Name: key

1. You are asked to measure the percent iron in a steel sample you believe to be about 85% Fe by mass. You dissolve four replicate samples in nitric acid and dilute them by mass to a concentration of 3 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 (in mg L^{-1}) of the initial solution and the volume of the aliquot required to make the final solution for analysis. BE SURE TO NEATLY WRITE OUT ALL CALCULATIONS INCLUDING UNITS OR YOU WILL NOT RECEIVE CREDIT.

$$1.0000\,g\ \text{sample} \times \frac{0.85\,g\ Fe}{1\,g\ \text{sample}} \times \frac{1000\,mg\ Fe}{1\,g} \times \frac{1}{0.05\,L} = 17{,}000\ \frac{mg\ Fe}{L}$$

$$M_1V_1 = M_2V_2$$

$$17{,}000\ \frac{mg\ Fe}{L} \times X = 3\ \frac{mg\ Fe}{L} \cdot 100\,mL$$

$$X = 0.0176\,mL$$

(10 pts) Is this a reasonable dilution scheme considering the equipment available in this course? If not, suggest another scheme and compare the relative merit of each.

17.6 µL is a pretty small volume, maybe add an additional dilution step so there are larger masses & thus more sig figs.

However, serial dilutions have inherently larger dilution errors. These can be somewhat eliminated by diluting samples on a mass bases.

2. You weigh the volume of water delivered by an automatic pipette 10 times. The pipette is adjusted to deliver 4.50 mL. The mass of the water delivered was found to be 4.62 ± 0.08 g. Assume the density of water is 1.00 g cm^{-1}.

(2 pts) Define random error.

- Always present
- random direction & magnitude
- quantify using replicate measurements

(2 pts) Do you observe evidence of random error in the measurement described above? If yes, what is the magnitude of the error?

yes 0.08 g

(2 pts) Do you observe evidence of systematic error in the measurement described above? If yes, what is the magnitude of the error?

yes 0.12 g

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

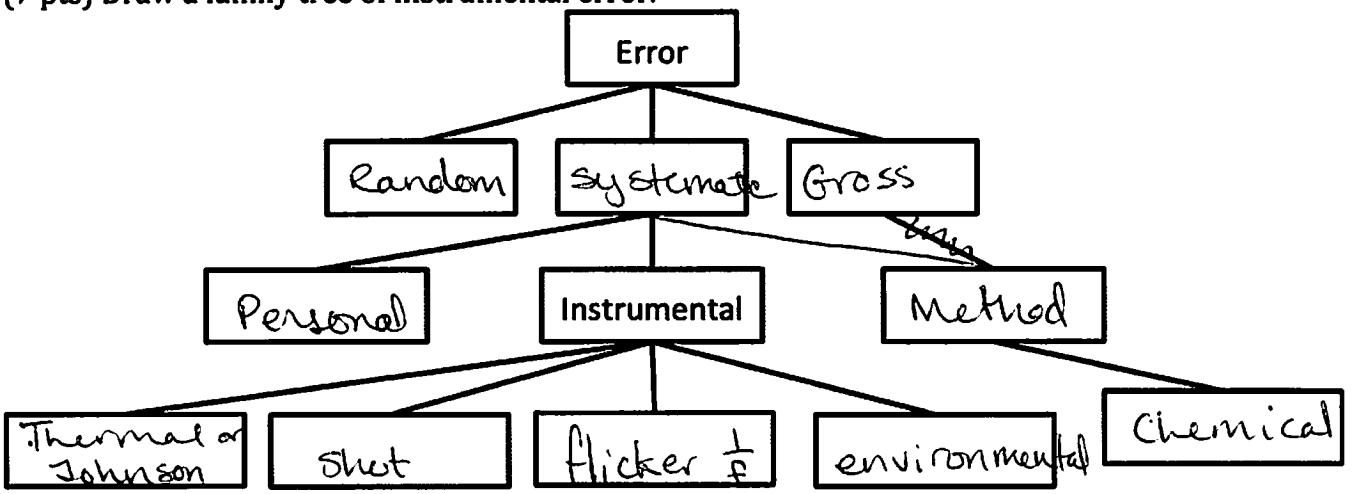
Random error, although always present, is readily detected & quantified using replicate measurements.

Detecting systematic error is much more difficult.

(2 pts) List at least four ways you could assess a method for systematic error.

- Analyze standard Reference Materials
- Blanks
- Analyze the same sample by multiple techniques
- Analyze the same sample by different labs
- Use lab fortified blanks
- QA/QC checks

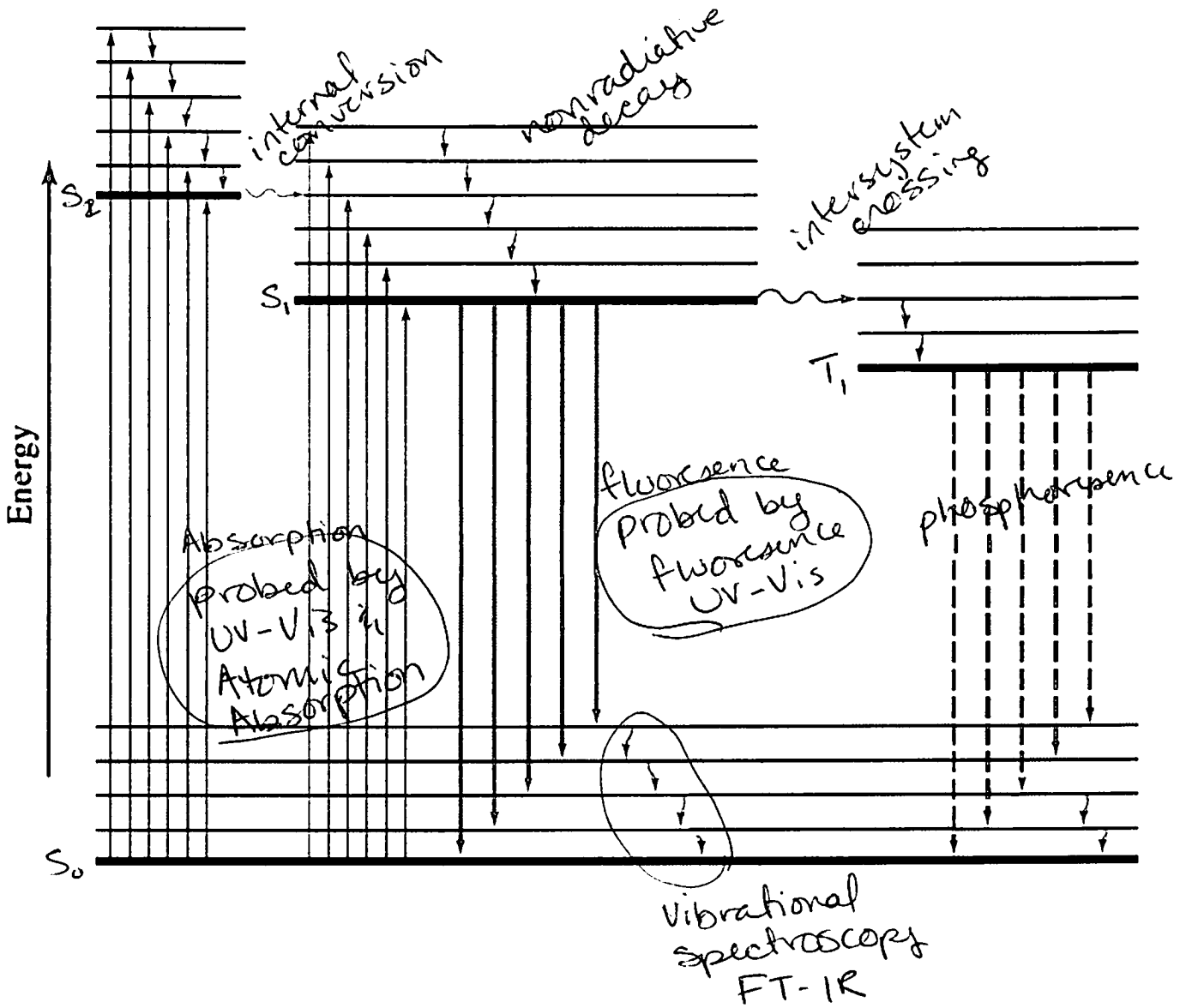
(7 pts) Draw a family tree of instrumental error.



(3 pts) Provide a 1-sentence description of 3 of the 4 types of instrumental error you listed above.

- Thermal noise - movement of e^- in a circuit component
- Shot noise - e^- crossing a junction
- $\frac{1}{f}$ or flicker - low frequency noise from using inexpensive components
- environmental - noise from the environment classes getting out; elevators; traffic; 60-Hz electricity.

4. (10 pts) Label the Jablonksi diagram below.
Indicate the excited and ground singlet and triplet states.
Indicate the following transitions: absorption, fluorescence, phosphorescence, nonradiative decay, internal conversion and intersystem crossing.
Label the transitions probed by at least 4 types of spectroscopy studied.



5. (2 pt each) State the identity of each instrument shown on the computer screen. Then describe the distinguishing features of the instrument that helped you with the identification.

ID	Instrument	Distinguishing Features
Ex.	Atomic fluorescence	Fluorescence: Bent geometry Atomic: no excitation monochromator
A	Single beam UV-Vis Photodiode array	• Polychromatic light interacting w/ sample • Polychromator
B	FT-IR	interferometer
C	Flame AA	chopped source flame
D	Molecular fluorence	bent geometry two monos
E	Double beam in space UV-Vis	• Two detectors • reference & sample
F	Atomic Fluoresence	• bent geometry • no exitation mono
G	Single beam UV-Vis PMT	• monochromator before sample. •
H	ICP-OES	Echelle wavelength selection & prism Area detector
I	double beam in Time UV-Vis	only one detector (time vs space)
J *	Raman	• Laser source • bent geometry

* could easily be Atomic fluor
I took any Fluorescence technique

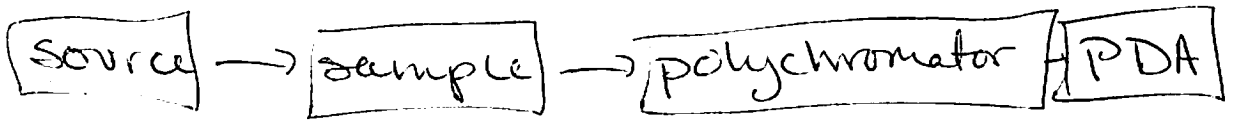
(2 pts) What is the advantage of double beam instruments?

double beam instruments adjust for short term fluctuations in source intensity & detector & amplifier responses

(4 pts ea) Select two instruments from the previous page. Draw a box diagram of the instrument, label each part and describe what purpose it serves. Then suggest an appropriate source, wavelength selector, and detector.

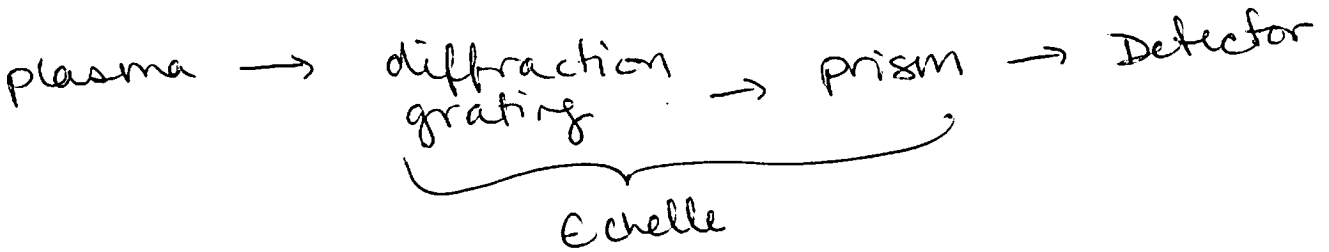
Instrument: A

source	Wavelength selection	detector
Deuterium arc tungsten filament	polychromator	photodiode array

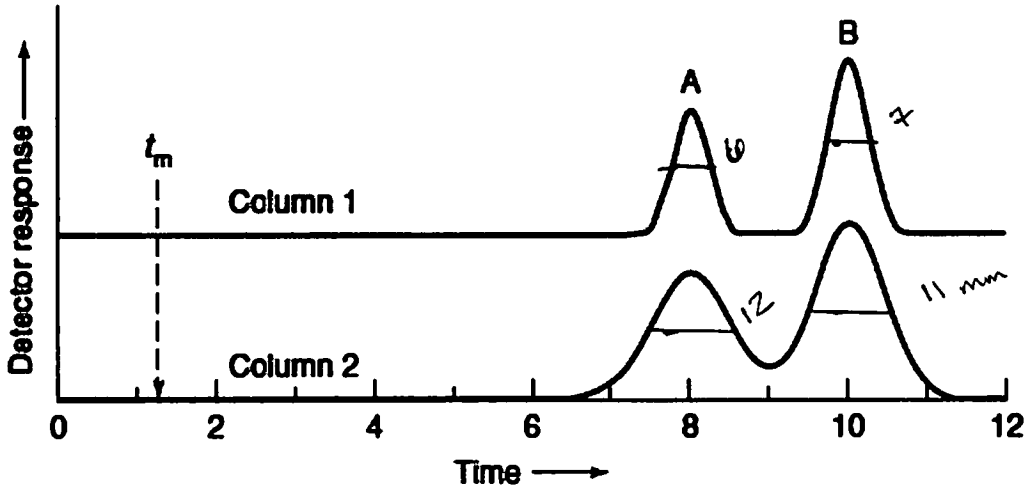


Instrument: H

source	Wavelength selection	detector
ICP - Inductively Coupled plasma	Echelle { grating + prism	CID charge injection device



6. Chromatograms of compounds A and B (shown below) were obtained at the same flow rate with two columns of equal length. (1 pt ea)



Which column has more theoretical plates? Why?
column 1 because it has better resolution

Which column has a larger plate height? Why?
column 2 because $N \propto \frac{1}{H}$

Which column gives higher resolution? Why?
column 1 because peaks are better separated

Which column gives a greater relative retention? Why?
neither, the relative retention is the same

Which compound has a higher retention factor? Why?
B is retained longer on the column

Which compound has a greater ~~partition coefficient~~ distribution constant? Why?
B has a greater distribution constant b/c it spends more time in the mobile phase

What is the numerical value of the unadjusted retention? ~~Why?~~

$$\gamma = \frac{t_{r2}}{t_{r1}} = \frac{10}{8} = 1.25$$

(6 pts) Estimate the resolution of compounds A and B in each column. Is quantitative resolution achieved? Use a ruler to assist in estimating the needed values from the chromatogram.

$$\text{Resolution} = \frac{0.589\ \Delta t_r}{W_{1/2\ ave}}$$

$W_{1/2}$ ave mm	t (min)
6.5 mm	0.62
11.5	1.0 min

21 mm = 2 min

$$R_{\text{column 1}} = \frac{0.589 \quad 2\text{min}}{0.62\text{min}} = 1.9 = R$$

$$R_{\text{column 2}} = \frac{0.589 \cdot 2\text{min}}{1.1\text{ min}} = 1.07 = R$$

Quantitative resolution is only achieved in Column 1

(5 pts) Diagram, label, and describe the function of each component of a HPLC.

solvent + sample → column → detector

1. solvent + sample injected onto the column
2. column separates solutes
   each solute retained for different times on the column.
3. solutes detected individually.

(2 pts) Suggest two detectors that can be used in conjunction with this instrument.

ICP-MS ICP-OES

MS UV-Vis

ELSD

Almost anything.