CHEM 314
2014 Exam 1

Name: key

1. You are asked to measure the percent iron in a steel sample you believe to be about 50% Fe by mass. You dissolve four replicate samples in nitric acid and dilute them by mass to a concentration of 30 mg Fe $L^{-1}$ for analysis by Flame AA. You begin by dissolving 1.0000 g of steel and dilute it to a final volume of 50 mL. Then you dilute an aliquot of your solution to a final volume of 100 mL for analysis.

(10 pts) Calculate the concentration of the initial solution and the volume of the aliquot required to make the final solution for analysis. BE SURE TO SHOW YOUR CALCULATIONS OR YOU WILL NOT RECEIVE CREDIT.

$$1.0000\,g\ metal \times \frac{0.5\,g\ Fe}{1\,g\ metal} \times \frac{1000\,mg\ Fe}{g\ Fe} \times \frac{\quad}{0.05\,L} = 10{,}000\ \frac{mg\ Fe}{L}$$

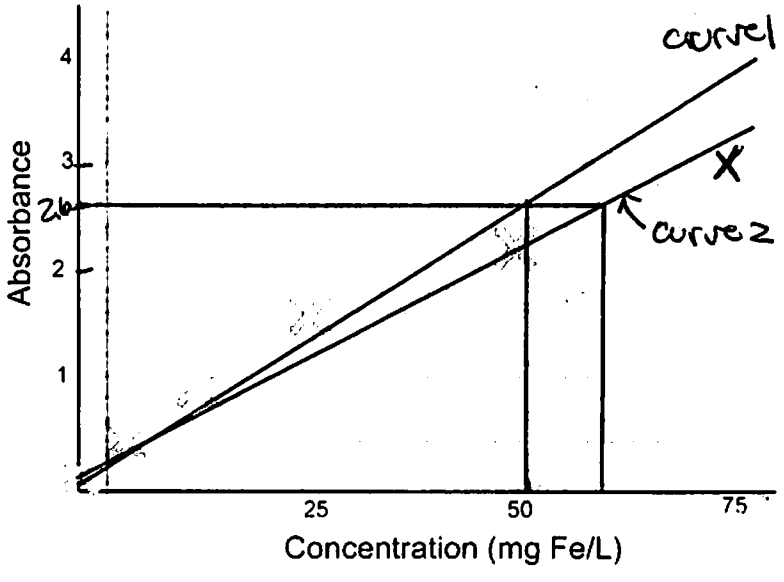
$$M_1V_1 = M_2V_2$$

$$10{,}000\ \frac{mg\ Fe}{L}\ X = 100\,mL \cdot 30\ \frac{mg\ Fe}{L} \qquad X = 0.3\,mL$$

You also prepare calibration standards of 0, 5, 10, 25, and 50 mg Fe $L^{-1}$. You run Flame AA on your samples and standards. After the analysis, you plot your data (shown below). The average absorbance value of your samples is 2.6.

(2 pts) Draw the line of best fit through the data and estimate the concentration of Fe in your sample solution.

53 mg/L




(3 pts) You know that it is a bad idea to extrapolate your calibration curve, so you quickly dilute a new high standard at 75 mg Fe $L^{-1}$ and run it. The resulting absorbance measurement is 2.9. Add this value to your plot and estimate the concentration of Fe in your sample solution.

57 mg/L



/15

(5 pts) Describe your confidence in your measurement. If you are not 100% confident, describe what you believe to be wrong with reference to the appropriate information from class. List at least four reasons.

Low

- low r-squared value
- Absorbance too high (above 1.5) nonlinear range of Beer's Law
- Flame AA linear b/w 0.1 - 10 ppm
- there is a linear calibration up to ~25 ppm

(5 pts) What aspects of experimental design were right in this experiment? List at least 3 things that were well-designed or turned out right.

- intercept near zero
- lots of standards
- choice of instrument
- 4 replicate measurements of sample
- good dissolution method

(5 pts) If you are not confident in your measurement, list ways you would perform the measurement differently to give you more confidence. List at least 3 things you might change.

- dillutions by mass
- dilute sample to a lower concentration
- more standards in linear range
- replicate measurements
- QC checks

2. Consider random and systematic errors.

(3 pts) Define random error.

- always present
- uncontrollable
- not directional

(2 pts) How can you quantify random error?

Precision. Measure replicates of the same sample & calculate standard deviation

(3 pts) Give an example of how you would quantify random error in the experiment described in the first problem?

multiple/replicate measurements of the same sample.

(3 pts) Define systematic error.

- affects data in a predictable way
- assignable cause
- hard to detect & quantify

(2 pts) Compare the relative difficulty of detecting and quantifying random and systematic error.

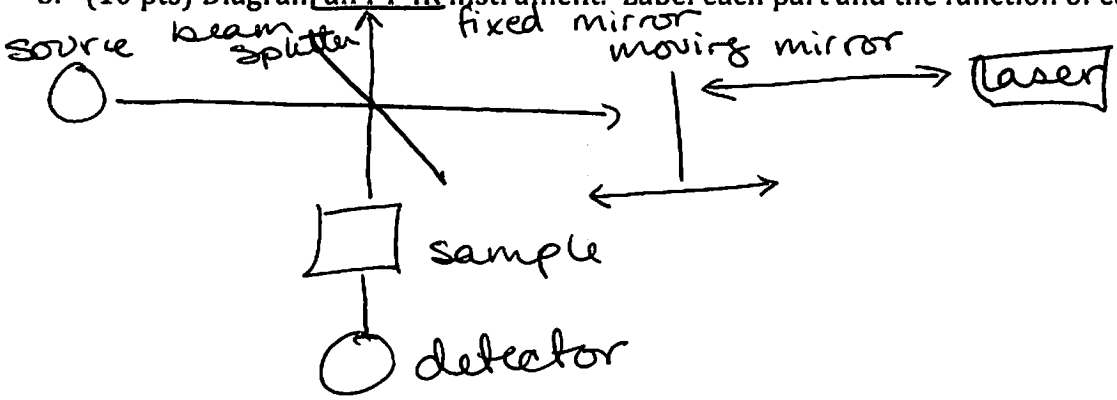
- ~~Calibration~~

systematic error much harder to detect & quantify. Random error is always present & easy to quantify

(4 pts) List at least four ways you can assess your method for systematic error

- calibration
- blanks
- standard reference materials
- alternate methods / other labs
- QC checks

3. (10 pts) Diagram an FT-IR instrument. Label each part and the function of each part.

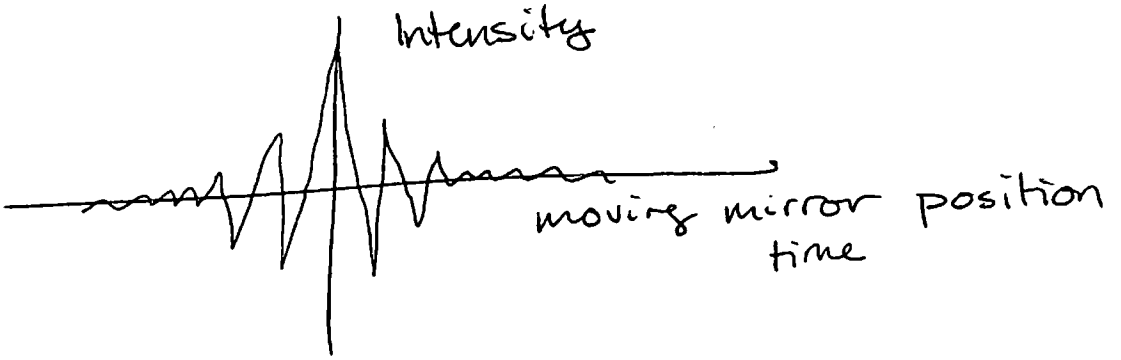



1. Globar source - broad spectrum many λ IR source
2. beam splitter - splits & recombines beam
3. fixed mirror - unmoving. Distance = zero position of moving mirror
4. moving mirror - moves in time causing interference in recombined beam.
5. Laser - determines exact position of moving mirror at
6. sample - absorbs IR radiation according to its the energies vibrational of functional groups.
7. Detector - detects all λ at once.

(7 pts) Describe how FT-IR measurements are made by the instrument.

1. the radiation from the source is split at the beamsplitter. some goes to moving mirror, some to fixed mirror.
2. Radiation from mirrors is recombine in an interference pattern (that changes in time) depending on position of moving mirror at the time of reflection
3. The sample absorbs radiation based on energies of vibrations of its functional groups.
4. Detector detects all $\lambda_4$ at once.

(3 pts) Draw an example interferogram. Be sure to label the axes.



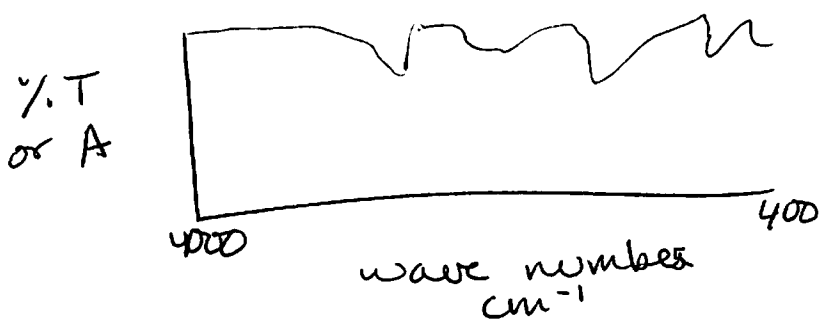

(5 pts) Describe the information contained in the interferogram.

An interferogram is the interference pattern (sine waves) for all wavelengths incident on a detector at a given time or moving mirror position

(5 pts) Describe how the interfereogram is converted to the familiar output spectrum.

Fourier transform converts the interferogram into its component sine waves & intensities, so that they can be plotted as wave number ($cm^{-1}$) vs intensity, %T or Absorbance.

(3 pts) Draw an example output spectrum. Label the axes.



4. The following data are for a liquid chromatographic column:
length = 24.7 cm  flow rate= 0.313 mL $min^{-1}$  $V_m$= 1.37 mL  $V_s$= 0.164 mL

A chromatogram of a mixture of species A, B, C, D provided the following data:

| Species | retention time (min) | width of peak (FWHM; min) |
|---|---|---|
| $t_m$ | 3.1 | |
| A | 5.4 | 0.41 |
| B | 13.3 | 1.07 |
| C | 20.1 | 3.16 |
| D | 21.6 | 3.72 |

(2 pts) Calculate the amount of time species B spends in the solid phase.

$t_A - t_m =$ 10.2 minutes

(5 pts) Calculate the number of theoretical plates and plate height for Species A.

$$N = \frac{L}{H} = 5.54\left(\frac{t_r}{\omega_{1/2}}\right)^2 = 5.54 \cdot \left(\frac{5.4}{0.41}\right)^2 = 961$$

$$H = \frac{L}{N} = \frac{24.7\,cm}{961} = 0.0260\,cm$$

(3 pts) For species C and D, calculate the resolution. Is quantitative separation achieved?

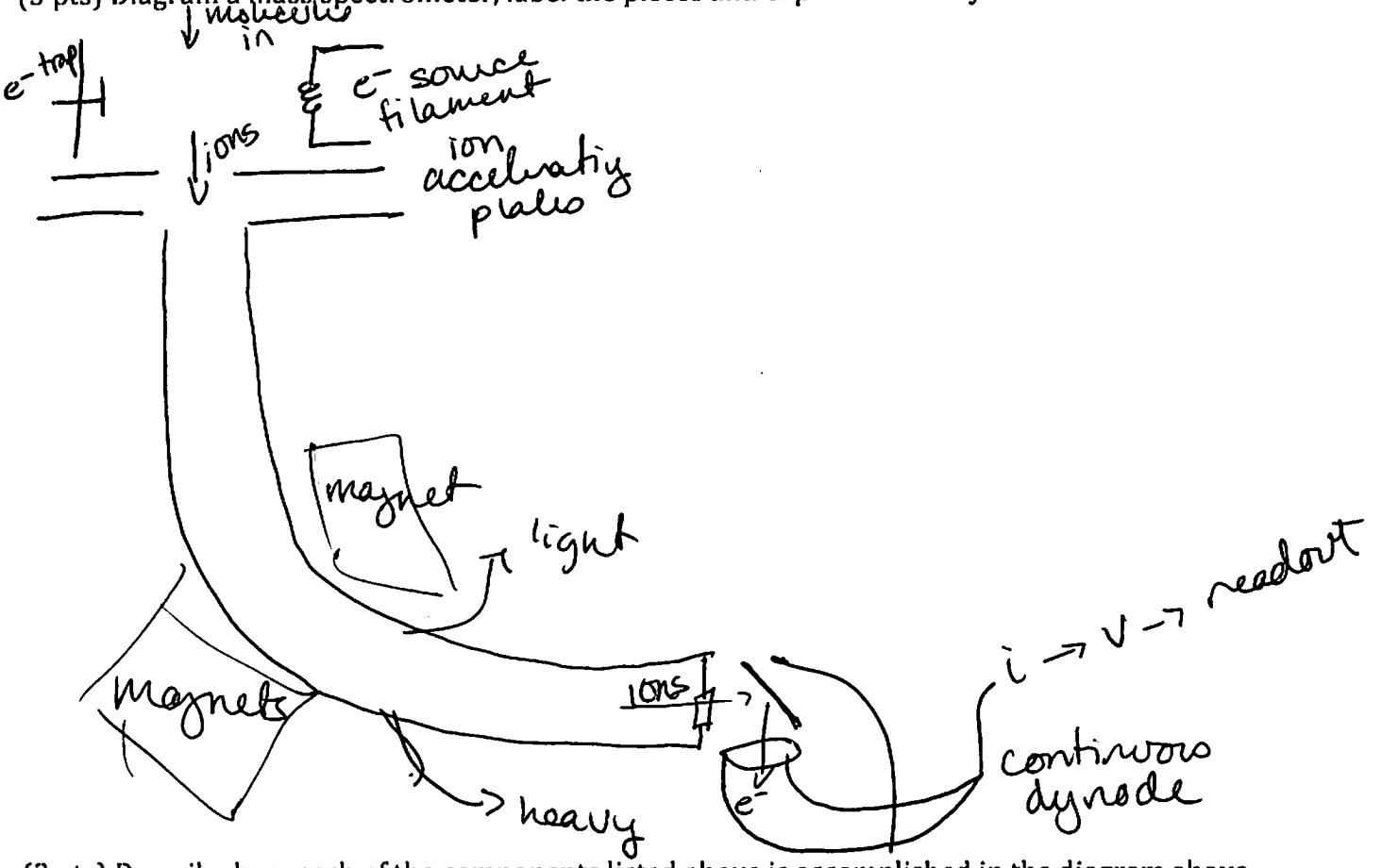
$$R = \frac{0.589\,\Delta t_r}{\omega_{1/2\,avg}} = \frac{0.589 \cdot 1.5}{3.44} = 0.2567$$

$R < 1.5$, so quantitative resolution was not achieved.

5. (2 pts) List the four components of a mass spectrometer

1. Ionization
2. Acceleration of ions
3. Ion separation / selection
4. Ion detection

(5 pts) Diagram a mass spectrometer, label the pieces and explain how they work.




(3 pts) Describe how each of the components listed above is accomplished in the diagram above.

1. ions are made through collision w/ electrons.
2. Ions are accelerated ~~with~~ by holding plates at a potential difference.
3. Ion selection is made by varying magnetic field to deflect a specific $\frac{m}{z}$ to the detector light ions are deflected too much & crash heavy ions not enough & crash
4. ions are converted to electrons & multiplied in a continuous dynode.