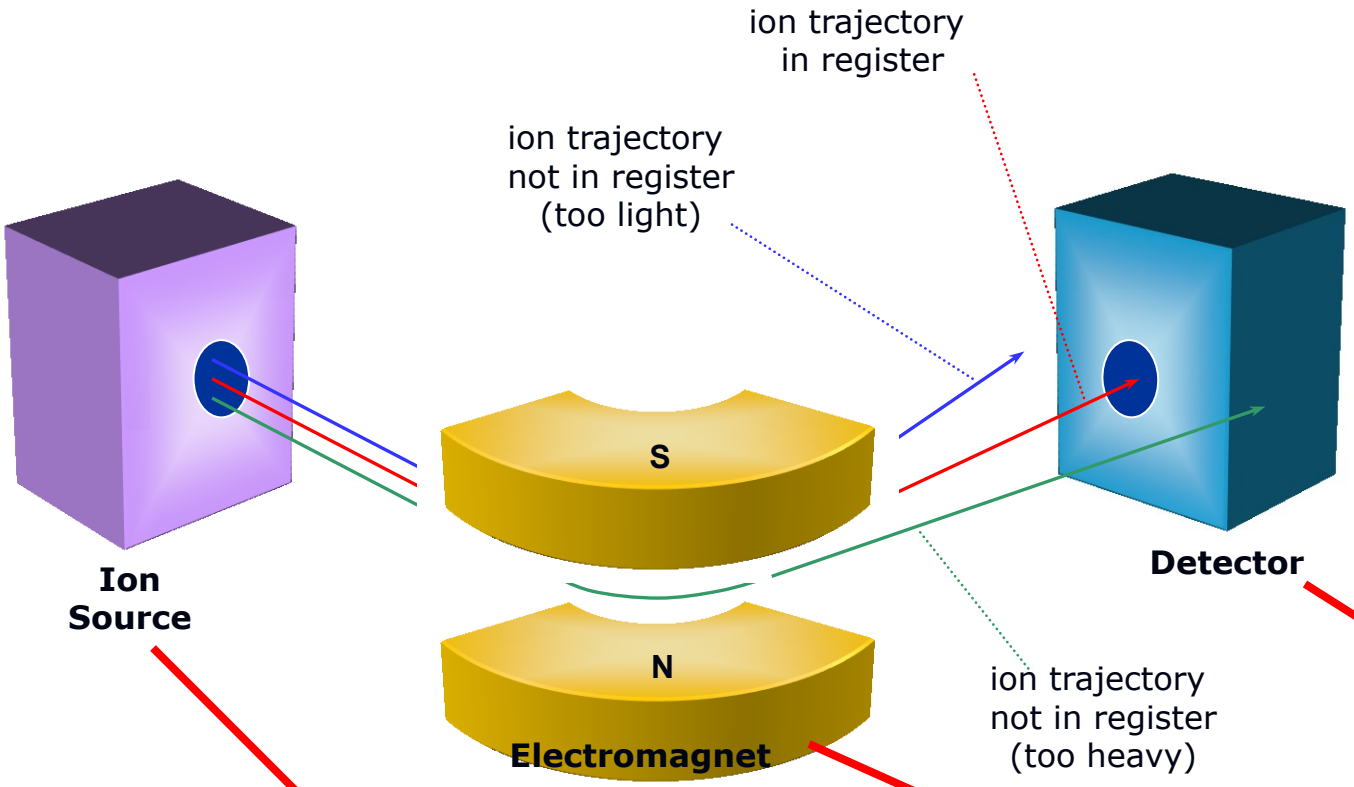
Time-Of-Flight Mass Spectrometry (TOFMS)

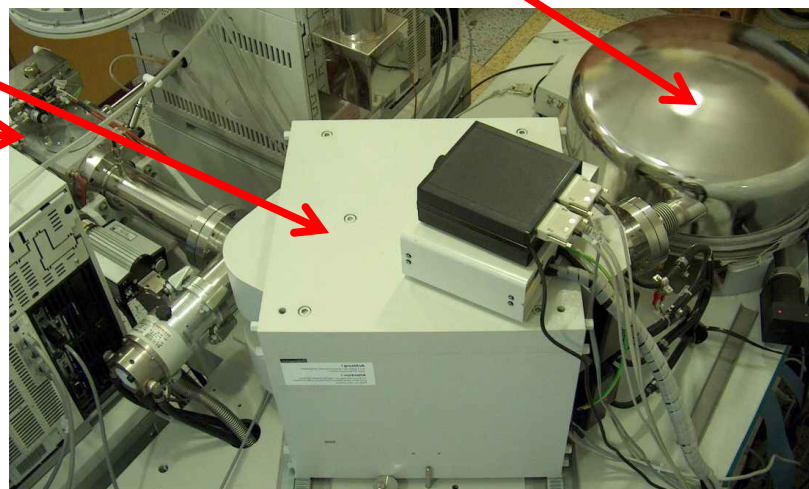
- It uses differences in transit time through a drift region to separate ions of different masses
- An electric field accelerates all ions into a field-free drift region with the same initial kinetic energy for all the ions produced
- It operates in a pulsed mode so ions must be produced or extracted in pulses
- Since the ion kinetic energy is $0.5mv^2$, lighter ions have a higher velocity than heavier ions and reach the detector sooner (e.g., ions of m/z 500 arrive in ~ 15 μs and m/z 50 in ~ 4.6 μs
- By TOF-MS, up to 50 000 full spectra can be measured in a second
- Since full spectra are available, peak deconvolution software enabling to differentiate non-separated GC peaks may be applied
- The TOF ultra-fast scanning is suitable for fast GC where peak widths can be much less then a second



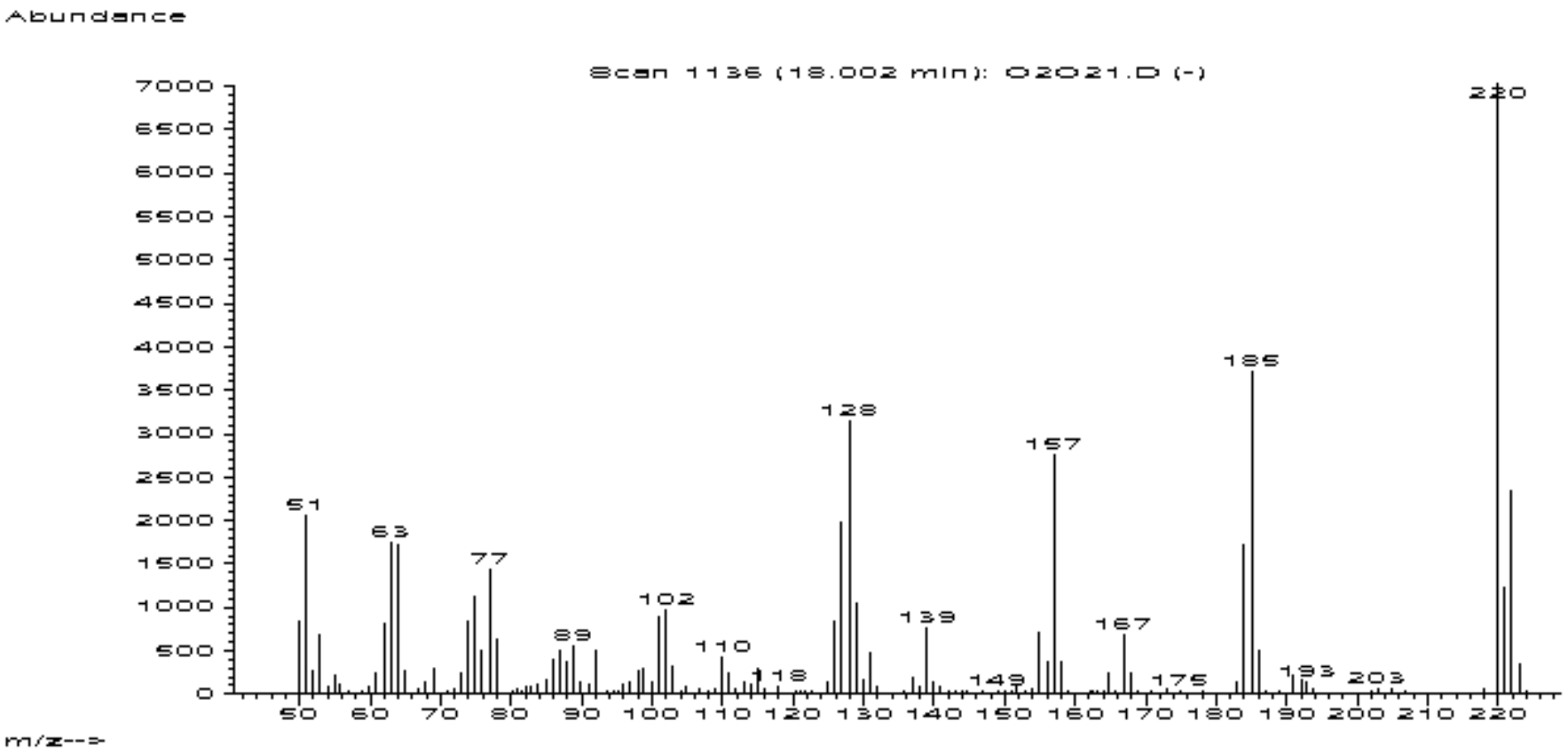


Magnetic Sector Mass Analyzer

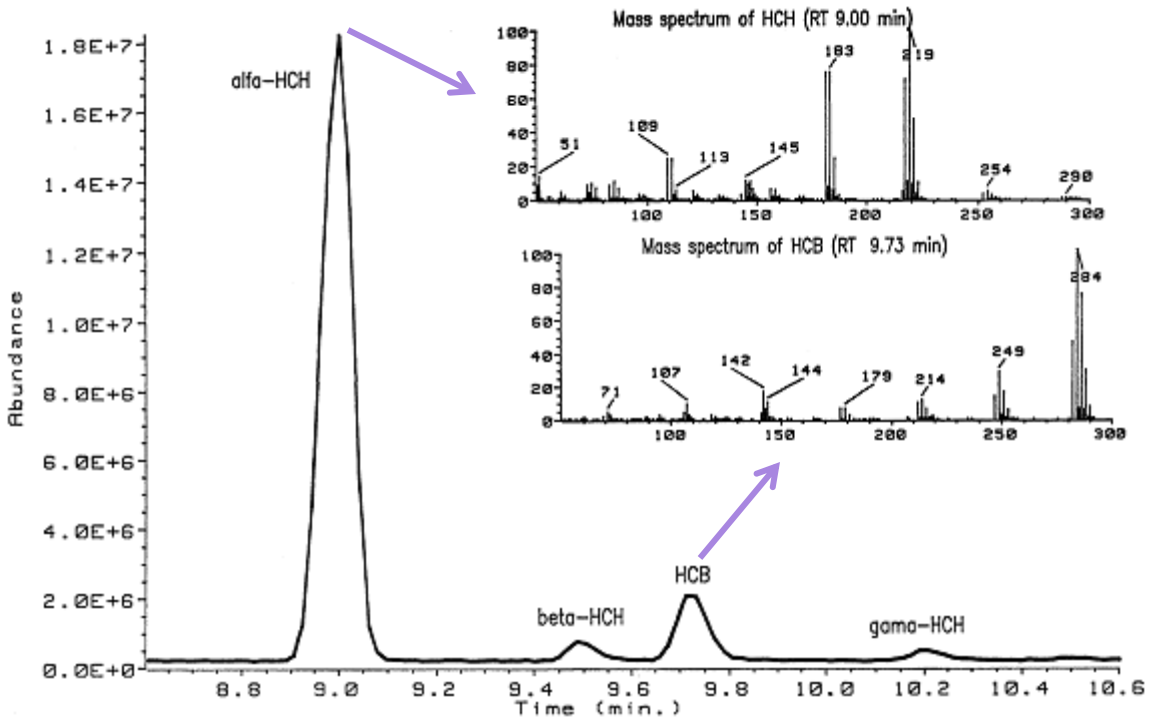




Mass spectra



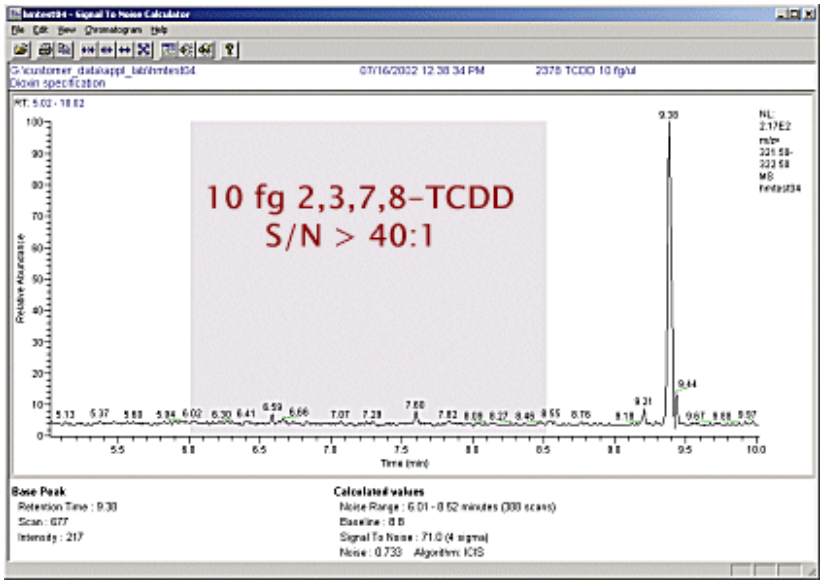
- The scanning mode provides mass spectra. They are recorded (scanned) at regular intervals (typically 0.5 – 1 /s; much faster if TOFMS is used) during the GC separation and stored in the instrument data system for subsequent qualitative or quantitative evaluation.
- From mass spectra, it is often possible to deduce structural features (mass spectral interpretation) but this requires experience and can be very time-consuming, particularly as a complex mixture might contain hundreds of components.

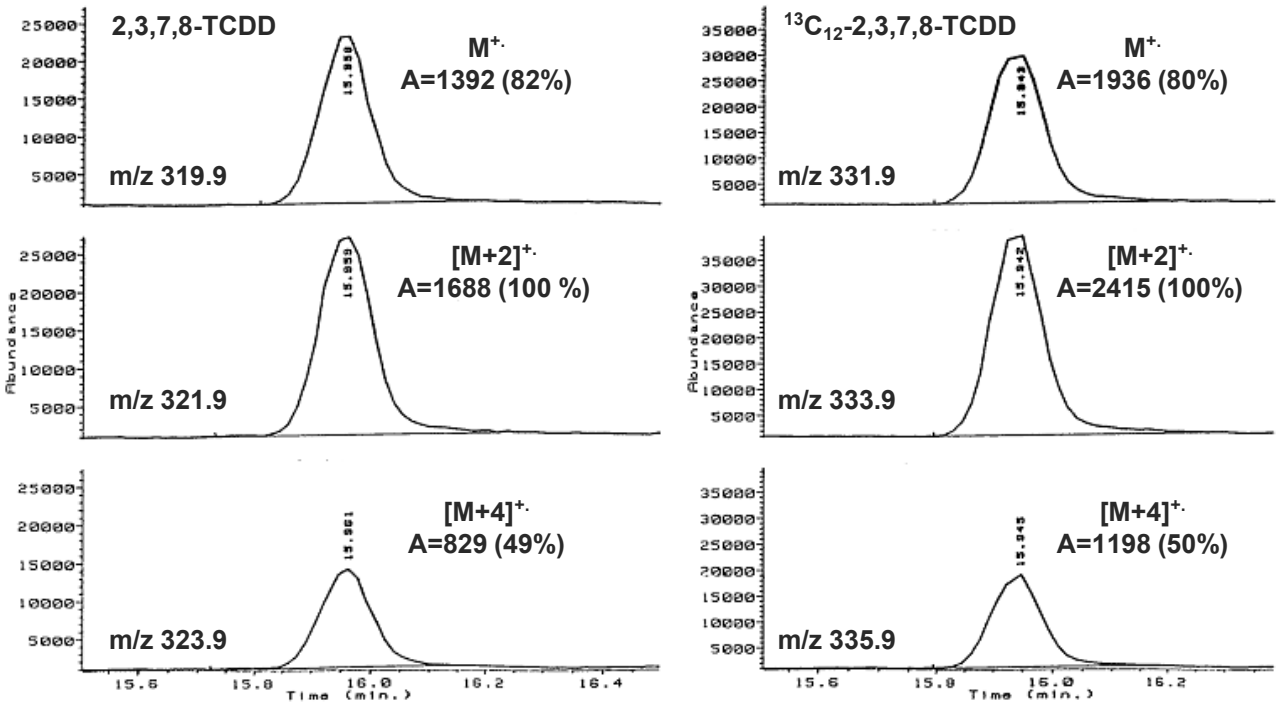


- The spectra can also be compared with those stored in mass spectral libraries. Although library searching is a very useful and timesaving technique, it is important to remember that such searches do not identify compounds – analysts do!

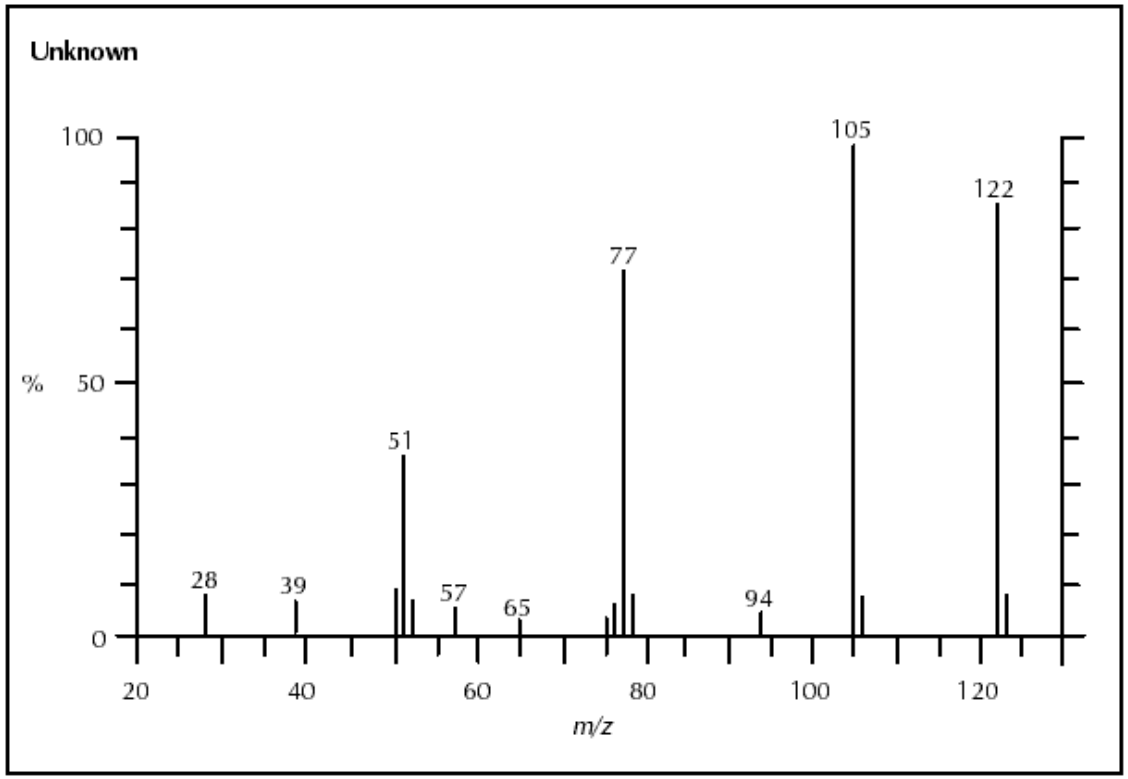
What is the SIM (or MID) Mode in Mass Spectrometry ?

- **SIM (Selected Ion Monitoring) or MID (Multiple Ion Detection) is much more sensitive technique suitable for trace quantitative analysis. Here, instead of scanning a whole spectrum, only a few ions (generally, the most abundant but characteristic selected from the mass spectrum) are detected during the GC run.**
- **This can result in as much as a 500-fold increase in sensitivity, at the expense of selectivity. Depending on the analyte, low picogram to even low femtogram amounts can be measured using this powerful technique.**
- **Stable isotope-labeled internal standards can be employed.**





HRMS/LRMS-SIM chromatogram from the analysis of 2378-TCDD in a soil extract by the isotope dilution method



Some formulae corresponding to nominal *m/z* = 122

Formulae	Actual mass
$C_4H_4N_5$	122.046668
$C_4H_{10}O_4$	122.057903
$C_6H_4NO_2$	122.024201
$C_6H_6N_2O$	122.048010
$C_6H_8N_3$	122.071819
$C_7H_6O_2$	122.036776
C_7H_8NO	122.060585
$C_7H_{10}N_2$	122.084394
$C_8H_{10}O$	122.073161
$C_8H_{12}N$	122.096970
C_9H_{14}	122.109545

These are based on the following relative atomic masses:

C =	12.0000000
H =	1.0078246
N =	14.0030738
O =	15.9949141

- **In general, more ions have the same nominal mass**
- **To distinguish between them certain MS resolution is needed**

- **For example, to separate these 2 ions we need a resolution of 5 124**

R = 122 / (122.060585 – 122.036776) = 5 124

Conversion of Analytical Results into the Toxic Equivalent (TEQ)

- This conversion is based on the assumption that all the 2,3,7,8-substituted PCDDs and PCDFs (17 cong.), as well as the dioxin-like PCBs (12 cong.), bind to the same receptor, the Ah receptor, and show comparable qualitative (toxic) effects, but with different potencies
- These differences in toxicity are expressed in the toxic equivalency factors (TEFs)
- TEF of the most toxic 2378-TCDD = 1

Congener	I-TEF	WHO-TEF	Congener	I-TEF	WHO-TEF
2378-TCDD	1	1	2378-TCDF	0.1	0.1
12378-PeCDD	0.5	1	23478-PeCDF		
123478-HxCDD	0.1	0.1	12378-PeCDF	0.05	0.05
123678-HxCDD	0.1	0.1	123478-HxCDF	0.1	0.1
123789-HxCDD	0.1	0.1	123789-HxCDF	0.1	0.1
1234678-HpCDD	0.01	0.01	123678-HxCDF	0.1	0.1
OCDD	0.001	0.0001	234678-HxCDF	0.1	0.1
			1234678-HpCDF	0.01	0.01
			1234789-HpCDF	0.01	0.01
			OCDF	0.001	0.0001

$$TEQ = (PCDD_i \times TEF_i) + (PCDF_i \times TEF_i) + (PCB_i \times TEF_i)$$

Quality assurance/quality control (QA/QC)

Quality assurance
Preventive measures (quality of facilities, personnel and education, equipment and service, calibration, internal and recovery standards)

Quality control
Control measures (internal – blank and reference material analyses, external – interlaboratory comparison, audit)

Reasons
- repeatibility of measurements
- comparison of results between laboratories
- political and economical importance of results

Terminology

Calibration
Limit of detection and quantification
Sensitivity and specificity
Accuracy, trueness, precision
Method validation and verification
Internal standards
Recovery and surrogate recovery standards
Certified reference materials
interlaboratory calibration tests,
GLP

Standard operational procedure

- General information (terminology, principles, range of use, limitations, safety procedures, toxicology, waste treatment)
- Directives
- Consumables and chemicals (glass, standards, solvents, reference materials)
- Equipment (sampling and analytical equipment, service)
- Calibration (standards, procedures)
- Analytical scheme (method validation and verification)
- Quality control (internal - blank, reference material, external – intercalibration)
- Data interpretation
- Annexes

Mokrá - půdy 2002 - 4

vyhodnoceno: 25.4.2003

Koncentrace ng/g

Číslo vzorku	toluen	02-753	02-752	02-740	02-741	02-742	02-743	02-744	02-745	02-746	02-747	02-748	02-749	02-750	02-751	
Lokalita	GC blank	Lab. blank	RM	454 Hosten	Čihálky	332 Vodojem	Velká Bata1	Velká Bata2	Prostřed kopec	420Vel Bata	Chlumek 1	Chlumek 2	Horák mysl.	Nové pole	jižní CVM	LOQ
Číslo zadav				303S	304S	305S	306S	307S	308S	309S	310S	311S	312S	313S	314S	
Datum odbě				14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	14.11.02	KALIB30
Navážka (g)	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0	5,0
Ředění	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Naftalen	0,10	1,86	26,74	12,5	6,6	7,5	5,2	5,5	11,8	13,5	7,1	6,6	8,6	5,9	8,5	0,10
Acenaftyle	-	0,02	0,58	0,8	0,3	0,7	0,4	0,5	2,2	1,8	0,6	0,5	1,2	2,4	0,8	0,10
Acenaften	-	0,04	1,22	1,4	0,3	1,4	1,6	0,6	5,3	3,4	2,5	0,8	2,0	5,4	1,2	0,10
Fluoren	-	0,04	2,26	1,7	0,6	1,4	1,3	0,7	4,9	3,8	2,0	1,0	2,2	4,7	1,5	0,10
Fenantren	-	0,12	23,96	24,9	6,4	20,5	18,8	8,4	69,1	59,4	14,2	13,6	29,5	109,3	16,8	0,10
Antracen	-	-	1,12	2,0	0,4	1,9	3,4	1,1	6,1	5,2	2,1	1,4	2,9	16,9	1,8	0,10
Fluoranten	-	-	27,78	68,2	13,7	58,0	42,0	24,2	213,0	162,5	40,7	37,6	82,5	450,2	42,9	0,10
Pyren	-	-	19,38	50,5	9,7	45,6	35,4	20,2	159,3	123,6	32,0	28,6	63,8	377,2	33,0	0,10
Benz(a)ant	-	-	4,60	17,9	2,9	14,4	14,7	9,1	61,5	49,3	18,3	13,1	26,3	206,3	13,6	0,10
Chrysen	-	-	11,50	32,4	7,3	25,6	18,4	12,2	102,6	75,9	22,3	16,8	41,2	204,2	20,0	0,10
Benzo(b)flu	-	-	18,30	61,0	11,7	32,2	23,6	20,4	169,5	128,2	28,0	29,4	67,7	261,1	31,2	0,10
Benzo(k)flu	-	-	6,04	18,1	3,8	14,4	11,0	7,9	56,4	41,9	13,0	11,2	22,4	134,8	11,6	0,10
Benzo(a)py	-	-	8,34	27,6	3,5	23,6	20,3	13,3	92,8	71,6	24,2	18,4	38,4	285,9	21,3	0,10
Indeno(123	-	-	8,22	33,1	6,4	21,4	14,8	11,1	98,7	72,0	22,6	19,6	41,0	216,1	20,7	0,10
Dibenz(ah)	-	-	0,82	2,7	0,6	2,4	1,6	0,9	7,1	8,3	1,8	2,3	4,1	25,8	1,8	0,10
Benzo(ghi)	-	-	11,26	29,7	5,3	20,6	14,8	11,4	83,9	61,4	19,4	16,3	36,0	181,8	18,5	0,10
Suma PA	**0,10**	**2,08**	**172,12**	**384,5**	**79,5**	**291,6**	**227,3**	**147,5**	**1144,2**	**881,8**	**250,8**	**217,2**	**469,8**	**2488,0**	**245,2**	**1,60**
100% D-PA	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	2 000	
ředění	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	
D8-naftaler	0%	0%	88%	72%	79%	66%	65%	80%	62%	66%	21%	61%	75%	81%	81%	
D10-fenant	0%	0%	90%	77%	91%	68%	72%	86%	77%	79%	88%	79%	85%	94%	92%	
D12-peryle	0%	0%	86%	74%	34%	67%	73%	86%	83%	83%	89%	82%	93%	101%	96%	

GC blank ..... slepý vzorek přístroje GC-MS - nástřik čistého rozpouštědla do plynového chromatografu

Lab. blank ..... laboratorní slepý vzorek - analyzovaný celým analytickým postupem s čistými rozpouštědly a všemi použitými materiály

GPC blank ..... slepý vzorek GPC chromatografu

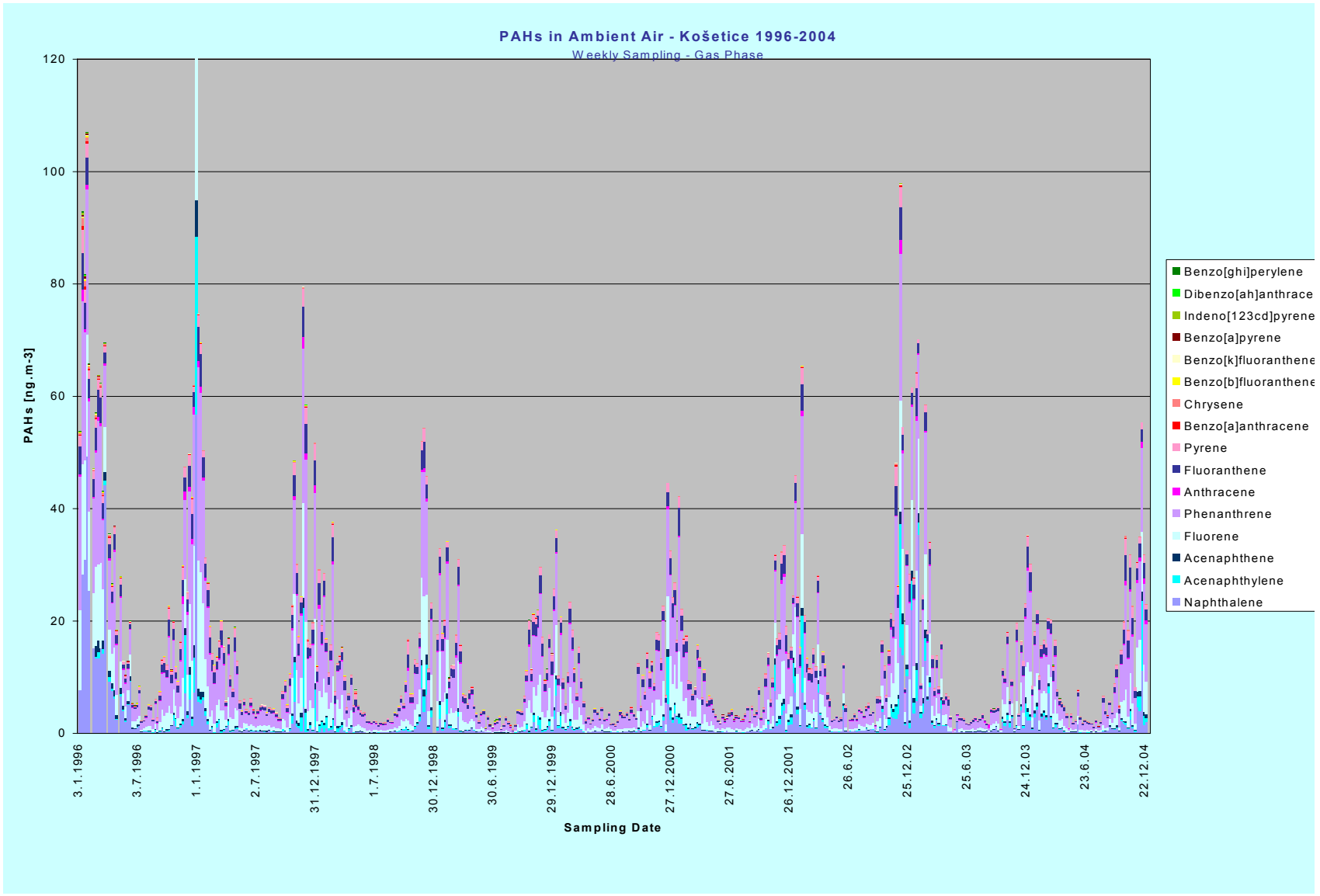
blank, GF blank ..... terénní slepé vzorky - pasivní odběr na polyuretanovou pěnu a skleněné vlákno

CRM ..... analýza certifikovaného referenčního materiálu

RM ..... analýza laboratorního referenčního materiálu

NQ ..... nekvantifikováno - analyt byl překryt interferentem

LOQ ..... meze stanovitelnosti


PAHs in Ambient Air - Košetice 1996-2004
Weekly Sampling - Gas Phase
PAHs [ng.m-3]
120
100
80
60
40
20
0
3.1.1996
3.7.1996
1.1.1997
2.7.1997
31.12.1997
1.7.1998
30.12.1998
30.6.1999
29.12.1999
28.6.2000
27.12.2000
27.6.2001
26.12.2001
26.6.02
25.12.02
25.6.03
24.12.03
23.6.04
22.12.04
Sampling Date
Benzo[ghi]perylene
Dibenzo[ah]anthrace
Indeno[123cd]pyrene
Benzo[a]pyrene
Benzo[k]fluoranthene
Benzo[b]fluoranthene
Chrysene
Benzo[a]anthracene
Pyrene
Fluoranthene
Anthracene
Phenanthrene
Fluorene
Acenaphthene
Acenaphthylene
Naphthalene