Overview of Experiments VI-VIII

CU- Boulder

CHEM-4181

Instrumental Analysis Laboratory

Prof. Jose-Luis Jimenez

Spring 2007

Lecture will be posted on course web page

Reminder of SCE Procedure and Dates

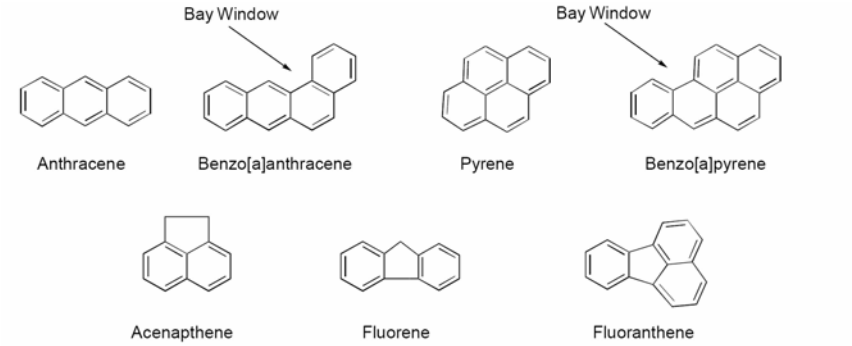
- By 10:00 AM Mon Mar 12: email to TAs & Jose w/ groups
- By 9:00 AM Fri Mar 16
  - email sent to TAs & Jose, explaining your idea
  - We will give you feedback about whether idea is ok, or if you need to find new one
- By 9:00 AM Wed Mar 21
  - 2-3 page proposal sent electronically to TAs & Jose
    - 1 page introduction/motivation:
      - Question / hypothesis
      - Sample collection and storage
      - Properly cite AT LEAST 1 journal article
    - 1 page on analytical procedure & instrument
      - Properly cite AT LEAST 1 journal article
    - 1 page on chemicals needed, safety aspects, and waste generated
  - We will review the proposals and inform you of problems

Experiments VI-VIII

- Weeks of Mar 5 to Mar 19
- Three types instruments
- E6: PAHs in diesel exhaust
  - GC-MS
- E7: PAHs in cigarette smoke
  - HPLC w/ fluorescence & absorbance detection
- E8: Heavy metals in water
  - Electrochemistry

Polycyclic Aromatic Hydrocarbons

- Multiple fused benzene & pentadiene rings:



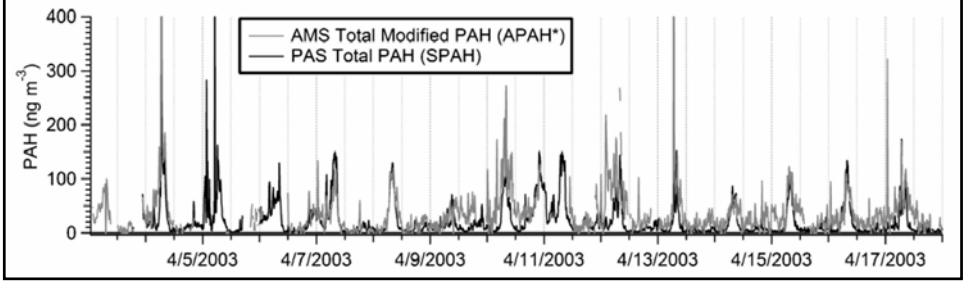
- Several are very toxic, mutagenic, and carcinogenic
- Produced in combustion processes (cars, trucks, your toaster when bread burns…) before soot

PAHs in Ambient Air

+Model
MASPEC-13429; No. of Pages 19
ARTICLE IN PRESS
Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
International Journal of Mass Spectrometry xxx (2007) xxx–xxx
Mass Spectrometry
www.elsevier.com/locate/ijms

Detection of particle-phase polycyclic aromatic hydrocarbons in Mexico City using an aerosol mass spectrometer

Katja Dzepina[a,b], Janet Arey[c], Linsey C. Marr[d,1], Douglas R. Worsnop[e], Dara Salcedo[f], Qi Zhang[a,2], Timothy B. Onasch[e], Luisa T. Molina[d,3], Mario J. Molina[d,g], Jose L. Jimenez[a,b,*]

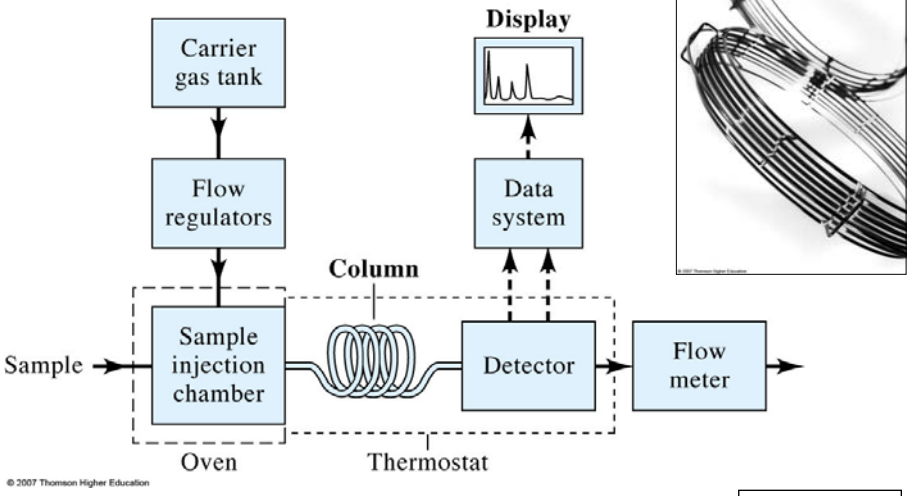


E7: PAHs in Diesel Exhaust

- Summary:
  - Extract soot w/ methylene chloride
  - Solvent exchange w/ hexanes in microscale flash column
    - http://orgchem.colorado.edu/hndbksupport/colchrom/colchromprocmicroflash.html
  - Analyze for 3 PAHs w/ GC-MS
- Practical aspects
  - Time consuming, so a person should work on standards while another starts extraction
- Safety:
  - Diesel exhaust is a "probable human carcinogen"
    - PAHs among several other toxics. Wear gloves
  - Pay attention to waste
- Quality control
  - Calibration, blank spike, and standard addition

Gas-Chromatograph (GC)

- Objective: separate compounds in mixture

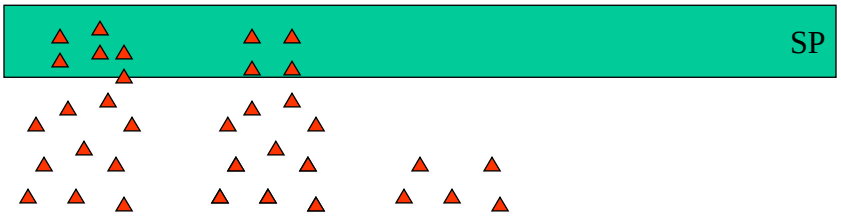


Figs 27-1 and 27-6, Skoog

Clicker Q

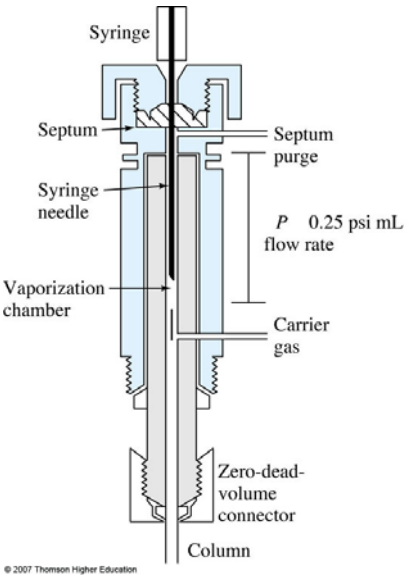
- What causes separation of compounds in GC? Different compounds…
  - A. have different velocities in the gas-phase (Boltzmann)
  - B. stick differently to the surface of the column
  - C. have different solubilities in helium
  - D. partition differently to the coating of the column
  - E. I don't know

Schematic of Column Chromatography



- If analyte has some affinity to the stationary phase, it will be retarded
  - Equilibrium $K = \frac{C_s}{C_M}$
  - Kinetics
    - Molecular mass transfer: diffusion
  - Emerge at the detector after "*retention time*" t_R

GC Injector and Sample Loop



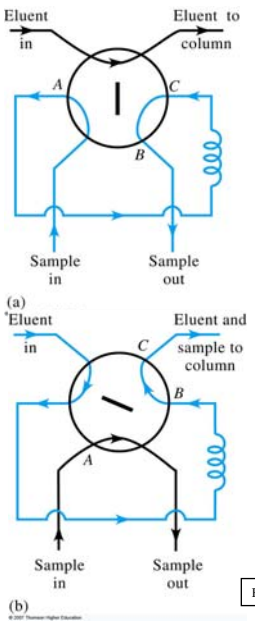
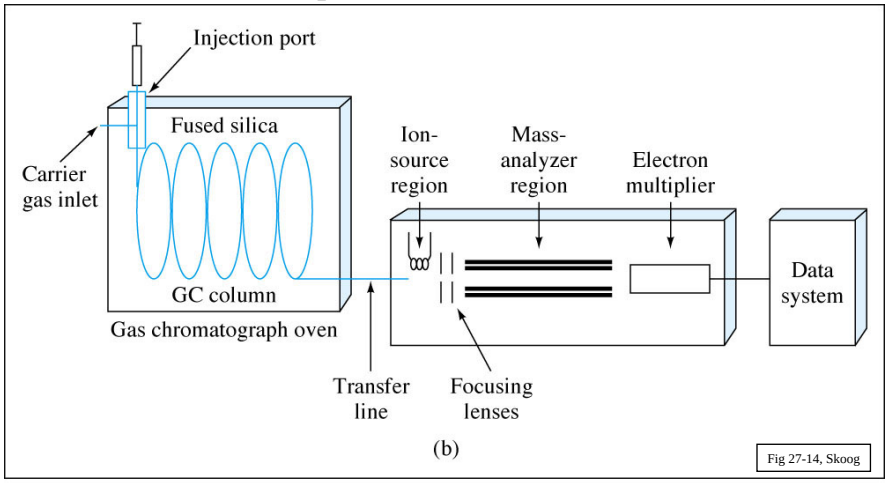


Fig 27-4 & 27-5, Skoog

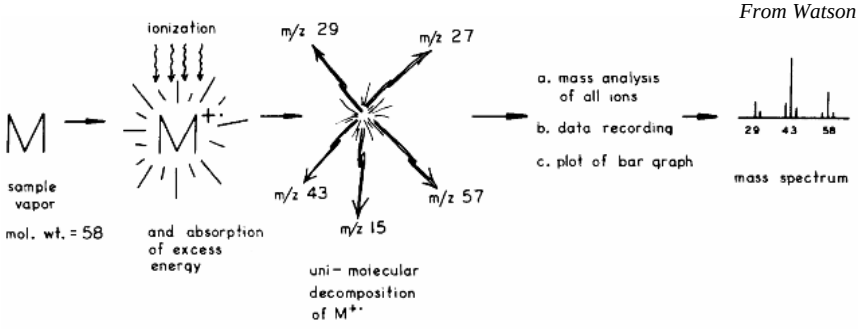
GC-Mass Spectrometer

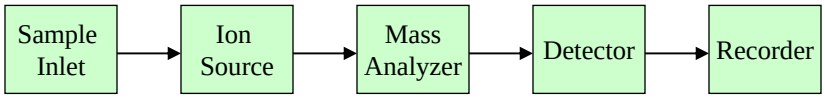
- Detection by injecting sample into vacuum, creating ions, analyzing ions w/ MS
- One of several possible GC detectors (FID…)



Concept of Mass Spectrometry

From Watson





E6: PAHs in Cigarette Smoke

- Summary:
  - Pull cigarette smoke through a filter using vacuum
  - Filter is extracted w/ solvent
  - Analyze extract w/ HPLC w/ fluorescence & absorbance detection
  - http://www.chem.uoa.gr/Applets/AppletChrom/Appl_Chrom2.html
- Practical aspects
  - Chromatography will take 4-5 hrs. One member of group should run standards (provided) while another collects cigarette samples
- Safety:
  - Gloves: you'll be handling PAH standards, also solvents (acetonitrile, methanol, methylene chloride)
  - Remove flammable materials when lighting cigarettes
  - Pay attention to waste
- Quality control
  - 3-point calibration curves
  - Spike: inject standard and extract in the same way as sample

High-Performance Liquid Chrom. (HPLC)

- Conceptually very similar to GC, but several hundred atm, so more elaborate and expensive equipment

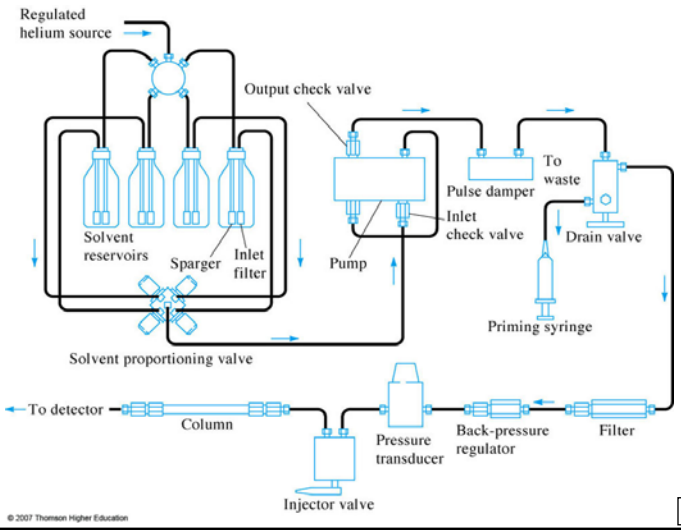


Fig 28-3, Skoog

Clicker Q

- Why is high pressure needed in HPLC?
  - A. To remove gases from the liquid phase
  - B. To increase the solubility of the analytes in the eluent
  - C. To allow heating of the column to higher temperatures
  - D. To flow the liquid through tiny particles
  - E. I don't know

Absorbance Detection

- Just like UV/Vis used before, but at end of column

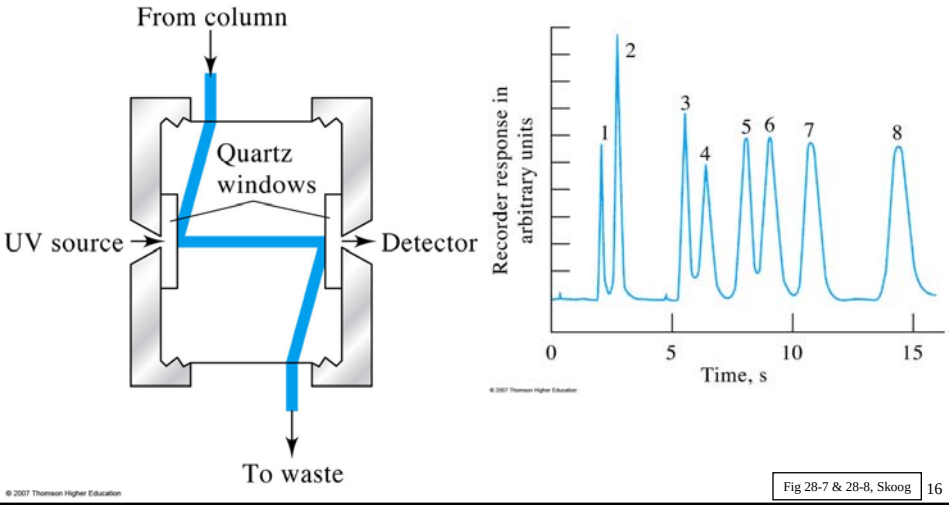


Fig 28-7 & 28-8, Skoog

E8: Metal Ions in Water

- Summary:
  - Analyze H_2O samples for Pb, Cd, and Zn ions
  - Annodic Stripping Voltammetry (ASV)
- Safety
  - Concentrated nitric acid solutions
    - Goggles, bicarbonate
  - Toxic Hg and Pb
    - Gloves
- Quality control
  - Standard addition for all 3 samples

ASV

- Analyte is first deposited from solution into an electrode by applying a potential
- Then potential is reversed, and analyte is redissolved ("stripped") into solution again
  - Measure potential (species) & current (amount) needed to do this

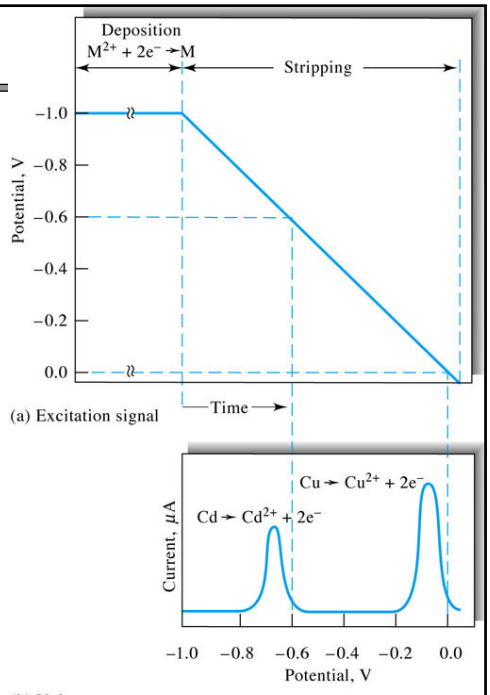


Fig 25-34, Skoog