

CHM 440 Final
Fall 2011

Name _____

1. (15 points) Match the **best answer** given the following:

1. chemical ionization _____

2. fast GC _____

3. base peak _____

4. 70 eV _____

5. solvent delay _____

6. multi-capillary fast GC _____

7. 10^{-3} – 10^{-6} _____

8. electron impact _____

9. second of three in MS/MS/MS _____

10. GC/MS mass analyzer you used _____

11. m/z _____

12. SIM _____

13. MS/MS/MS _____

14. column bleed _____

15. TIC _____

A. all others are normalized to this

B. cigarettes cause lung cancer

C. hard ionization

D. 15 + 20 daltons

E. MS vacuum pressure in torr

F. total ionization chromatogram

G. double dispersing MS

H. metastable peak

I. typical electron impact ionization energy

J. mass to charge

K. phosphine reagent gas

L. quadrupole

M. specific ionized mass

N. best for solvent determination

O. soft ionization technique

P. tandem mass spec product ion

Q. usually only a collision cell

R. saves ionization filament life

S. increases as oven temperature increases

T. only an isotope's abundance

U. x/y matrix of raw data

V. carefully sacrifices resolution for run time

W. M – 1 peak

X. produces lots of 28 + 32 dalton peaks

Y. decreases as oven temperature increases

Z. a bundle of capillaries used

AA. total ionization current

BB. selected ion monitoring

CC. mass fragment fragmented again

DD. total ion current

EE. mass spectrograph

2. (10 points) A tandem mass spectrometer (MS/MS/MS) with a nonpolar capillary column was tuned in the following manner for a run containing a single $1\ \mu\text{L}$ injected sample containing hexane as the solvent and octane (C_8H_{18}) as the analyte. The ionization method was electron impact. The temperature program was 30°C for 1 min, then $15^\circ/\text{min}$ to 250° .

During the entire run, the first MS was set to allow only m/z 57 to pass into the second MS (the collision cell) while the third MS ran a full scan from 10—350 daltons.

Draw and label a reasonable mass spectrum for the second of the two chromatographic peaks that elute in this experiment. Label the formula of the 4 largest peaks in your spectrum.

3. (15 points) What are the formula and the charge of the four largest peaks around m/z 208 in the MS of CCl_2Br_2 . Is there more than one formula possibility for any of those peaks? If so include it.

4. (10 points) One of the mass spectra attached to this test is from normal butane and a second from 1-butene. Identify which is which and provide formula for the four largest peaks **in each spectrum you choose**.

5. (15 points) A TIC generated from a forensic blood sample contains hundreds of peaks, frankly too many to reasonably examine for the poison of interest, dimethyl mercury, DMHg. Describe a selected ion monitoring experiment with that same blood sample that would allow you to most easily pick out a chromatographic peak for DMHg.

- a) To begin with, create the problematic TIC data set as I described it, clearly labeling each axis.
- b) Next, describe the process by which you'd used SIM, including, specifically, the MS instrumental settings necessary to solve your problem. Leave chromatographic conditions completely out of this problem
- c) Finally draw the SIM chromatogram that shows your success. Make sure all its axes are labeled correctly too.

6. (20 points) One of the mass spectra attached to this test is that of $\text{CH}_3\text{CH}_2\text{-S-CH}_2\text{CH}_2\text{CH}_3$, ethylpropyl sulfide. Choose the correct spectrum from the attached spectra; mark it clearly as your choice for ethylpropyl sulfide, and detail reasonable formula for the six most intense peaks in the space below.

Isotope	Atomic mass	Natural abundance (%)	At. Mass x Natural Abundance
^{196}Hg	195.965807	0.15	0.293948711
^{198}Hg	197.966743	9.97	19.73728428
^{199}Hg	198.968254	16.87	33.5694445
^{200}Hg	199.968300	23.10	46.1926773
^{201}Hg	200.970277	13.18	26.48788251
^{202}Hg	201.970617	29.86	60.30842624
^{204}Hg	203.973467	6.87	14.1297718
		S = 100	S = 200.5991407

7. (15 points) A sample of soil from the bottom of a contaminated ship channel near Houston Texas was analyzed for dimethyl mercury, $(\text{CH}_3)_2\text{Hg}$, a highly toxic organometallic compound. The soil sample was handled in the following manner: 6.25 grams of soil were shaken with 100.0 mL of "ultrapure" hexanes, a solvent in which $(\text{CH}_3)_2\text{Hg}$ is very soluble. After $(\text{CH}_3)_2\text{Hg}$ extraction, the solvent was filtered to remove suspended soil particles. A 1.00 mL aliquot of that solvent was diluted to a final volume of 25.00 mL with fresh hexanes. One μL of that solution was injected into the hot injector of a GC-MS programmed in SIM mode for analysis. The GC-MS had previously been calibrated in the following manner: standards of $(\text{CH}_3)_2\text{Hg}$ in hexane were injected to yield a LLS data set plotting $\text{pg } (\text{CH}_3)_2\text{Hg}/\mu\text{L}$ injected versus the summed abundances of a group of selected ions in the mass spectrum of the DMHg chromatographic peak using the following selected ions 202, 217, 232 m/z. The best fit equation of that data was $y = 7.853 \times 10^2 + 2.97 \times 10^6 x$ $R = 0.9992$.

One microliter of the solution from the soil extract that was injected, splitless, into the GC/MS's hot injector yielded a very complex total ion chromatogram because many of the ship channel's soils components were soluble in hexanes; however, when generating the extracted sample's SIM chromatogram using the 202, 217, and 232 m/z only a single chromatographic peak appeared. The summed abundance of the SIM ions was 432650 in the mass spectra of that SIM peak. The Texas Environmental Quality limit for dimethyl mercury is 58 ppb in soil. What was the concentration of $(\text{CH}_3)_2\text{Hg}$ in the ship channel's soil in ppb? Does it violate Texas law?