ENVIRONMENTAL CHEMICAL ANALYSIS III

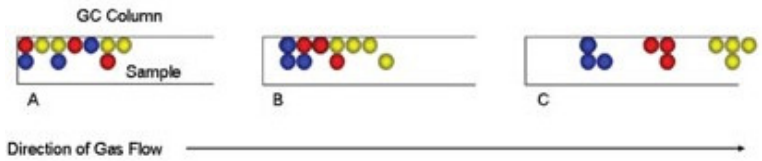
Chromatographic Methods

Gas Chromatography (GC)

Gas chromatography is a separation process in which a gaseous solute is carried through the column by a gaseous mobile phase, also called ***carrier gas***.

Stationary phase: A nonvolatile liquid, coated on a solid support, or a solid.

Separation of a 3-component mixture inside a GC column

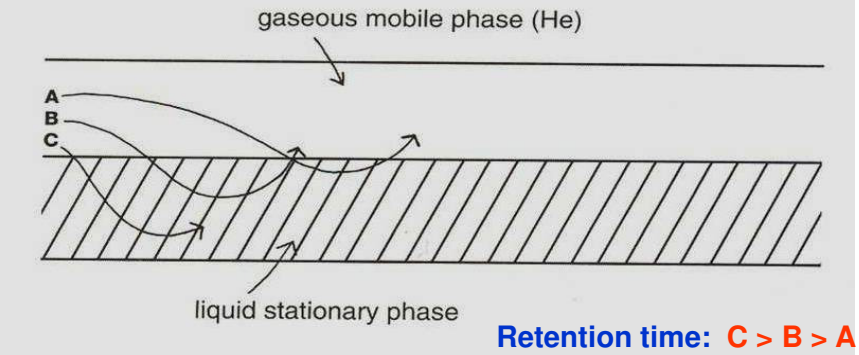


Which component has the highest affinity for (or "solubility" to) the stationary phase?

Image available at http://www.labnews.co.uk/feature_archive.php/2079/5/blood,-sweat-and-tears---gc/ms-in-forensic-toxicology

Gas Chromatography (GC)

Note: In order to be carried through the column the sample components must be gases or volatile liquids



Retention time: C > B > A

Volatile = high vapor pressure = low boiling point

Volatility: A > B > C **Solubility in the s.p. C > B > A**

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GC INSTRUMENTATION

Theory: http://www.youtube.com/watch?v=4Xaa9WdXVTM

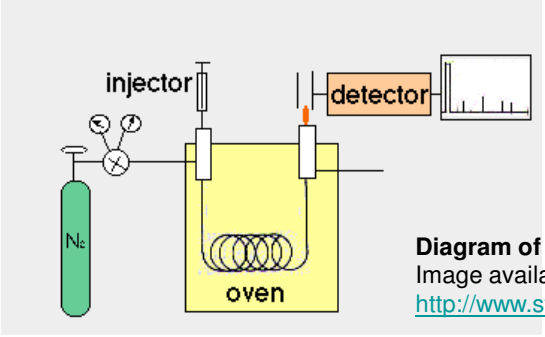

Diagram of a typical gas chromatograph. Image available at http://www.sfu.ca/bisc/bisc-429/GLC.html

Carrier gas (usu. He) = the mobile phase; Carries the components of a mixture from the **injection port** (where the sample is introduced) through the **column** and into the detector

- The **column**, housed in an **oven** for temperature control, contains the stationary phase, which separates the components of a mixture

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Applications of GC

GC works well for the separation and quantitation of:

- ***Volatile*** or ***semivolatile*** organic compounds

  Examples:

  - HCs, Low MM organics
  - Volatile organic compounds, VOCs, like low MM halogenated compounds in drinking water
    - Chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2)
  - Pesticides and their residue
  - PAHs

- Thermally stable compounds

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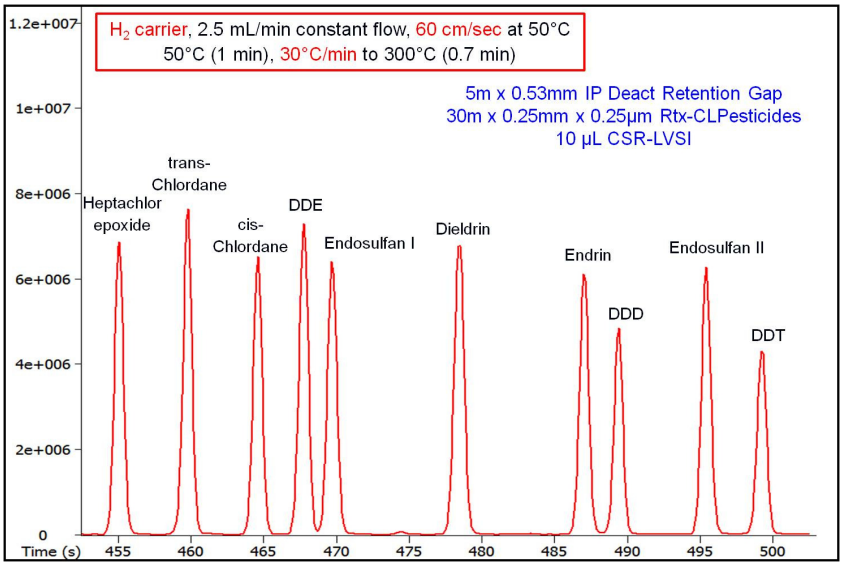

GCMS separation of organochlorine pesticides. Image available at http://blog.restek.com/?p=5956

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

- **Similar in separation principle to GC but**
  - it is a liquid-phase separation
  - it is usually a room temp. separation
  - it is used for the separation of non-volatile analytes (high MM)
- **Not as common as GC for environmental samples**
  - Most pollutants are volatile; GC is faster
- **Ion chromatography** – used ion-exchange columns to separate ions in water samples
  - Ex. Nitrates and phosphates (nutrients) analysis

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Methods of Analyzing Water and Wastewater

Chemical parameters commonly determined in water

Chemical species	*Significance in water*	*Methods of Analysis*
Acidity	Indicates industrial pollution; acidic mine drainage	Titration
Alkalinity	Water treatment; algal productivity	Titration
Hardness (Ca^{2+}; Mg^{2+})	Water quality; Water treatment	Atomic absorption (AA); Titration
Metals (Like Pb, Cd, Hg, As, Cr)	Toxic pollutants	AA, ICP (Plasma Emission)
Anions (Like NO_3^- and PO_4^{3-})	Algal productivity; Toxicity; Water quality	Spectrophotometry (UV/vis); Ion chromatography (IC)

Analytes ***Instrumental methods***

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Methods of Analyzing Water..., Cont.

Chemical parameters commonly determined in water (Cont.)

Chemical species (Cont.)	***Significance in water***	***Methods of Analysis***
Organic carbon	Indicates organic pollution	Oxidation – CO_2 measurement
Organic contaminants	Indicates organic pollution	Activated carbon adsoprtion
Oxygen demand, BOD (Biochemical)	Water quality and pollution	Microbiological - titration
Oxygen demand, COD (Chemical)	Water quality and pollution	Chemical oxidation - titration
Pesticides	Water pollution	Gas chromatography (GC)

Analytes ***Instrumental method***

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Analysis of Solid Wastes and Wastewater

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Analysis of Solids and Wastewater

Sample matrix = anything in the sample except the analyte

Question 1. (a) What constitute the **matrix** in a sample of soil contaminated with oil spill? (b) What are the **analytes**?

A. (a) The matrix consists of the ***soil*** itself and ***soil components*** (like clay, silt, sand, microorganisms, humic substances, soil nutrients, etc.) other than the spilt oil

(b) The analyte would be the oil and its constituents (mostly ***hydrocarbons***)

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Analysis of Solids and Wastewater

Question 2

(a)How will you remove the analytes from the matrix?

(b) What ***instrumental method*** is appropriate for the qualitative and quantitative analysis of oil components , say before and after remediation?

A: (a) Extraction with an organic solvent, or vaporization (by heating the soil) followed by trapping (through sorption) of the vapor components

(b) GC (applies to volatile components) with a MS detector - to aid in identification of hydrocarbon components

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Analysis of Solids and Wastewater

The previous slide demonstrates the complications of analyzing solid wastes compared to aqueous samples like drinking water

- Solid wastes and wastewater have a ***more complex matrix*** than water (like drinking water)
  - Adds one step to the instrumental analysis procedure
    - ***Sample preparation*** - a necessary evil

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Sample Preparation for Solids and Wastewater

Wastewater

- ***Acid digestion*** - to analyze metals using AA or ICP
- ***Solvent extraction*** - to analyze organics (e.g. Benzene in wastewater) using GC or UV/Vis spectrometry

Solid waste

- ***Drying & acid digestion*** - to analyze metals using AA or ICP
- ***Solvent extraction*** - to analyze organics using GC, HPLC or UV/Vis spectrometry

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Sample Preparation for Solids and Wastewater

Solvent extraction

Images available at http://www.dionex.com

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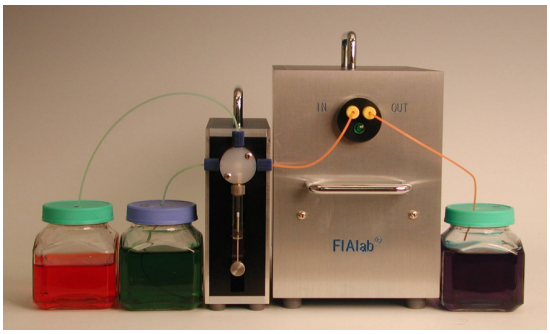
Some EPA Methods for the Analysis of Solids and Wastewater

Nitrogen, Nitrate-Nitrite in water and wastewater:
Method 353.2 (Colorimetric, Automated, Cadmium Reduction)

Visible spectrometry/spectroscopy

- NO_3^- is colorless, so a chemical reaction is done to produce a colored complex
- The colored complex absorbs visible light



Flow injection analyzer (FIA): Image available at http://www.flowinjection.com/whatsnew.html

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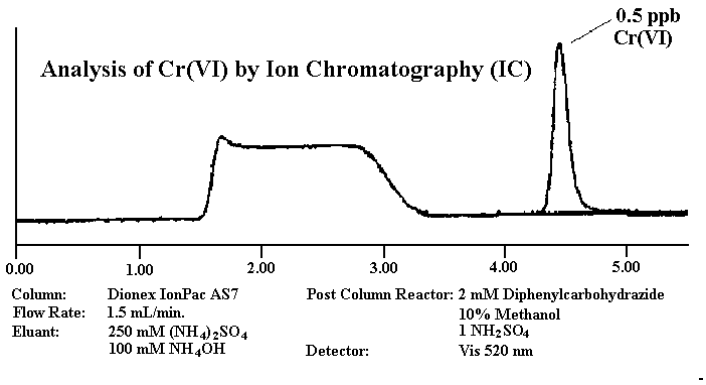
Some EPA Methods for the Analysis of Solids and Wastewater

Hexavalent Chromium [Cr(VI)] by Ion Chromatography (IC)



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Some EPA Methods for the Analysis of Solids and Wastewater

PAH analysis: EPA 8100 HPLC and EPA 8270 GC methods

Mercury in Solids and Solutions by Thermal Decomposition, Amalgamation, and Atomic Absorption Spectrophotometry: EPA Method 7473

Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma- Atomic Emission Spectrometry. EPA Method 200.7: EPA 821-R-01-010, January 2001

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Some EPA Methods for the Analysis of Solids and Wastewater

Organo-Halides in Wastewater, Soil, Sludge, Sediment, and Tissue by GC/HSD, EPA Method 1656, Revision A, EPA-821-R-00-017, September 2000

Organo-Phosphorus in Wastewater, Soil, Sludge, Sediment, and Tissue by GC/FPD, EPA Method 1657, Revision A, EPA-821-R-00-018, September 2000

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