CHEM 212
Exam 4
Fall 2014

Name Key

1. (15 pts) Diagram and describe the function of each part of a **GENERALIZED** mass spectrometer.

Ionization & acceleration → ion selection → detection

1. ions are generated from analyte molecules & accelerated by a potential difference into ion selector

(5pts) 2. Ions are separated on the basis of m/z

3. Ions are converted to e^- which are multiplied & generate a current, which is converted to a voltage & measured.

What does a mass spectrometer measure?

(2pts) m/z

What is the pressure inside a mass spectrometer (roughly)? Why is pressure controlled?

$\sim 10^{-9}$ bar

(3pts) Vacuum is maintained to minimize analyte ion - air collisions

(3pts) Referring to the diagram, where would you anticipate observing the following for pentobarbital

Molecular ion

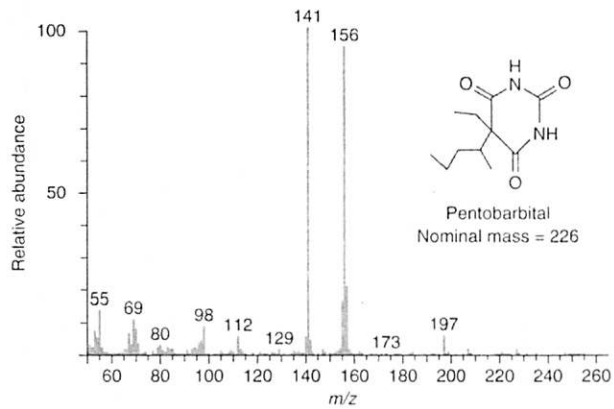
$\frac{m}{z} = 226$

Protonated molecule

$\frac{m}{z} = 227$

Base peak

$\frac{m}{z} = 141$

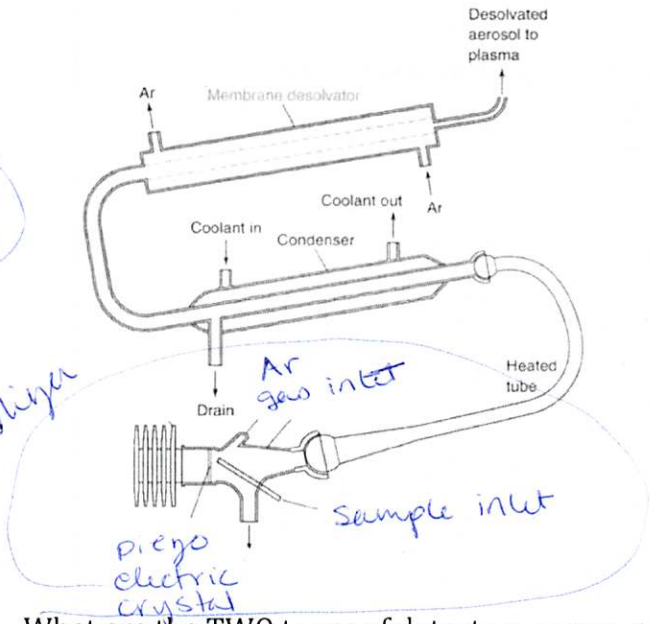


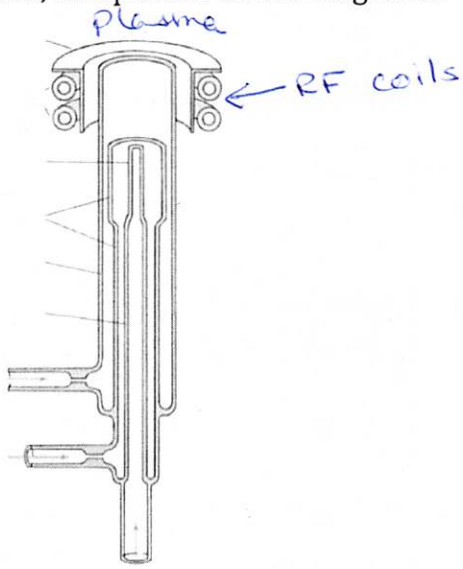
Which ionization method might have been used and what evidence leads you to this conclusion?

(2pts) electron ionization b/c fragmentation is significant & parent peak is not observed.

2. (20 pts) Consider the following diagrams of an ICP below. Label the sample inlet, gas inlet, piezoelectric crystal, nebulizer, radio frequency coil, and plasma on the diagrams.

1 ea
6 pts



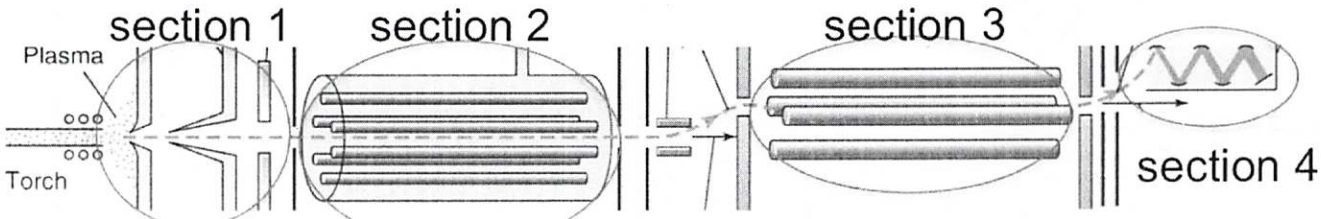


What are the TWO types of detectors are generally used with an ICP source?

2pts

Optical emission spectroscopy
mass spectrometry

Label and briefly describe the role of each of the instrument section shown below:



2ea
8pts

Section 1: sampling & skimmer cones limit the number of plasma ions entering the instrument. ions are also accelerated & preliminary vacuum achieved.

Section 2: collision cell or dynamic reaction cell reduces kinetic spread & minimizes isobaric interferences

Section 3: Quadrupole MS selects ions of a specific m/z

Section 4: Detection electron multiplication

Give an example of an isobaric interference?

4pts

interference of ions of similar m/z

ArO^+ detected as $^{56}Fe^+$

Ar_2^+ " " $^{80}Se^+$

$^{138}Ba^{2+}$ " " $^{69}GaO^+$

3. (15 pts) A solute with a partitioning coefficient of 4.0 is extracted from 10 ml of phase 1 into phase 2. What is the volume required of phase 2 to extract 99% of the solute in one extraction?

$$x^1 = \left(\frac{V_1}{V_1 + KV_2}\right)^1$$

99% in phase 2 means 0.01 left in phase 1

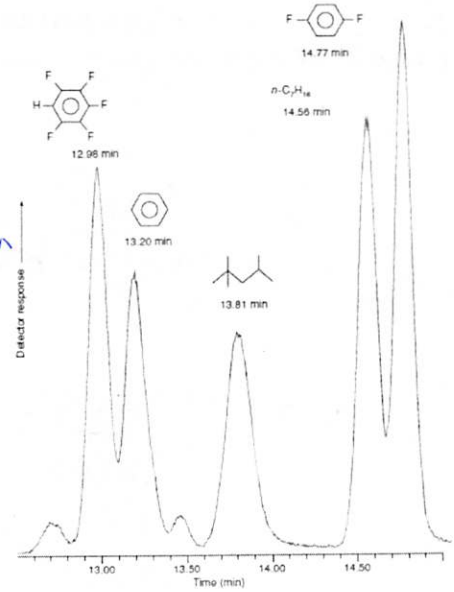
$$0.01 = \frac{10\,mL}{10\,mL + 4.0V_2}$$

$$0.1\,mL + 0.04V_2 = 10\,mL$$

$$9.99\,mL = 0.04V_2$$

$$V_2 = 249.75\,mL = 250\,mL$$

4. (20 pts) Consider benzene and pentafluorobenzene in the following chromatogram collected with a 30 m 0.530 mm open tubular column with a 3 um thick stationary phase. The retention time of the mobile phase is 1.06 minutes.
Find the adjusted retention times and retention factors for both compounds.



$t_r' = t_r - t_m = 13.20 - 1.06 \text{ min} = 12.14 \text{ min}$

(4 pts) $k = \frac{t_s}{t_m} = \frac{12.14 \text{ min}}{1.06 \text{ min}} = 11.45$

compound	t_r'	k
Benzene	12.14	11.45
pentafluorobenzene	11.92	11.24

Find the unadjusted relative retention time

(2 pts) $\gamma = \frac{13.20}{12.98} = 1.0169$

Given $w_{1/2}$ in table and calculate the number of plates N and H for each compound.

(8 pts) $N = \frac{5.55\, t_r^2}{w_{1/2}^2}$ $H = \frac{L}{N}$

(benzene) $N = \frac{5.55\,(13.20 \text{ min})^2}{(0.23)^2} = 18{,}280$

(benzene) $H = \frac{30{,}000 \text{ mm}}{18{,}280} = 1.64 \text{ mm}$

$N = \frac{5.55\,(12.98)^2}{(0.21)^2} = 21{,}203$

$H = \frac{30{,}000 \text{ mm}}{21{,}203} = 1.41 \text{ mm}$

compound	$W_{1/2}$	N	H
Benzene	0.23 min	18,280	1.64 mm
Pentafluorobenzene	0.21 min	21,203	1.41 mm

Determine the resolution between the two peaks using N=√N1N2

(4 pts) $N = \sqrt{18{,}280 \cdot 21{,}203} = 19{,}687$

$R = \frac{\sqrt{N}}{4}(\gamma - 1) = \frac{\sqrt{19{,}687}}{4}(1.0169 - 1) = 0.593$

Is this separation quantitative?

(2 pts) R is less than 1.5, so the separation isn't quantitative
No surprise from the chromatogram

5. (15 pts) Diagram, label and describe a GC-MS

see worksheet

5pts

List two types of chromatography that are commonly performed using a GC.

adsorption & partitioning

2pts

Suggest three methods of sample preparation

headspace, direct liquid injection.
solid phase micro extraction

2pts

What types of columns are used for GC-MS. List three advantages of these types of columns?

open tubular | increased resolution
low sample volume
high sensitivity
decreased retention times

3pts

Suggest at least three detectors that can be coupled with GC separation

Mass spectrometry
Flame Ionization detector
Thermal conductivity
Electron capture

3pts

6. (15 pts) Diagram, label and describe an HPLC.

see worksheet

5pts

List at least three types of chromatography can be performed using a HPLC?

2pts

adsorption size exclusion
affinity
ion

In what two ways can the mobile phase be applied to the column? Briefly describe each.

2pts

isocratic - uniform solvent mixture as a function of time

gradient - solvent mixture changes as a function of time

Why is HPLC performed at high pressures?

2pts

to force solvent through the packed column

HPLC uses a thin (several mm) column packed with tiny stationary phase beads. List at least two advantages of small particles.

2pts

- smaller pores, less of a multiple flow path problem (term A)
- shorter distance to diffuse to stationary phase (term C)
- lower detection limits
- smaller H with smaller particles
- H isnt sensitive to flow rate when particles are small

Suggest at least two detectors that can be coupled with HPLC separation

2pts

UV-Vis spectrophotometer
mass spectrometer
Evaporative Light scattering

/15