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Chemical Analysis in Environmental Chemistry

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Previous lectures

- Semi-volatile organic compounds – from sources to the environment
  - Part 1: Chlorinated and brominated compounds
  - Part 2: Emerging compounds, endocrine disrupting compounds

- Analytical chemistry
  - Monitoring and sampling strategies I

This lecture

- Analytical chemistry and environmental pollution
- Steps in quantification of contaminants
- Sample preparation and clean-up
- Chromatography
- Detection
- Data processing
- Examples
- Case study

Analytical Chemistry

Quantitation

How much of substance X is in the sample?

Detection

Does the sample contain substance X?

Identification

What is the identity of the substance X in the sample?

Separation

How can the compounds of interest be separated from the sample matrix for better quantitation and identification?

Environmental Pollution - Sources

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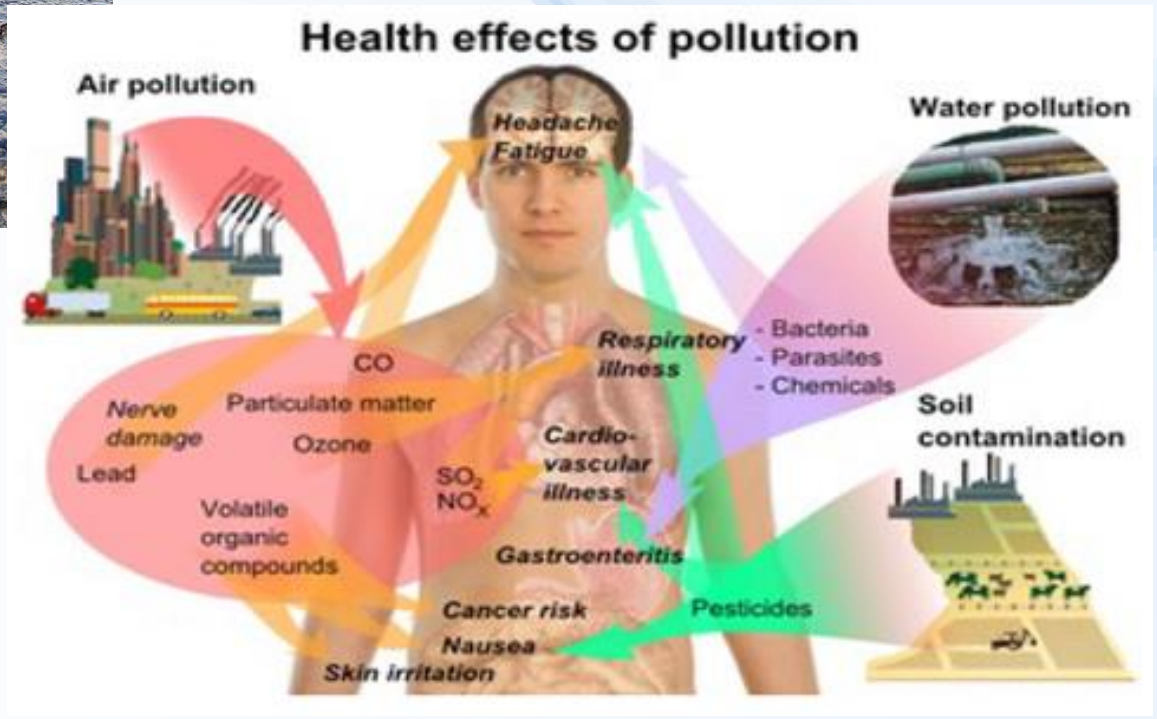
Environmental Pollution - Effects



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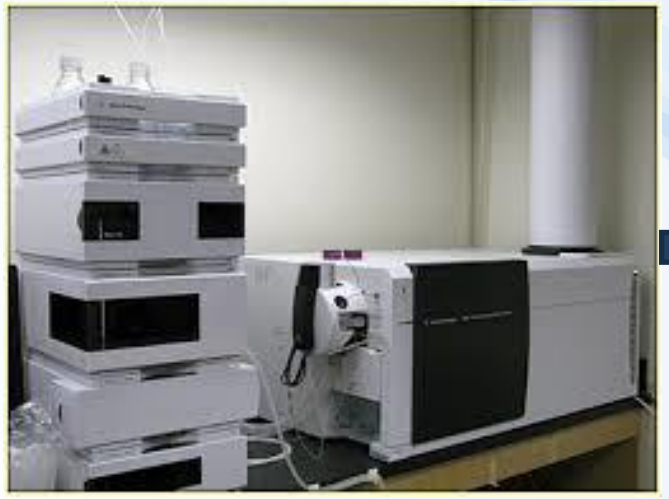
Chemical Analysis of Environmental Samples



compounds e.g.,

Pharmaceuticals

Personal care products

Drugs

Biocides

Polycyclic Aromatic Compounds

Phthalates

Antioxidants

Halogenated compounds

Dioxines

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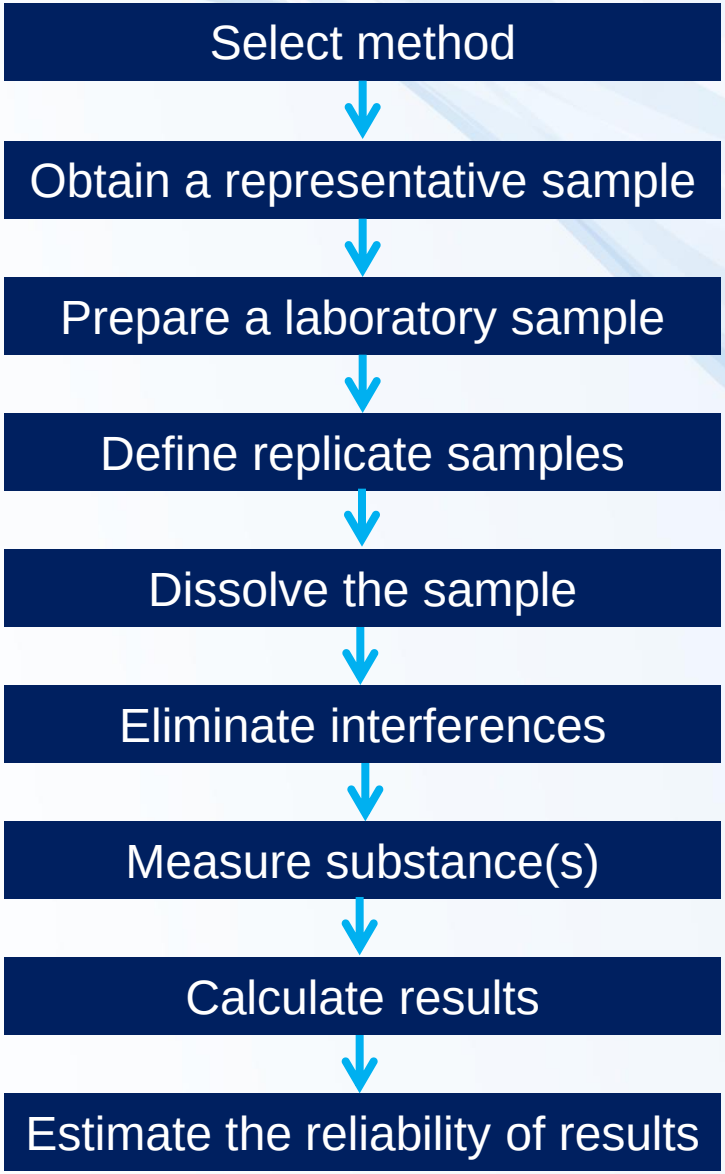
Steps in a Quantitative Analysis



Selecting a Method

- What is the problem?
- What is already known?
- Choosing a Method
- Testing Procedure
    - Standard Sample
    - Comparing methods
    - Standard addition to the sample
- Accuracy

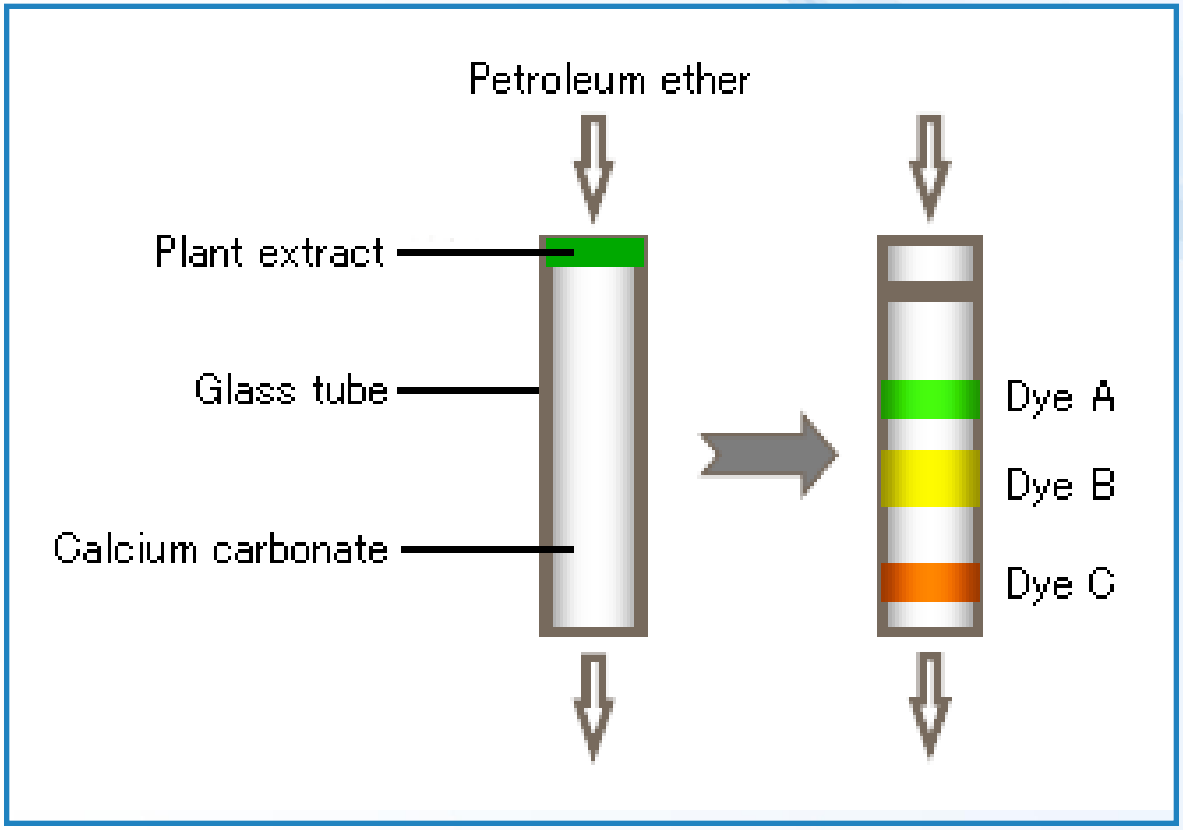
Sampling and Preparation

- Sampling uncertainties
- Representative
- Homogene
- Crushing, grinding, sieving, mixing
- Replicates
- Quanitative or Qualitative analysis

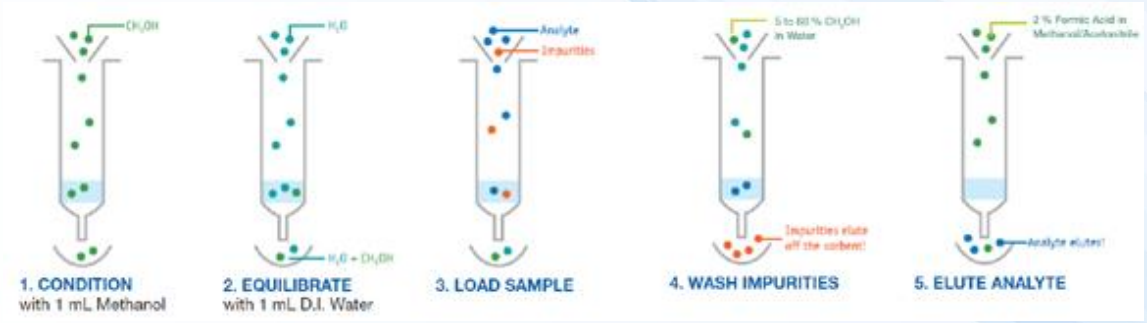
Eliminating Interferences – Sample Clean-up

- Solubility
- Partition coefficient
- Liquid/Liquid Extraction
- Solid Phase Extraction (SPE)
- Soxhlet Extraction
- Accelerated Solvent Extraction (ASE)
- Gel Permeation Chromatography (GPC)
- Evaporation
- Filtration

1906 - Tswett - Adsorption Chromatography



Solid Phase Extraction (SPE)



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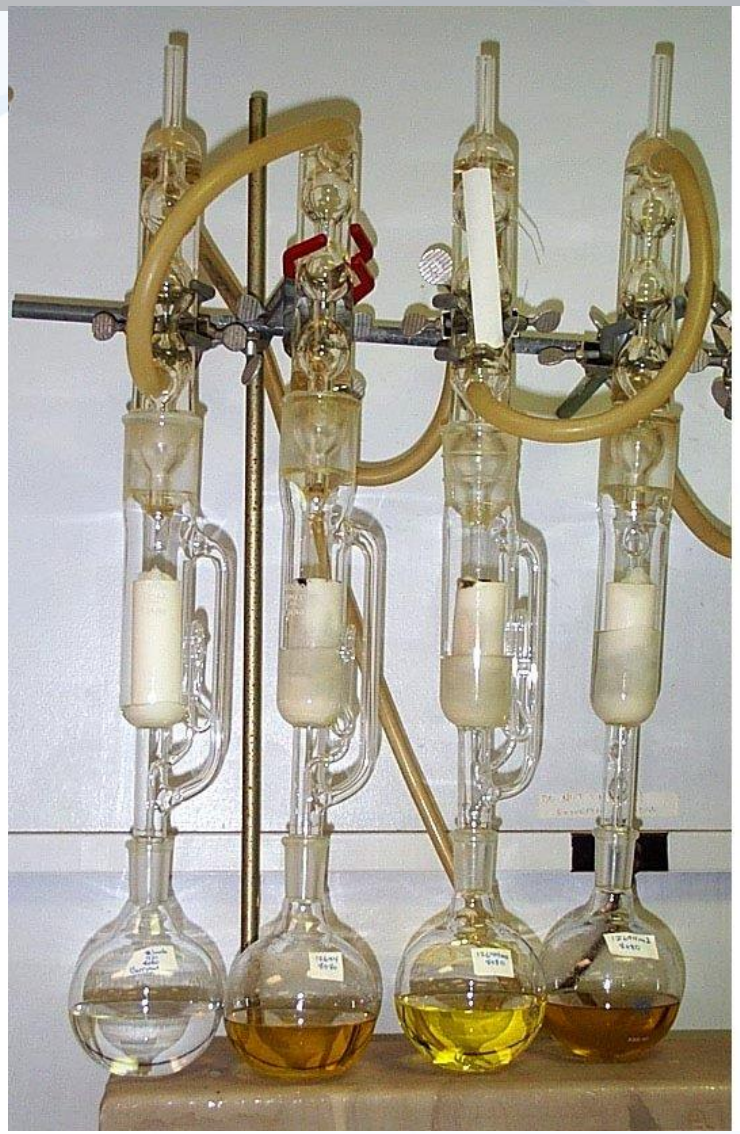
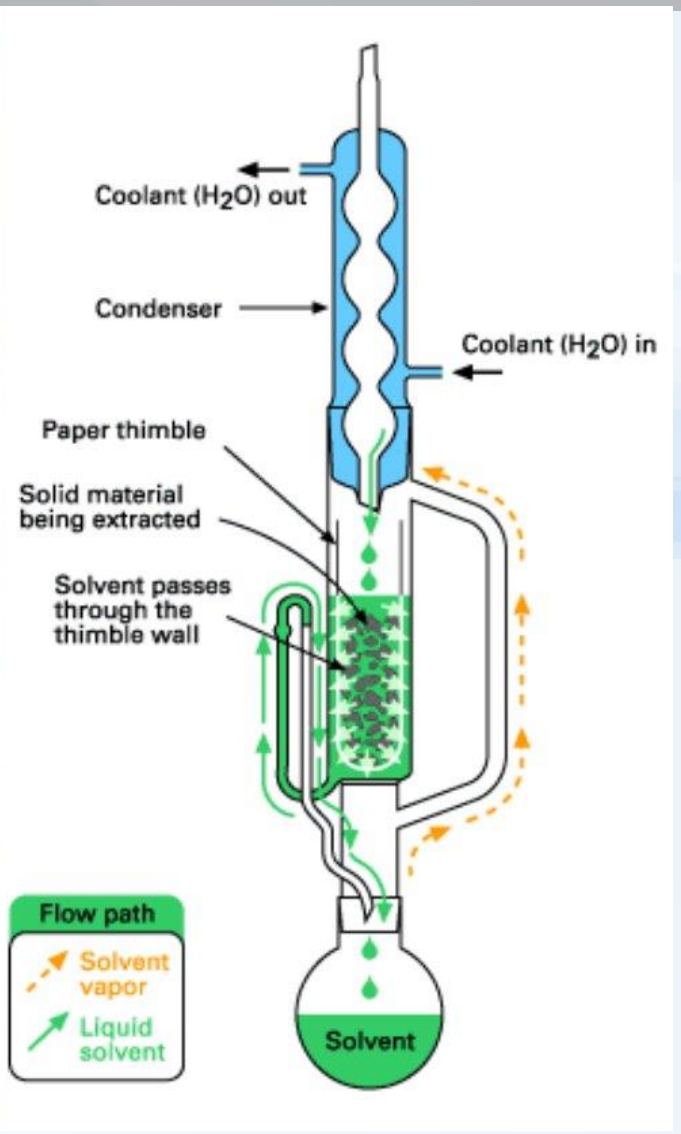
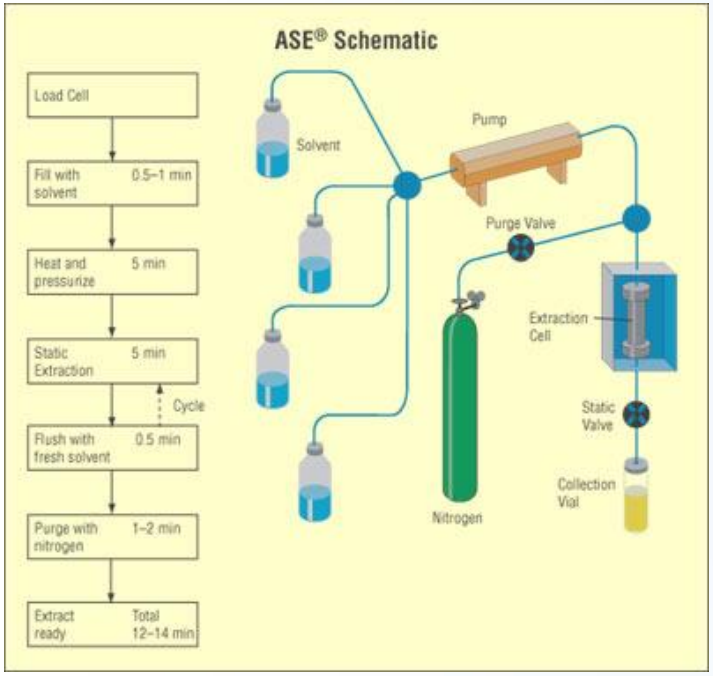
Soxhlet Extraction

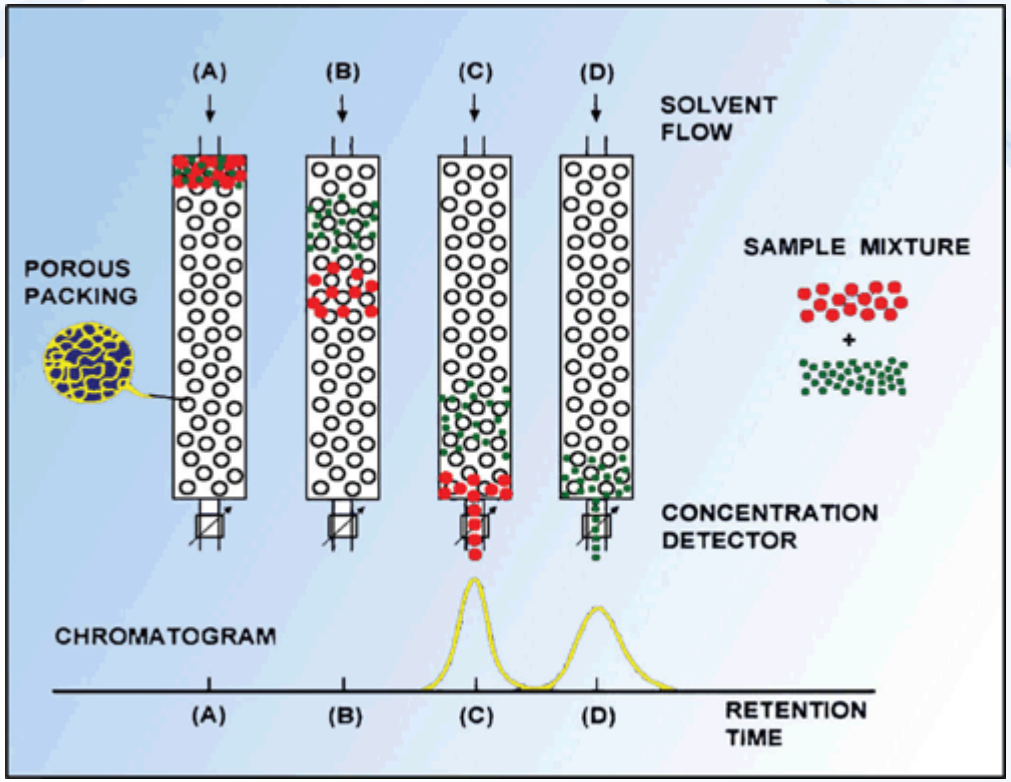




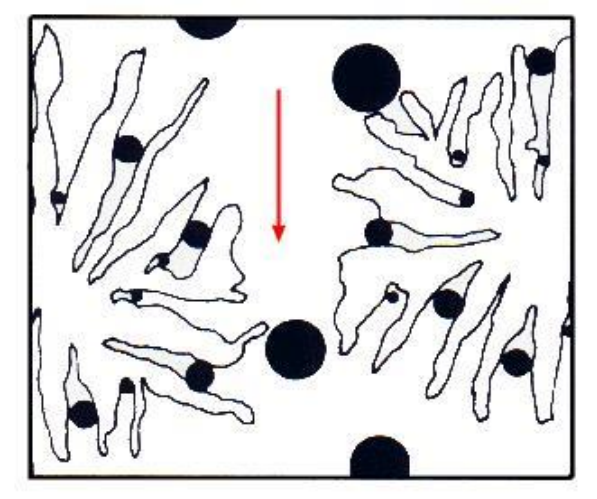
Accelerated Solvent Extraction (ASE)



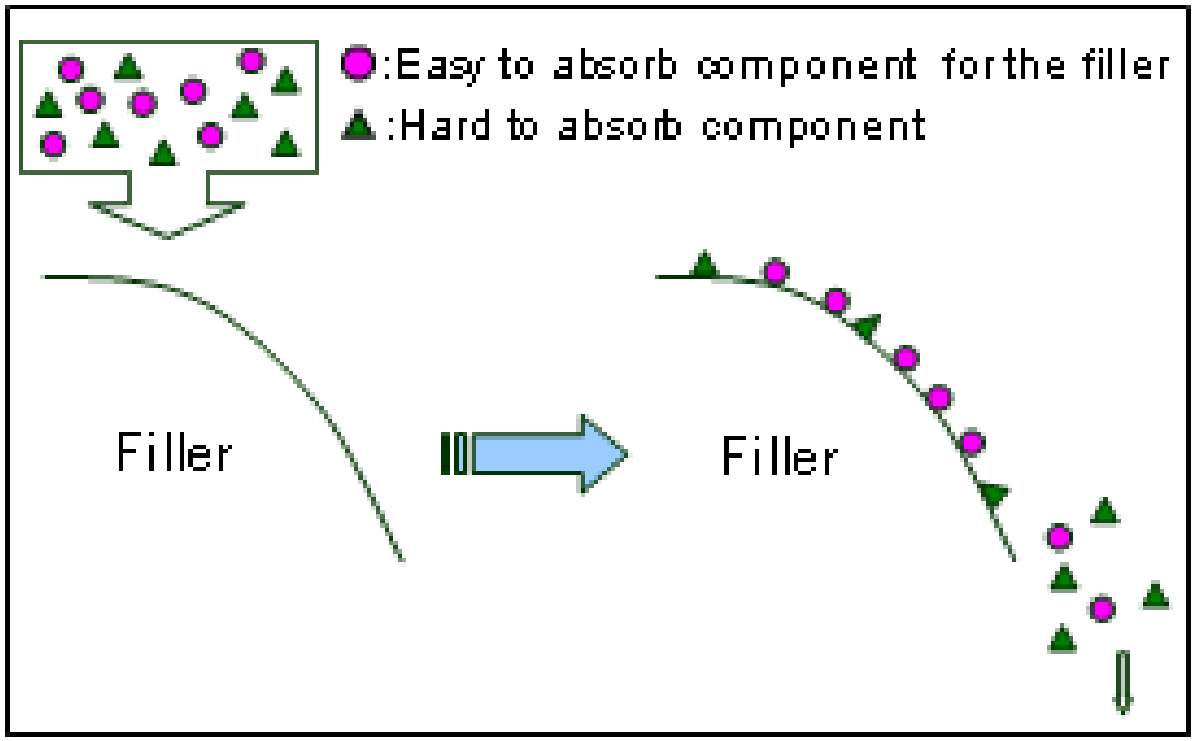
Gel Permeation Chromatography (GPC)



porous packing

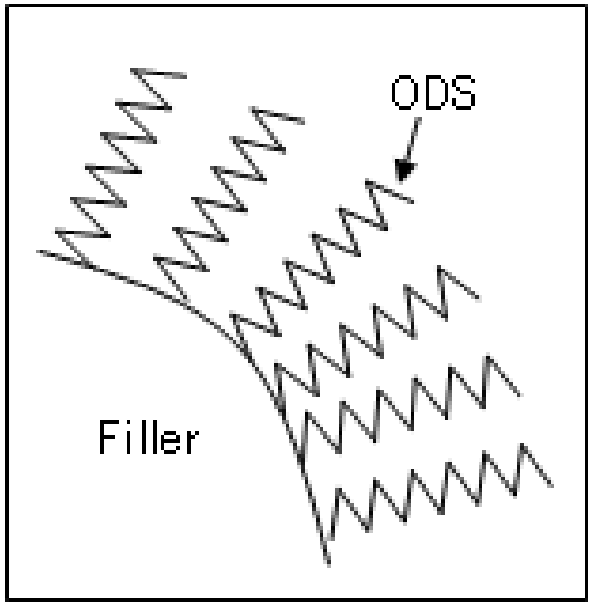


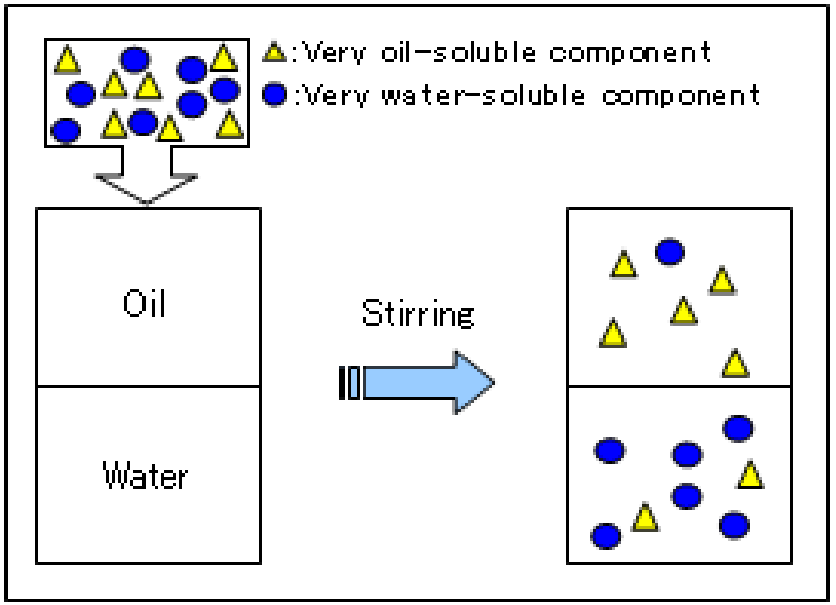
Adsorption Chromatography



http://www.hitachi-hitec.com/global/science/lc/lc_basic_4.html

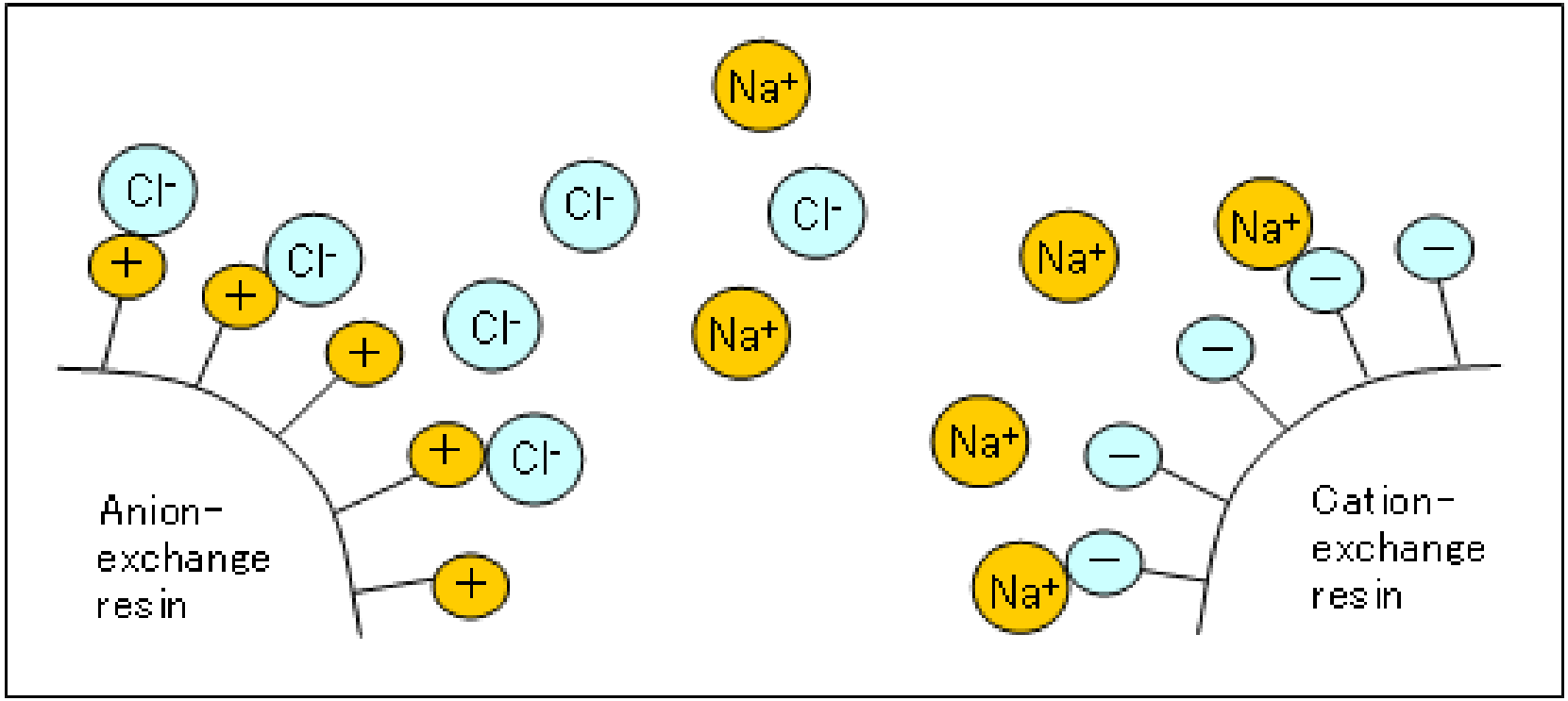
Partition Chromatography





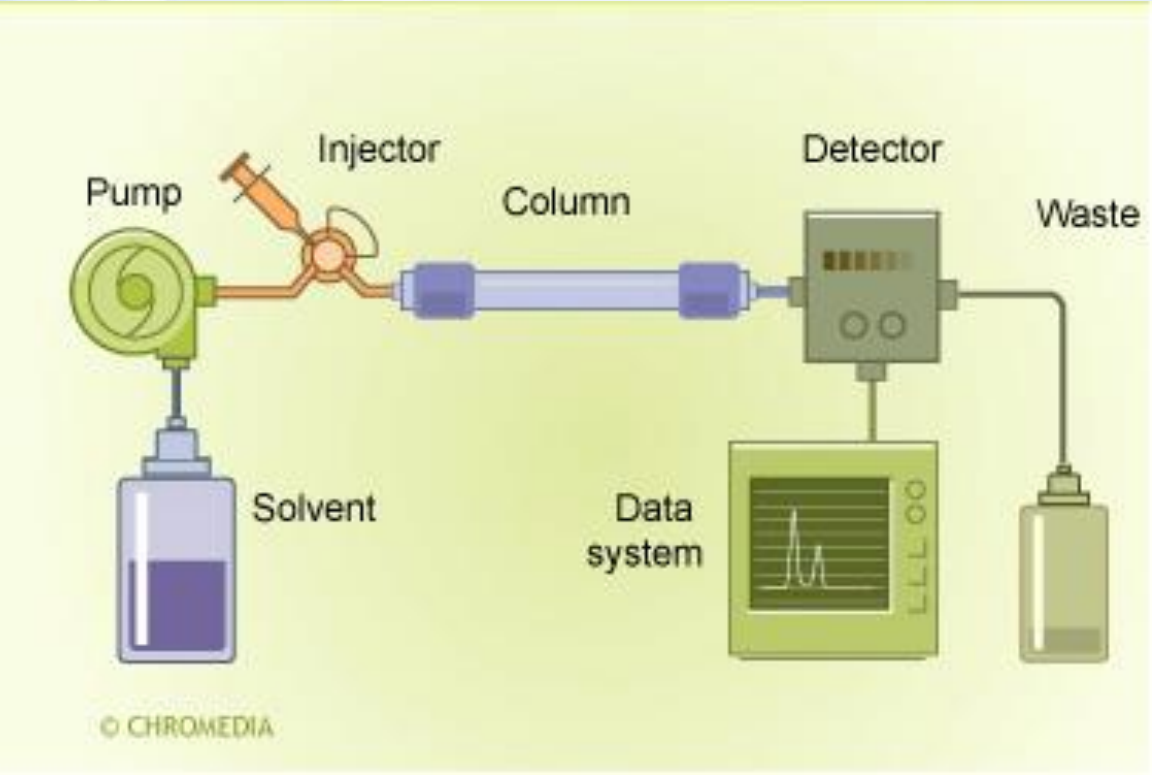
http://www.hitachi-hitec.com/global/science/lc/lc_basic_4.html

Ion Exchange Chromatography



http://www.hitachi-hitec.com/global/science/lc/lc_basic_4.html

High Performance Liquid Chromatography (HPLC)



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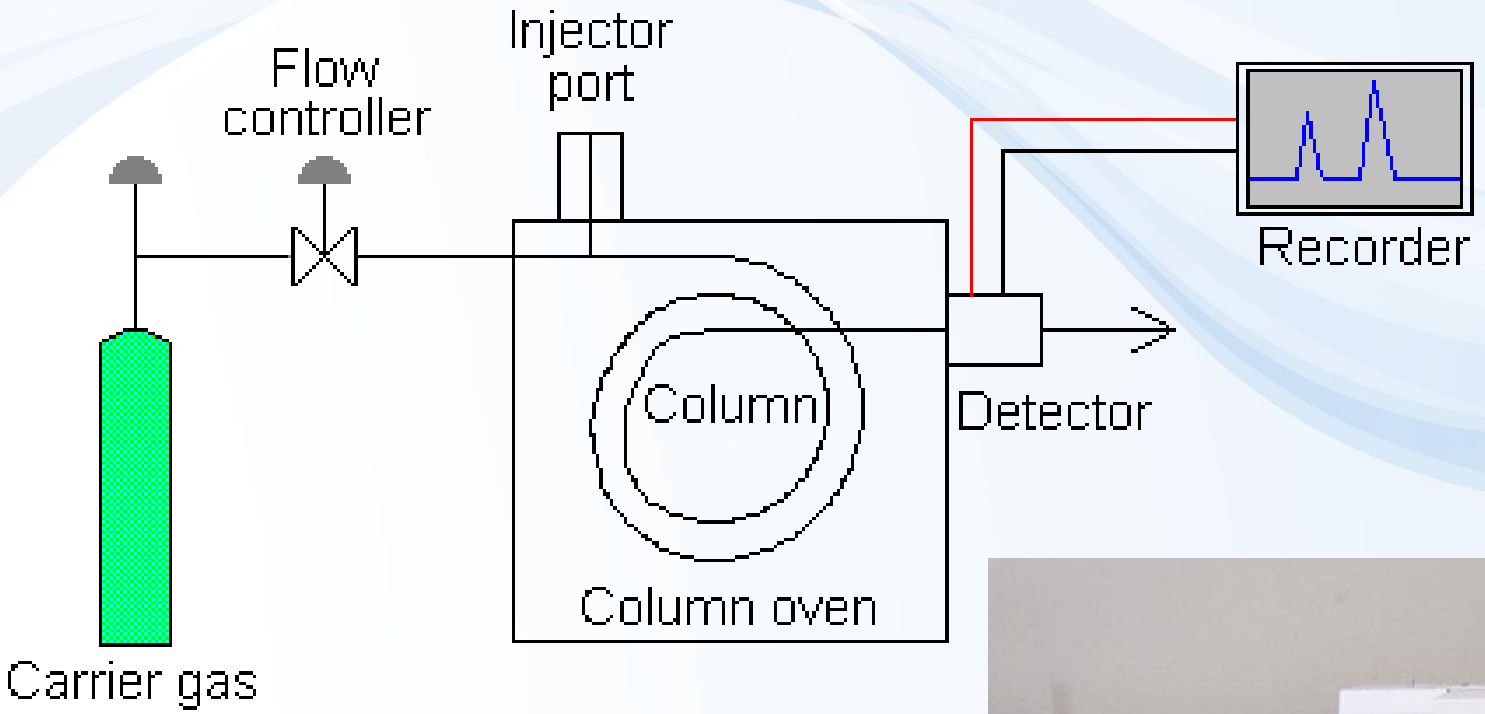
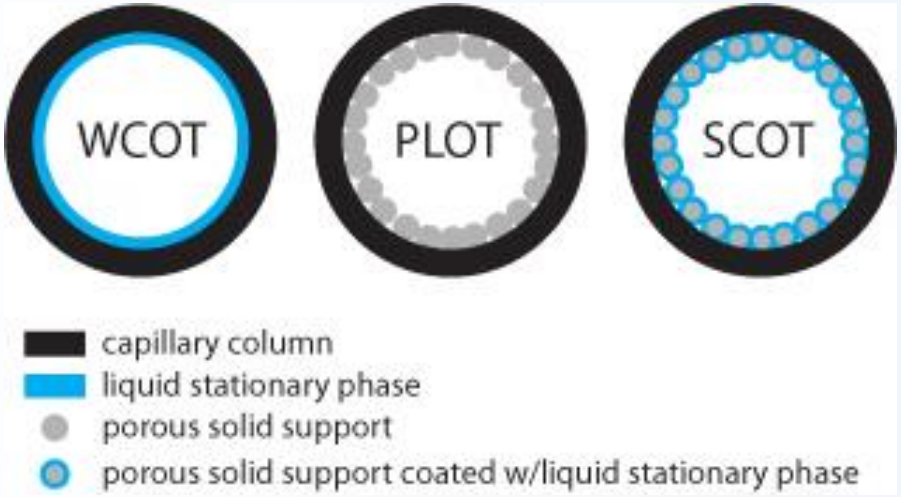
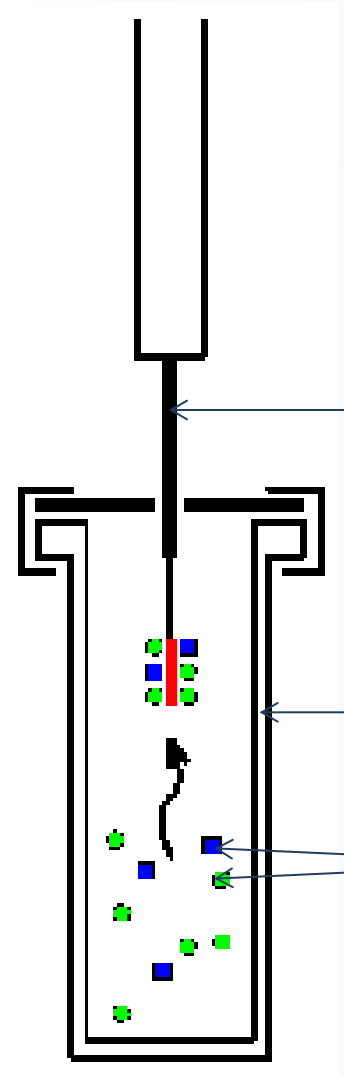
Gas Chromatography (GC)



GC column


WCOT
PLOT
SCOT
capillary column
liquid stationary phase
porous solid support
porous solid support coated w/liquid stationary phase

Solid-phase microextraction (SPME)



Fiber coated with extraction phase

Vial containing sample (liquid or gas)

Contaminants

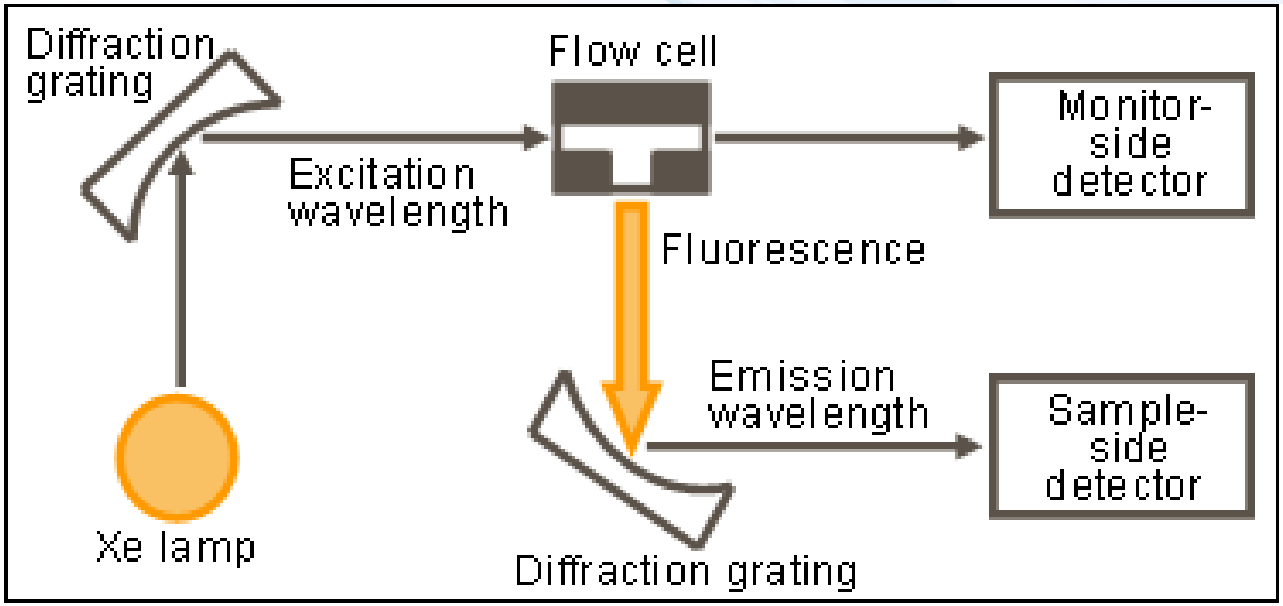
Detectors

Analytical signals:
Emission of radiation
Absorption of radiation
Scattering radiation
Reflection of radiation
Electrical current
Electrical resistance
Mass-to-charge ratio

Often used in Environmental Chemistry:
Fluorescence Detector
UV-VIS detector

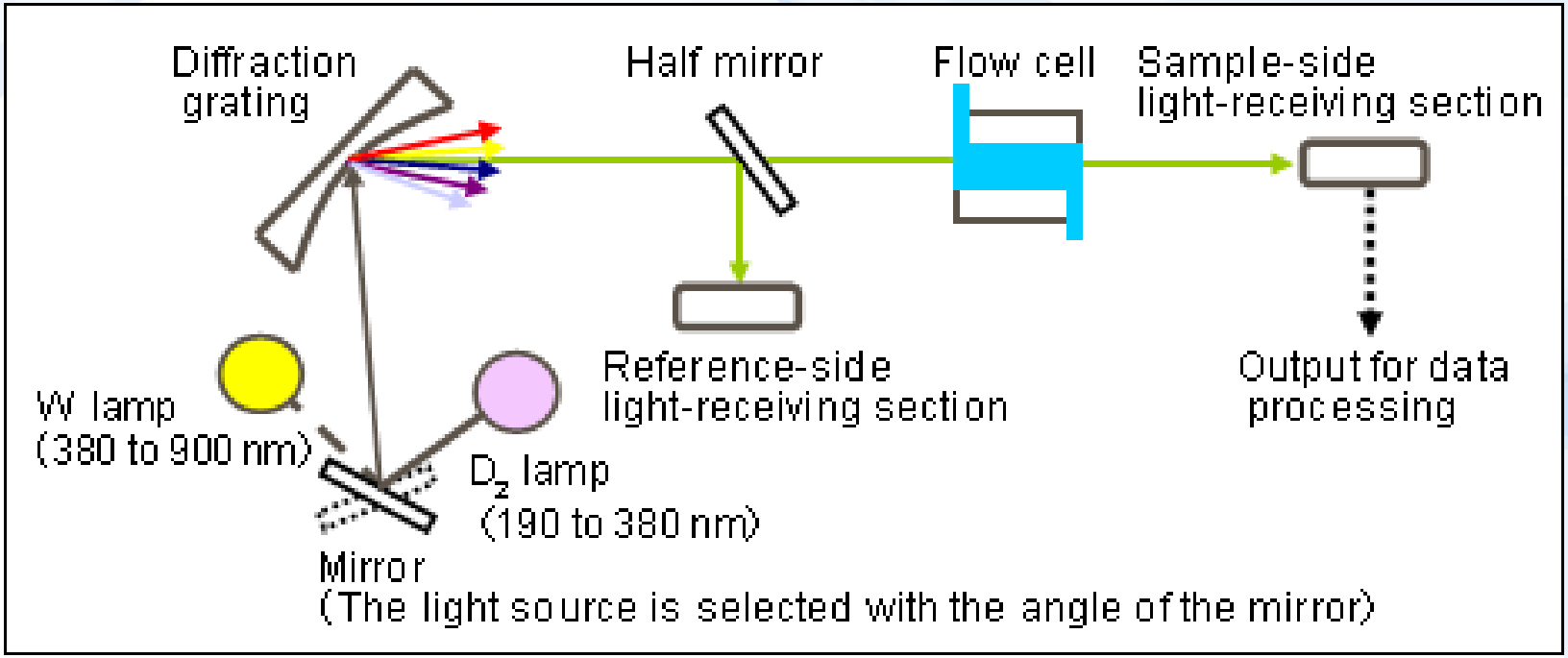
Mainly used in Environmental Chemistry:
Mass Spectrometry

Fluorescence Detector



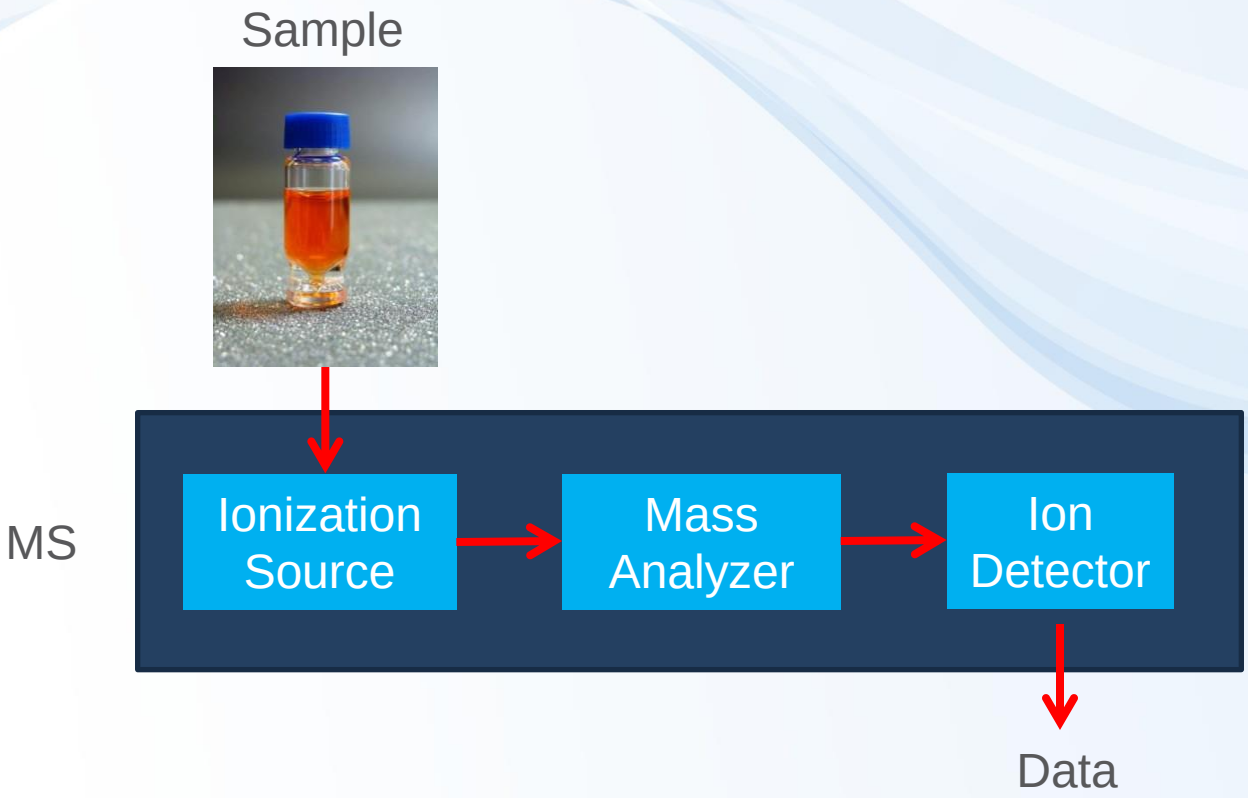
http://www.hitachi-hitec.com/global/science/lc/lc_basic_4.html

UV-VIS Detector

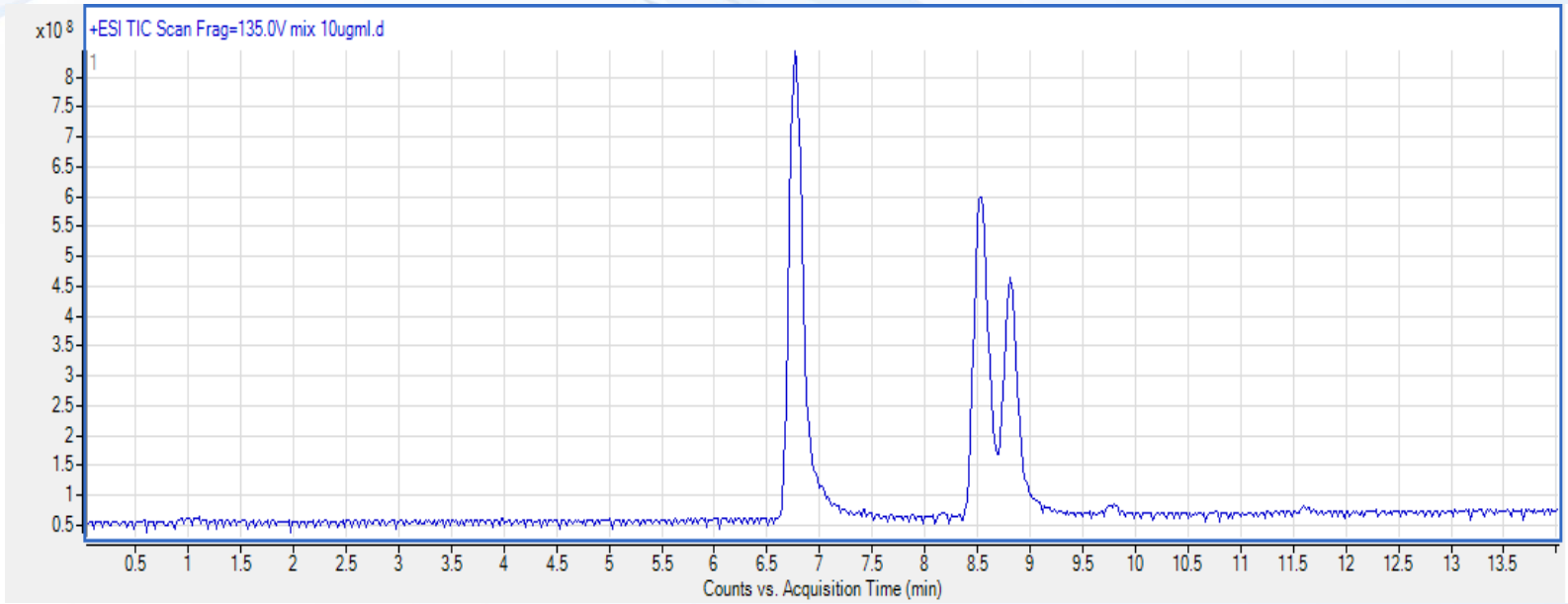


http://www.hitachi-hitec.com/global/science/lc/lc_basic_4.html

Mass Spectrometry (MS)



Chromatogram



Detector signal Intensity

Retention time (min)

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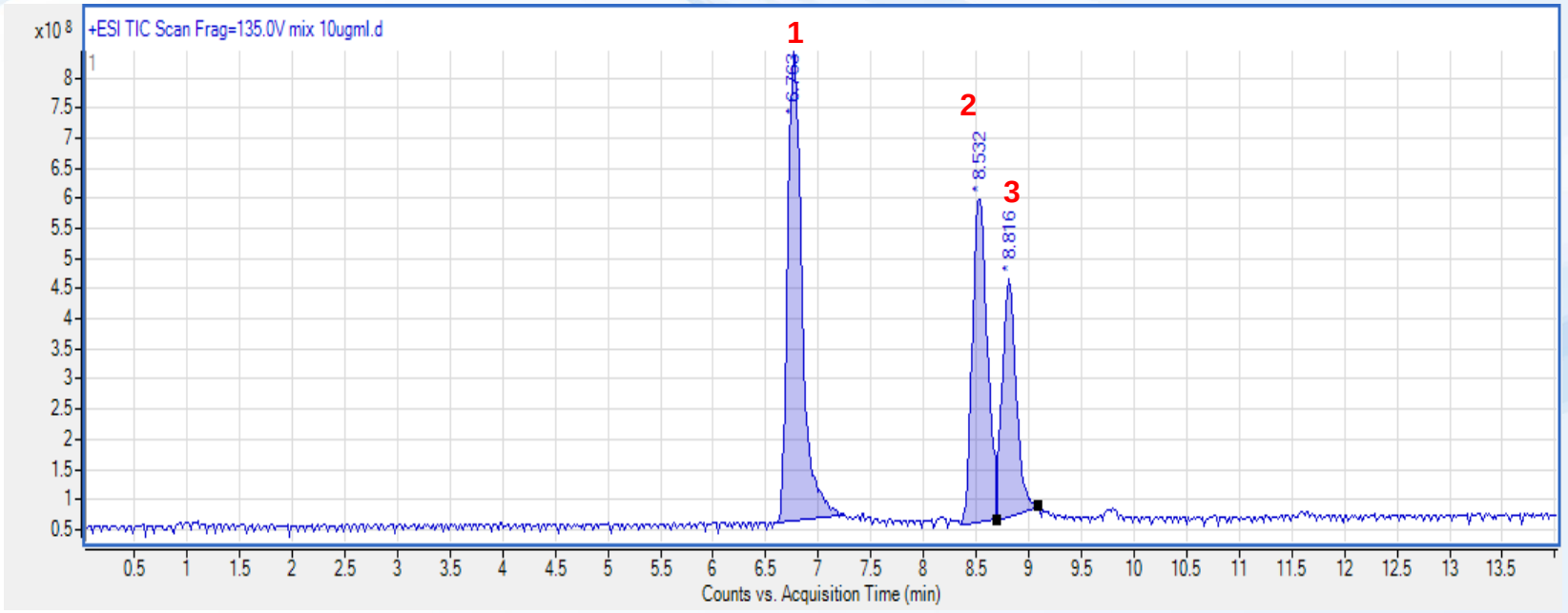
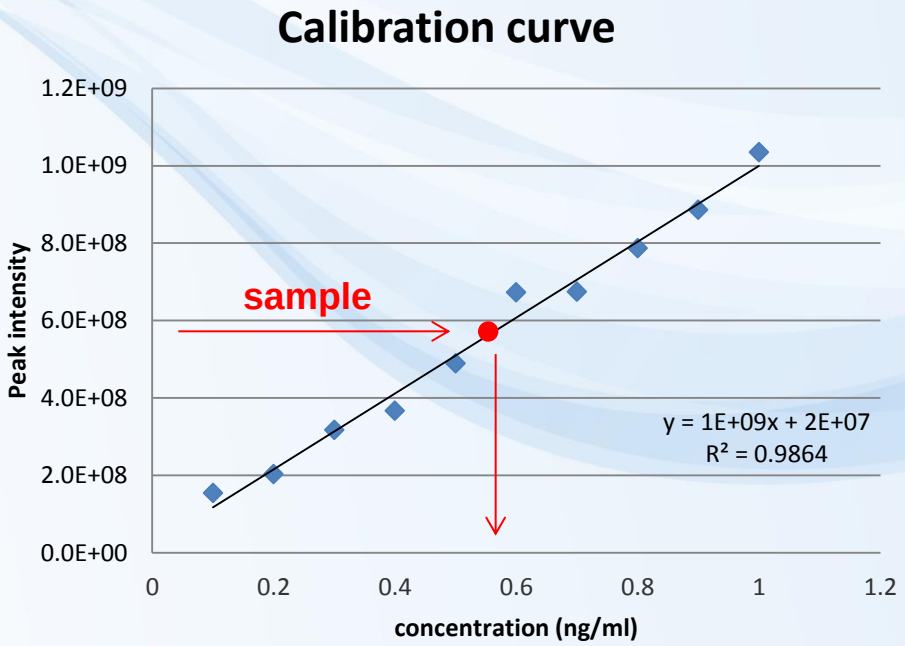
Peak Integration



Peak	RT	Area	Height
1	6.763	7496704442	779127844.4
2	8.532	5292010045	535611910.5
3	8.816	3649106823	394565640.2

Calibration Curve - Quantification



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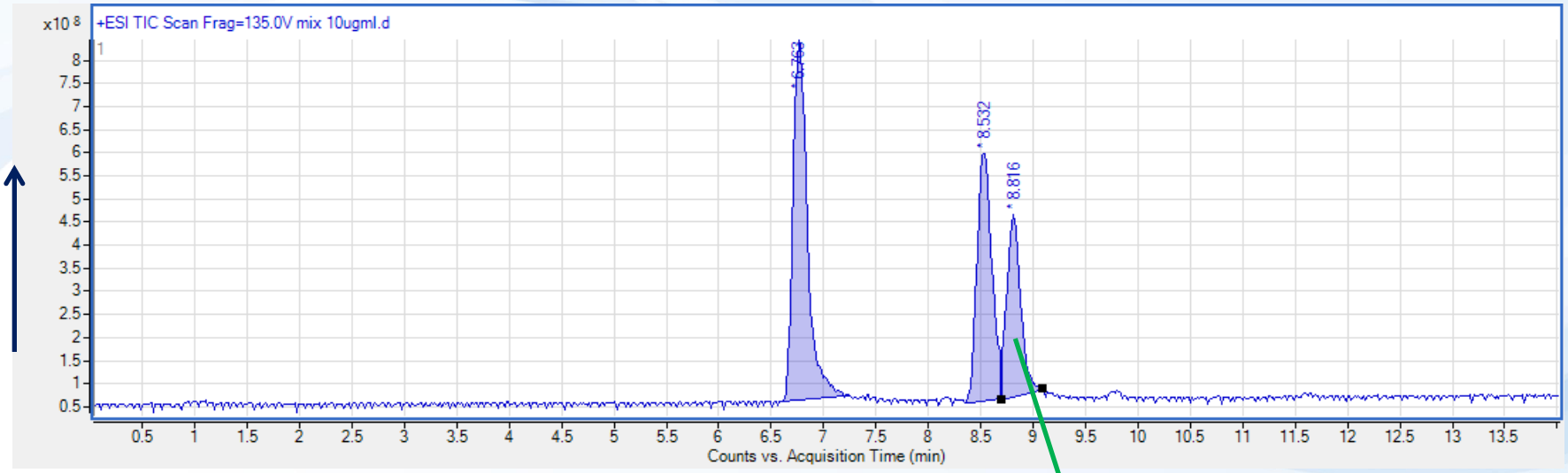
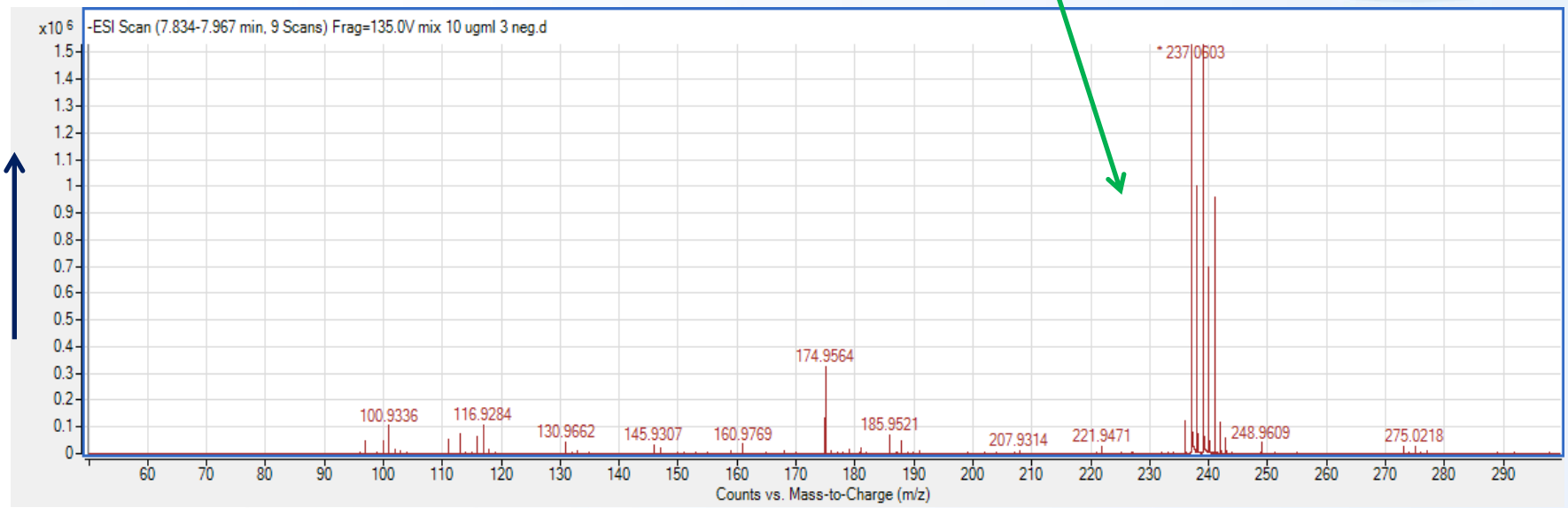
Mass Spectrum - Qualification



Detector signal Intensity



Detector signal Intensity

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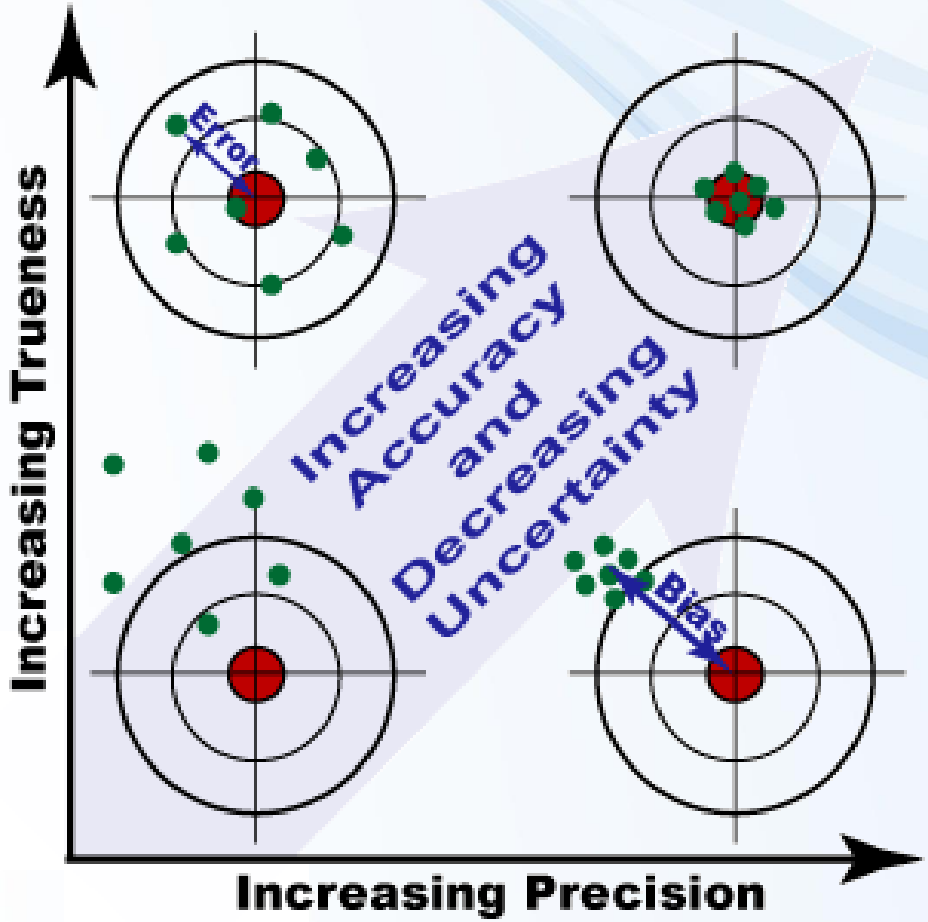
Retention time (min)

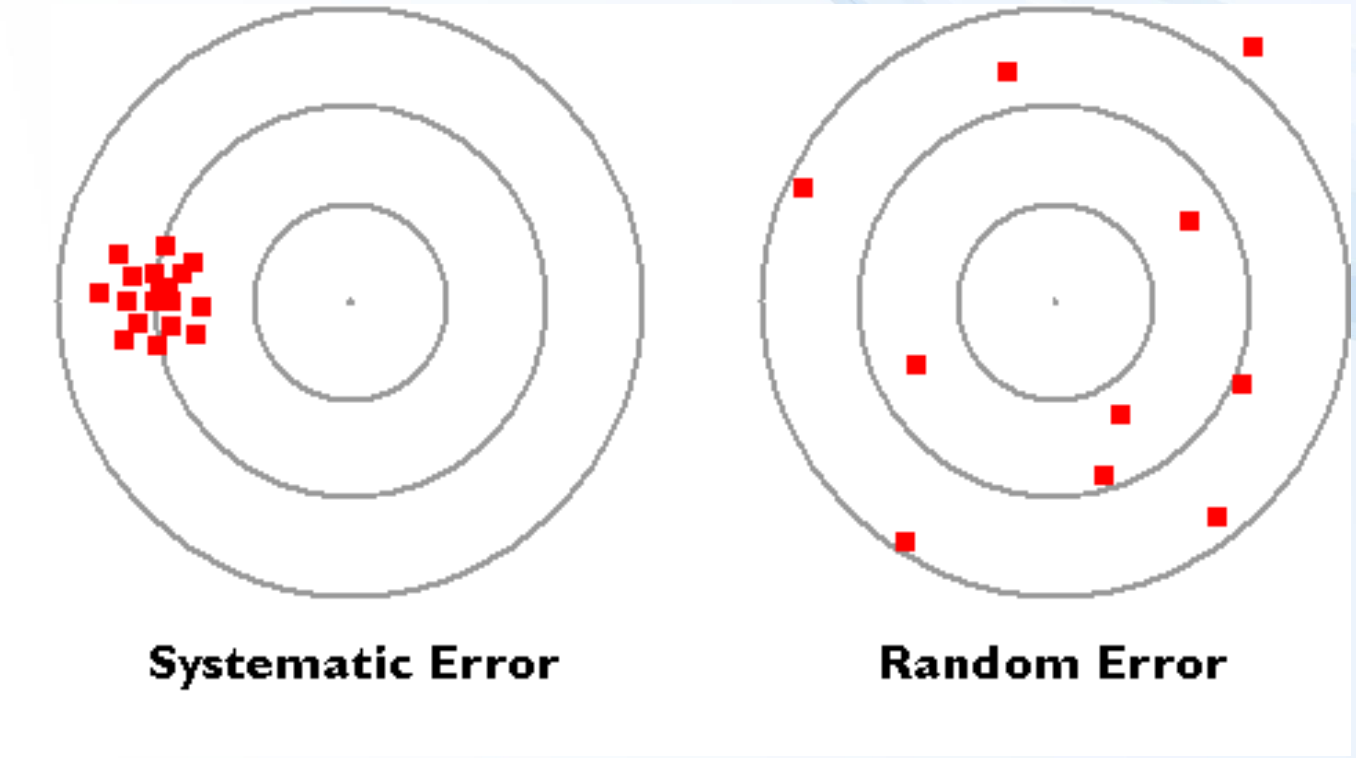
Errors

- Instrument
- Method
- Personal

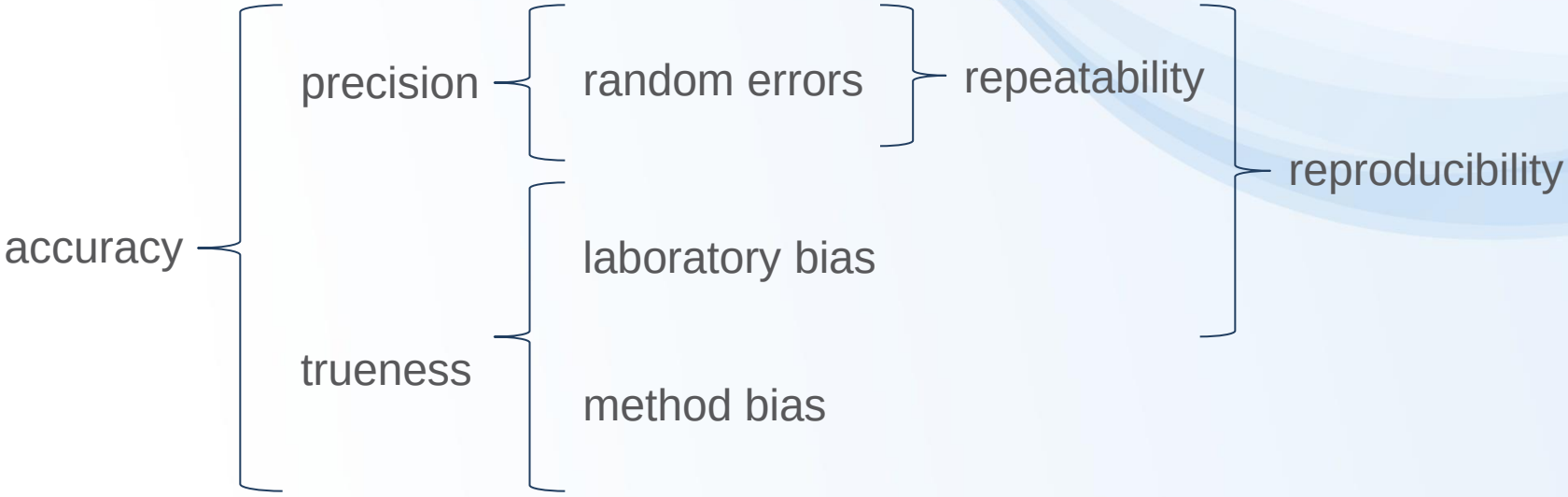
Accuracy, Precision and Trueness



Random and Systematic Errors



Measurement Errors



Eliminating Errors

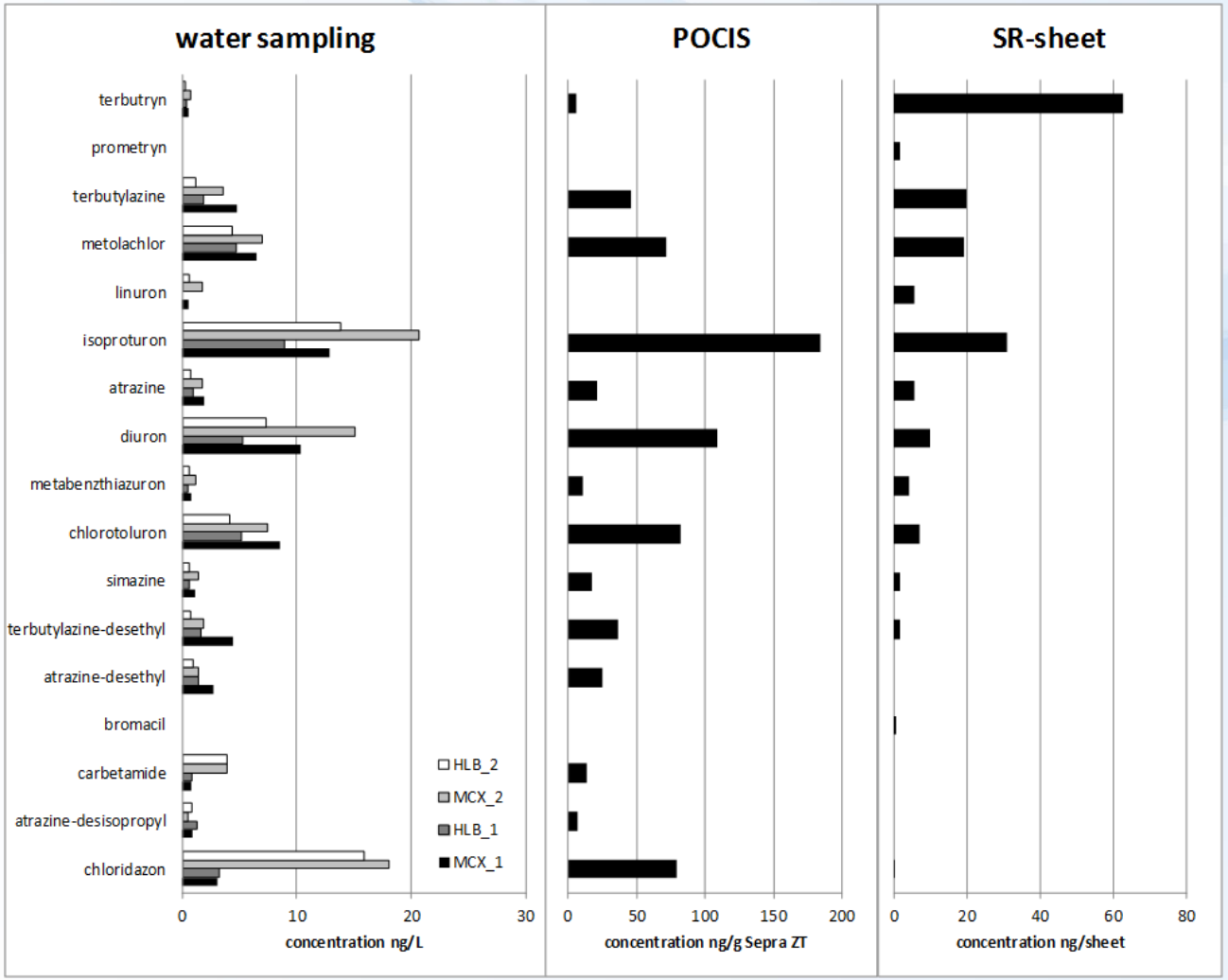
- Calibration
- Proper use of standards
- Proper use of internal labeled standards
- Blank material
- Reference material

Extraction tools for identification of chemical contaminants in estuarine and coastal waters to determine toxic pressure on primary producers

(Booij et al., Chemosphere 93 (2013) 107-114)

Method:

1. SPE / Soxhlet
2. Evaporation
3. LC-MS



Compounds:

Herbicides

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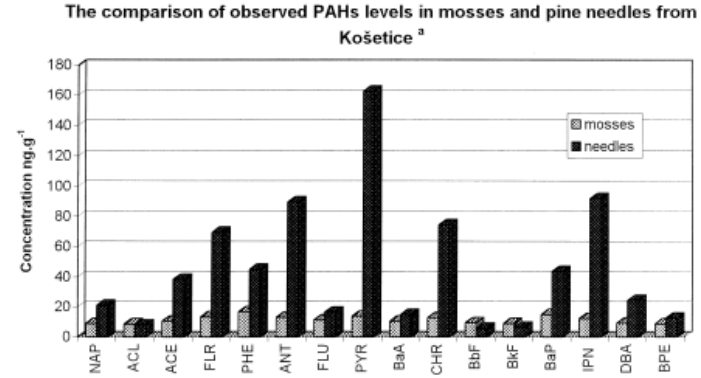
The use of mosses and pine needles to detect persistent organic pollutants at local and regional scales

(Holoubek et al., Environmental Pollution 109 (2000), 283-292)

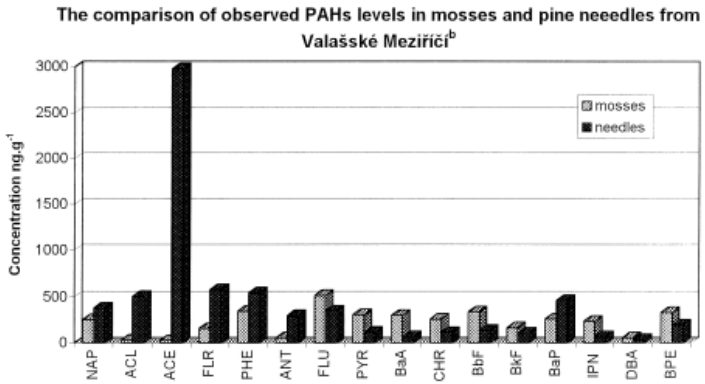
Method:

1. Drying
2. Mincing
3. Soxhlet
4. Evaporation
5. SPE
6. Evaporation
7. GC-MS

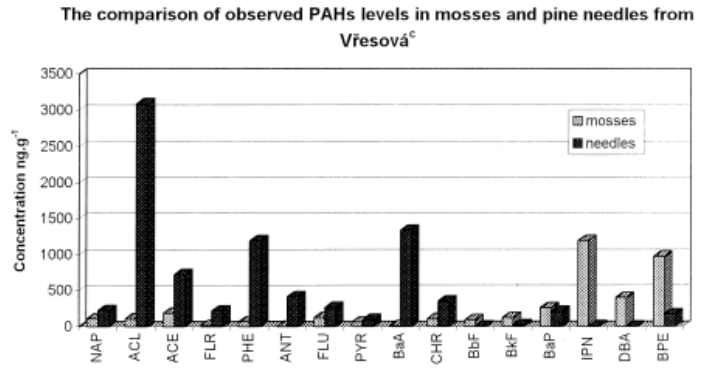
Compounds:
Polycyclic Aromatic Hydrocarbons (PAHs)



← Background site



← Industrial site



← Industrial site

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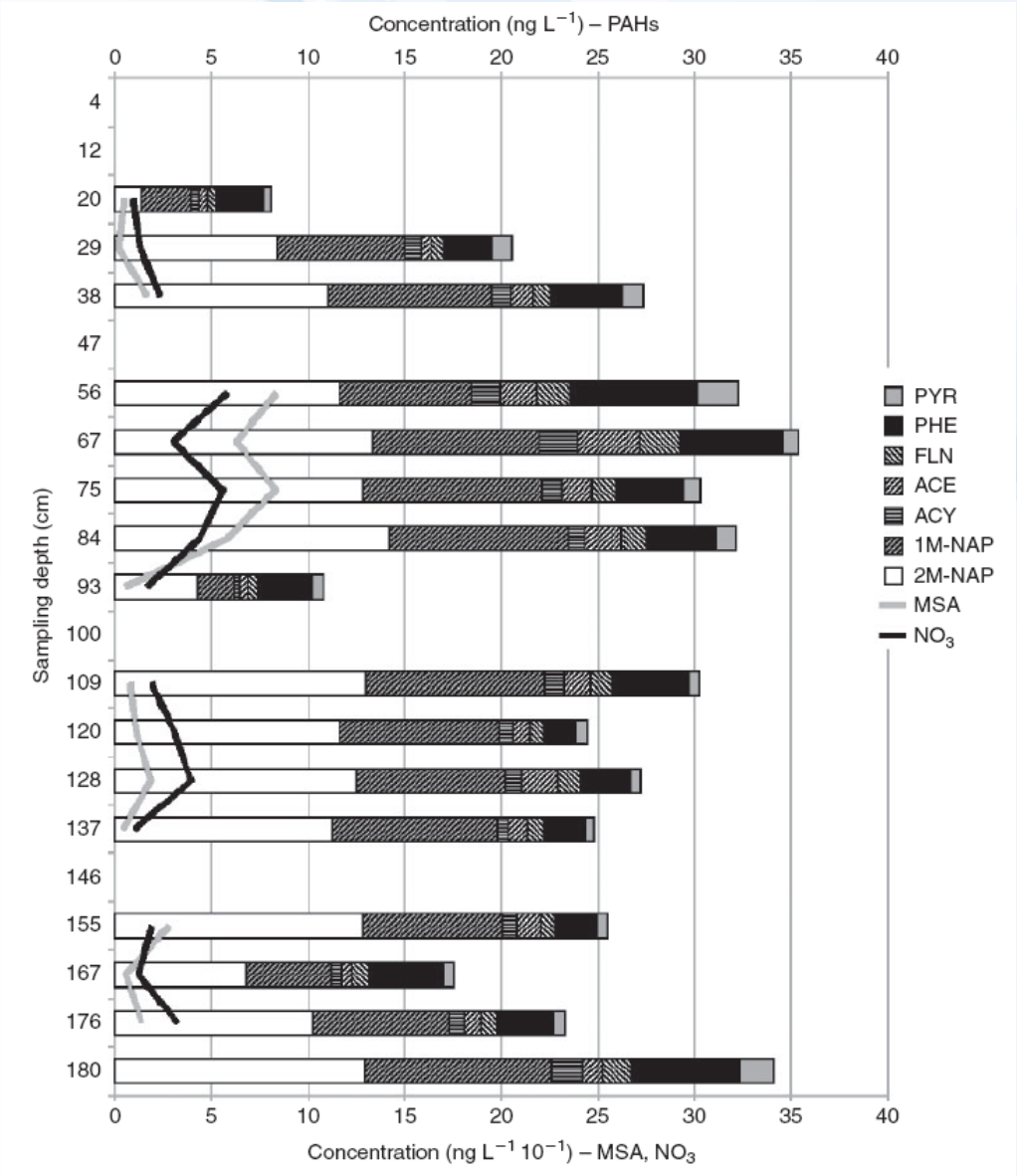
Contamination of Antarctic snow by polycyclic aromatic hydrocarbons dominated by combustion sources in the polar region

(Kukučka et al., Environ. Chem. 7 **(2010)** 504–513)

Method:

1. SPME
2. GC-MS



Compounds:

Polycyclic Aromatic Hydrocarbons (PAHs)

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PCDD, PCDF, PCB and PBDE concentrations in breast milk of mothers residing in selected areas of Slovakia

(Chovancová et al, Chemosphere 83 (2011) 1383–1390)

Method:

1. Sufuric acid/silica
2. SPE
3. GC-MS

Compounds:

Dioxins, Polychlorinated biphenyl (PCBs), Polybrominated diphenyl ethers (PBDE)

Conclusion:

Daily intake of dioxins and PCBs substantially exceeded the tolerable daily intake recommended by WHO.

Estimated daily infant intakes of $TEQ_{PCDDs/Fs}$, $TEQ_{dl\text{-}PCBs}$ (pg/kg b.w.) and PBDEs (ng/kg b.w.) in four Slovak areas.

Compounds	Krompachy $n = 10$			Košice $n = 8$			Šaľa $n = 14$			Nemecká $n = 1$
	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	
PCDDs/Fs	43.1	40.5	8.6–101	53.3	33.2	12.2–198	22.1	18.7	7.5–42.0	45.7
dl-PCBs	46.5	27.3	7.2–107	34.7	32.7	13.8–61.7	29.2	17.4	6.8–69.5	30.2
PBDEs	2.2	2.5	0.74–3.3	3.0	1.6	1.1–7.1	1.9	1.9	0.69–3.6	1.9

Identification and determination of trinitrotoluenes and their degradation products using liquid chromatography–electrospray ionization mass spectrometry

(J. Becanová et al. / International Journal of Mass Spectrometry ˇ 291 (2010) 133–139)

Method:

1. LC-MS and LC-UV

Optimization of LC-MS:

pH mobile phase

Capillary voltage

Fragmentor voltage

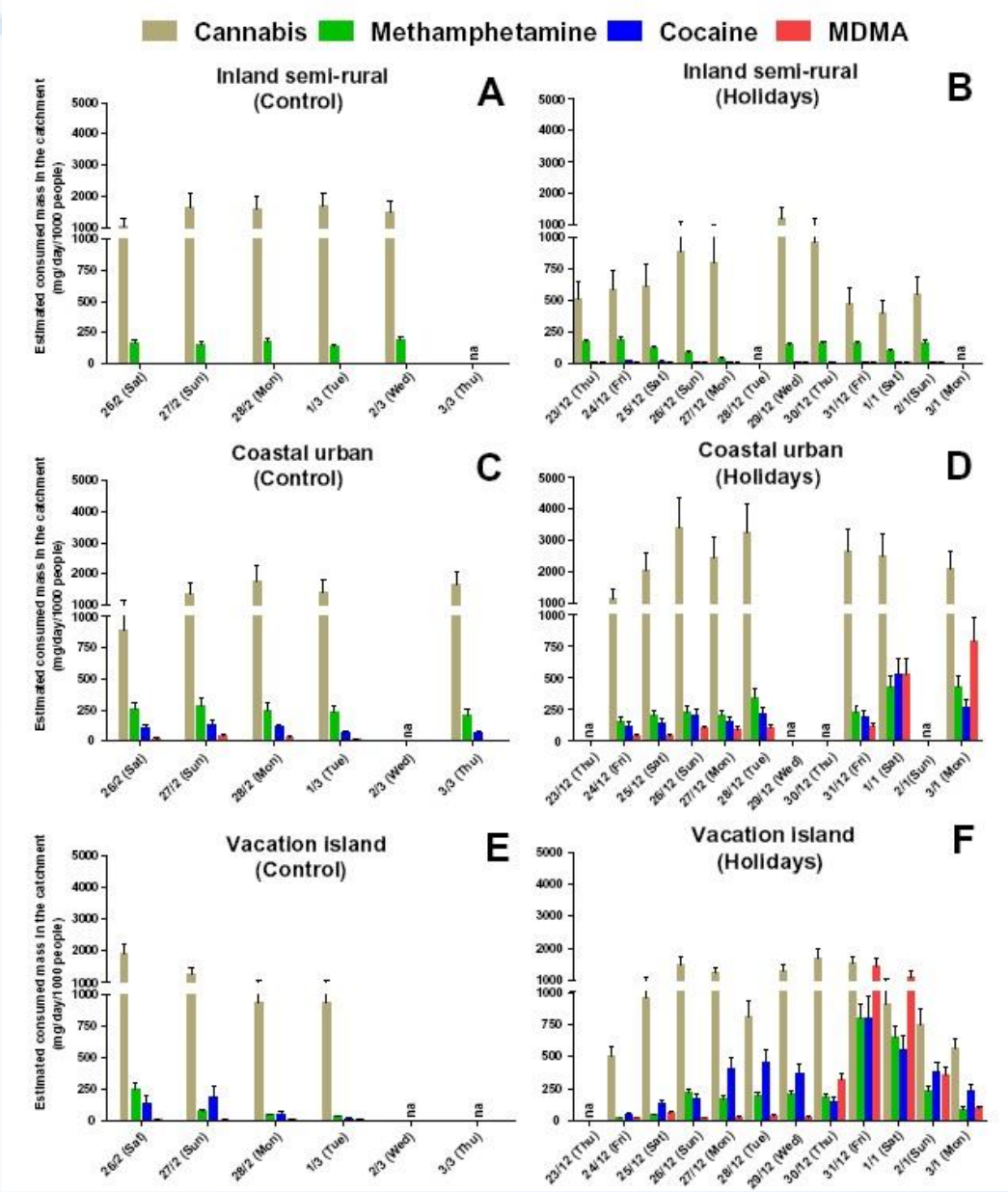
Collision energy

Profiles of illicit drug use during annual key holiday and control periods in Australia: wastewater analysis in an urban, a semi-rural and a vacation area

Yin Lai et al., Addiction, 2012, 108, 556–565

Method:
Waste water
Filtration
SPE
Evaporation
LC-MS/MS

Conclusion:
detecting changes in use of drugs



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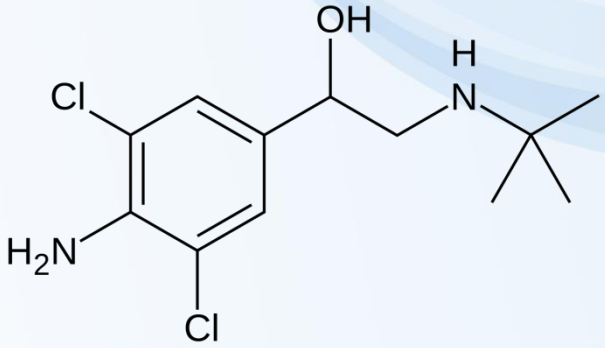
Determination of Clenbuterol in surface water

Workflow ?
Compounds class
Chemical properties
Sampling
Sample clean-up and extraction
Chemical analysis



http://www.chemspider.com/Chemical-Structure.2681.html
Mw 277
Log Octanol-Water Partition Coef (SRC):
Log Kow (KOWWIN v1.67 estimate) = 2.00

Boiling Pt, Melting Pt, Vapor Pressure Estimations (MPBPWIN v1.42):
Boiling Pt (deg C): 378.89 (Adapted Stein & Brown method)
Melting Pt (deg C): 138.02 (Mean or Weighted MP)
VP(mm Hg,25 deg C): 5.56E-008 (Modified Grain method)
Subcooled liquid VP: 7.66E-007 mm Hg (25 deg C, Mod-Grain method)

Water Solubility Estimate from Log Kow (WSKOW v1.41):
Water Solubility at 25 deg C (mg/L): 3320
log Kow used: 2.00 (estimated)
no-melting pt equation used

Water Sol Estimate from Fragments:
Wat Sol (v1.01 est) = 46916 mg/L

Sacher et al., Journal of Chromatography A, 938 (2001) 199–210

1 L water

SPE

LC-MS/MS

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