**Exercise #4: GC calculations and predictions**

*Chem 6614 Chemical Instrumentation*

**TABLE OF RUN CONDITIONS:**

Tinitial = 35 oC, thold = 0

Temperature ramp = 20o C/min

Tfinal = 200 0C, thold= 1 minute

Tinlet = 300 oC

Column = HP-1 (`OV-1` non-polar siloxane phase 10 m, 350oC MAOT ) silica capillary (0.2 mm ID,0.33 µ)

Split ratio: 1:100

He column flow = 1.6 mL/min

FID detector: P(H2) = 40 psi, P(air) =75 psi

Sampling method: wet needle

Reference mixture: 33.3 % octane (bp 125.6 oC) 33.3% heptane (98.5oC ) 33.3% hexane (68.7o C) v/v

**TABLE OF COLLECTED RUN DATA:**

**Chromatogram #1: Known reference mixture data**

Component tr,obs(min) Area (pA\*s)

Hexane 0.65 40.0

Heptane 0.90 65.1

Octane 1.10 98.2

**Chromatogram #2: unknown mixture of above components**

Component tr, obs(min) Area (pA\*s)

Hexane 0.63 10.1

Heptane 0.92 90.6

Octane 1.15 60.0

**4.1. Estimating Run behavior from Run conditions**

a) what is the total volume of the column ? \_\_**0.31**\_\_ mL

**V=L\*π(d/2)2 = 10 m \*(100 cm/m) \*3.14\*(0.02 cm/2)2 =0.314 cm3**

b) how long will a single run minimally take from the time of injection to completion of the GC

program cycle described in the run condition table above ?

**\_\_\_\_\_\_\_9.25\_\_\_\_\_ min**

**200-35 = total ΔT= 165 C at 20oC/min => 165/20 minutes=8.25 minutes + 1.00 minute hold=9.25**

c) given the flow rate for He, use your answer above to compute the time it takes for a `plate’ of He to traverse the column (= minimum retention time=dead or `void’ time…c.f. p. 766 of text)

**0.31 mL =t\*flow rate (mL/min) = t\*1.6**

**t= 0.31/1.6=0.19 minutes=11.8 s** \_0.19\_ = tmin = tdead volume (min)

d) Based on just temperature ramp, initial column temperature and the boiling points of the components, what do you estimate the theoretical retention times, tr theory should be for hexane, heptane and octane ?

Component tr obs(min) tr,theory(min) T(bp) ΔT=T(bp)-T(initial) ΔT/ramp

Hexane 0.63 **1.68** 68.7 68.7-35=33.7 33.7/20=1.68

Heptane 0.92 **3.17** 98.5 98.5-35=63.5 63.5/20=3.17

Octane 1.15 **4.53** 125.6 125.6-35=90.6 90.6/20=4.53

Suggest a reason for why the theoretical retention times may not match observed.

*The materials are usually already volatilized in injector, so separation will depend more on chemical interactions on stationary phase than on the material reaching its boiling point in the column.*

**4.2. Theoretical Plate Count**

From the theory of Synge and Martin, the number of hops an species makes down a column’s stationary phase = N:

N = 16(tr/w­0.1)2

Where tr = the retention time of the species, w0.1 = width of the peak at 10% height assuming a symmetric peak. The corresponding `height equivalent of the theoretical plate,” HETP = H is the distance of each theoretical hop a species takes before re-adhering to the stationary phase.

If L is the length of the column in cm, then:

H= L(cm)/N

Compute both N and L for Octane using the conditions above assuming w0.1 = 0.075 minutes

N= \_\_\_\_\_\_\_16\*(0.63/0.075)2=18063\_\_\_\_\_\_\_\_\_\_\_\_\_\_

H=\_\_\_\_1200 cm/18063= 0.066\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ cm

4.3 **. Estimating Unknown Mixture composition**

a) Assuming no changes in sensitivity or run character between unknown and known, compute the apparent sensitivity, Sk of the components in pA\*s/% using the known mixture data below

Known Reference GC Data

Component Area (pA\*s) %V Sk = Area/%V

Hexane 40.0 33 40.0/33.0=1.21

Heptane 65.1 33 65.1/33=1.97 U-do these

Octane 98.2 33 98.2/33=2.97

b) Given the Sk above, we can solve for the unknown %Vk unk (raw) .For example, letting k=1 (hexane)

S1 = observed Area of hexane in unknown

%V1 unk(raw)

1.21 = 10.0

%V1 unk(raw)

%V1 unk (raw) = 10.0/1.21=8.26

Finish the calculations for the two other components below:

Unknown GC mixture data

Component Area (pA\*s) Sk %Vk(raw)

Hexane 10.1 1.21 8.26

Heptane 90.6 1.97 90.6/1.97=46.99

Octane 60.0 2.97 60.0/2.97=20.20

c) Add up the %Vk(raw). They normally do not sum exactly to 100%. Rescale them to 100 as shown below: %Vk(final) = %Vk(raw) \* 100 and tabulate below.

Σ%Vk(raw)

Component %Vk(raw) %Vk(rescaled)

Hexane 8.26 100\*8.26/75.45 = 10.9

Heptane 46.99 100\*46.99/75.45 = 63.1

Octane 20.20 100\*20.20/75.45 26.8

Σ%Vk(raw) 75.45 100