Chemistry 4440 Third Test
Thursday, October 22, 2011

(***15 points***) Amy Winehouse was found dead in her apartment on July 23, 2011. Her blood alcohol level was a subject of great speculation. Samples of her blood were analyzed by GC/FID using a solid phase microextraction (SPME) for headspace sampling. The procedure involved 10-mL headspace vials containing 1.00 mL of Amy's blood with 10% Na_2SO_4 added to increase alcohol recovery and 100 mg/dL isobutanol as an internal standard and capped with silicon/PTFE septa. The vial's headspace gas was sampled after being heated to 50° C using a precleaned SPME fiber for 1 min and the fiber was then inserted in a 225° GC injector for 1 min before the GC's temperature program was begun. That temperature program was 40° initial for 4 minutes then 15°/min to 220°. The detector was an FID.

The chromatographic peak for ethanol in Amy's blood sample had an area of 1.998×10^4 pA*s. The LLS calibration for ethanol standards—handled identically as above—plotting mg ethanol/dL blood versus pA*s produced the following equation $y = 54.912x + 32.6$ ($R^2 = 0.99997$). And finally, if the isobutanol internal standard showed 87% recovery, what was the concentration of ethanol in singer Amy Winehouse's blood in percent by mass?

(***20 points***) Someone has decided to buy a fused silica capillary that is "coated with a polymer" and use it for CE. The polymer provides a neutral surface, unlike a naked fused silica capillary with ionized silanol groups (at pH above ~3). How can this polymer-coated capillary be used in CE? What CE modes that we've discussed would be successful with this capillary? If this won't work for some of the CE modes we've discussed, describe **which ones won't work** and why they won't work in detail? For the modes **it will work for**, describe, in detail, how it can be used.

(***15 points***) Since time is money in an analytical and forensic laboratory, deciding when the focusing step in CIEF is finished is important. Why is this not clearly defined? How does the analyst (you) make this decision and with what data? And what processes occur after the focusing step in CIEF and how does the analyst control these?

(**20 points**) We have discussed many different GC detectors. Draw a schematic diagram of any GC detector we've discussed, clearly labeling 1) all the important parts, and 2) those parts **functions** in the detector. Provide an example chromatogram of data from your detector, labeling the axes appropriately.

(**10 points**) Examine the reverse-phase HPLC data on the back of this page. A binary solvent, gradient elution program was used to accomplish the final chromatogram that I have labeled SUCCESS!

Make up two appropriate solvent formulations that could be successfully mixed to accomplish this chromatogram. Name your solvents A and B, detail the relative polarity of each pure solvent, and create a reasonable solvent program that might work to produce these data.

Show your answer on the same page as the chromatograms.

(***20 points***) Match the **best answer** given the following:

1. Cryogenic trapping _____

2. 80 mg ethanol/dL blood _____

3. splitless injection _____

4. split injection _____

5. solvent focusing _____

6. fiber used to sample headspace _____

7. no run buffer between bands _____

8. routinely > 100,000 theoretical plates _____
   (not U, V, or X)

9. Column: 30.0 m, HETP 3.5×10^{-2} cm_____

10. septum purge _____

A. 0.08% blood alcohol

B. 0.80% blood alcohol

C. 8.0% blood alcohol

D. for trace analysis

E. cigarettes still cause cancer

F. used to sharpen analyte peaks

G. prevents sample carryover

H. prevents early eluting peaks

I. prevents late eluting peaks

J. capillary electrophoresis

K. absorbance detector

L. photoionization detector

M. simple fiber extraction technique

N. chronic alcohol poisoning

O. solid phase microextraction

P. HPLC

Q. 105,000 theoretical plates

R. 86,000 theoretical plates

S. 860 theoretical plates

T. only a proportion of sample goes of column

U. CIEF

V. CZE

X. CITP with conductivity detection

Y. used for really low boiling analytes

Z. electron waterfall

Formulae that <u>may</u> be useful:

$$\Delta f = \frac{1}{3t_r}$$

$$c_x = \frac{(S_1 c_s V_s)}{[(S_2 - S_1) V_x]}$$

Beer's Law: $A = \varepsilon bc$

$$\nu = \sqrt{4kTR\Delta f}$$

$$\text{Frequency} = \frac{1}{\text{Conversion rate}}$$

Equation for a line: y = mx + b

$E = h\nu$

mass electron 9.11×10^{-28} grams

$$C_x = \frac{S_1 c_s V_s}{(S2 - S1)V_x}$$

$h = 6.626 \times 10^{-34}$ Js

$$i_{rms} = \sqrt{2Ie\Delta f}$$

$$s = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2 / N}{N - 1}}$$

speed of light = 3.00×10^8 m/s

$$\gamma = \frac{m}{S_s}$$

$c = \lambda\nu$

$$A = \log \frac{P_0}{P}$$

$A = -\log T$

$$E = \frac{1}{2} mv^2$$

$1J = kg \cdot m^2 \, sec^{-2}$

photons rest mass = 0