CHEM 3590 Test 1, October 5, 2018; 10:30-11:25 a.m; 124 Machray Hall; Instructor: H. Perreault.

Please answer all questions directly on exam paper. Each question is worth 20 points.

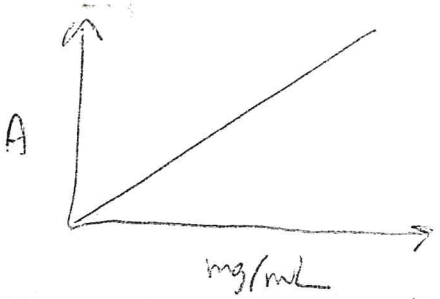
Name: ANSWER KEY **Student number:** 00000A

VERSION A

1. a) Four standard solutions are measured by UV spectrophotometry at 254 nm, of concentrations 2, 4, 8 and 16 mg/mL with corresponding absorbance values of 0.04, 0.08. 0.16, and 0.32. What is the path length of the measuring cuvette if the correlation coefficient (slope) is 0.04 ~~$mgL^{-1}cm^{-1}$~~? $mL\,mg^{-1}cm^{-1}$

   b) Which cuvette material would be best to use, polyvinyl chloride (PVC), quartz, or ordinary glass? Justify.

a) The slope obtained by the measurements is 0.02 $mL\,mg^{-1}$



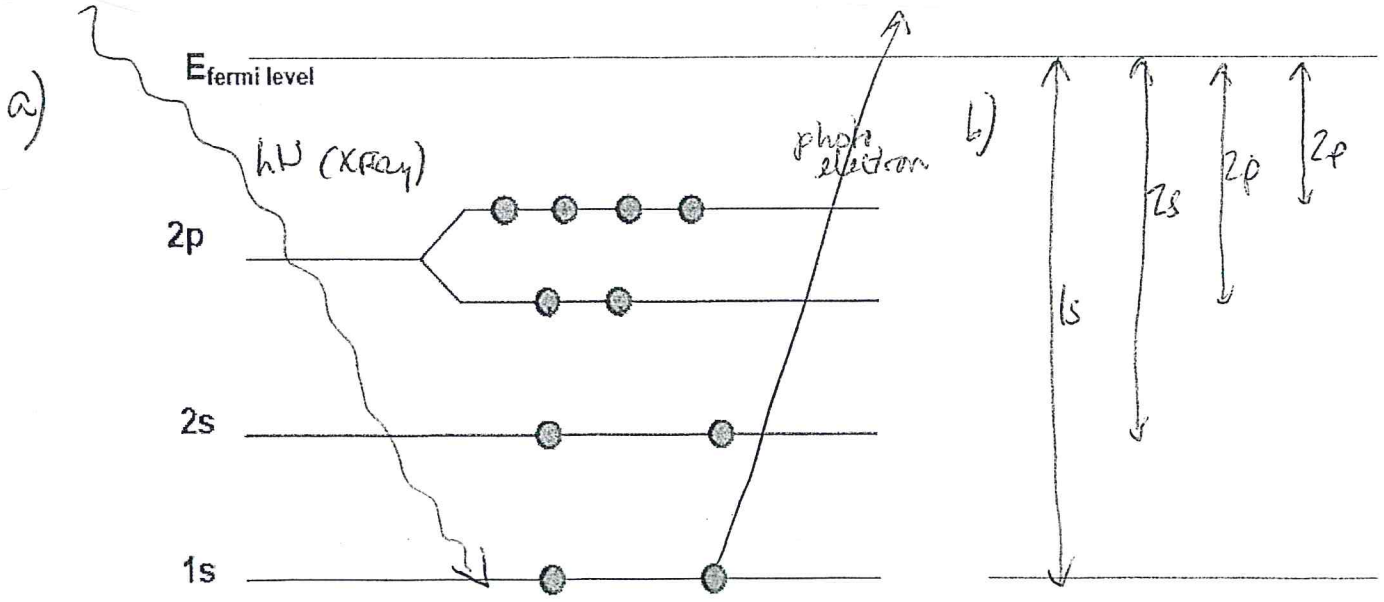
If the cell length is 1 cm, the coefficient obtained was 0.04

⇒ the cell has 1/2 the length, ⇒ 0.5 cm

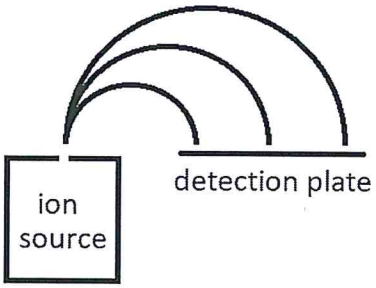
b) Quartz is the most transparent in the 254 nm range. Glass has metal ions that cause absorbance in that range and PVC is an organic polymer, likely to cause a high background at that wavelength.

2. a) By drawing/writing on the atomic energy diagram given below (left section), show what happens during an X-ray photoelectron emission event.

   b) On the right section of the diagram, draw vertical arrows to indicate the binding energy of the electrons in that particular atom.



3. a) Given that the radius of Pb^{2+} trajectory in a constant field SIMS magnetic analyzer is 35 cm, calculate the distance between the detection points of Pb^{2+}, Al^{3+} and Na^{+} after a 180° trajectory. Use the diagram below as example for guidance.



b) Primary ions (Cs^+, O_2^+) Strike the samples for ejection of secondary ions from the analyte: Pb^{2+}, Al^{3+}, Na^+.

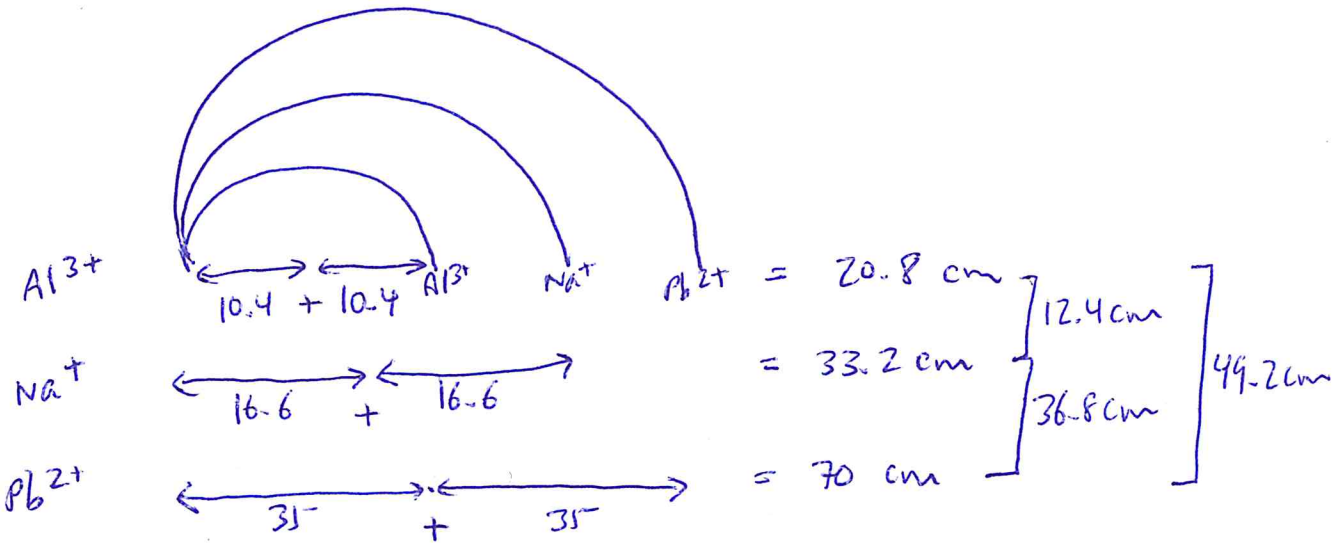
b) Why are Pb^{2+}, Al^{3+} and Na^{+} called secondary ions?

a) $m/z = \text{constant} \times R^2$

for Pb^{2+}: $\frac{207}{2} = ct \times (35)^2 \Rightarrow ct = 0.084$

Al^{3+}: $\frac{27}{3} = 0.084 \times (R)^2 \Rightarrow R = 10.35$ cm

Na^{+}: $\frac{23}{1} = 0.084 \times (R)^2 \Rightarrow R = 16.55$ cm



4. a) What are the main advantage and the main disadvantage of using axial viewing detection in ICP-OES?

   b) What is the role of the nebulization chamber in ICP-OES instruments?

   c) Why not measure the absorbance of elements rather than their emission in the plasma torch?

a) advantage: more sensitivity, as more light is viewed.
disadvantage: less selectivity, as no height adjustment is possible.

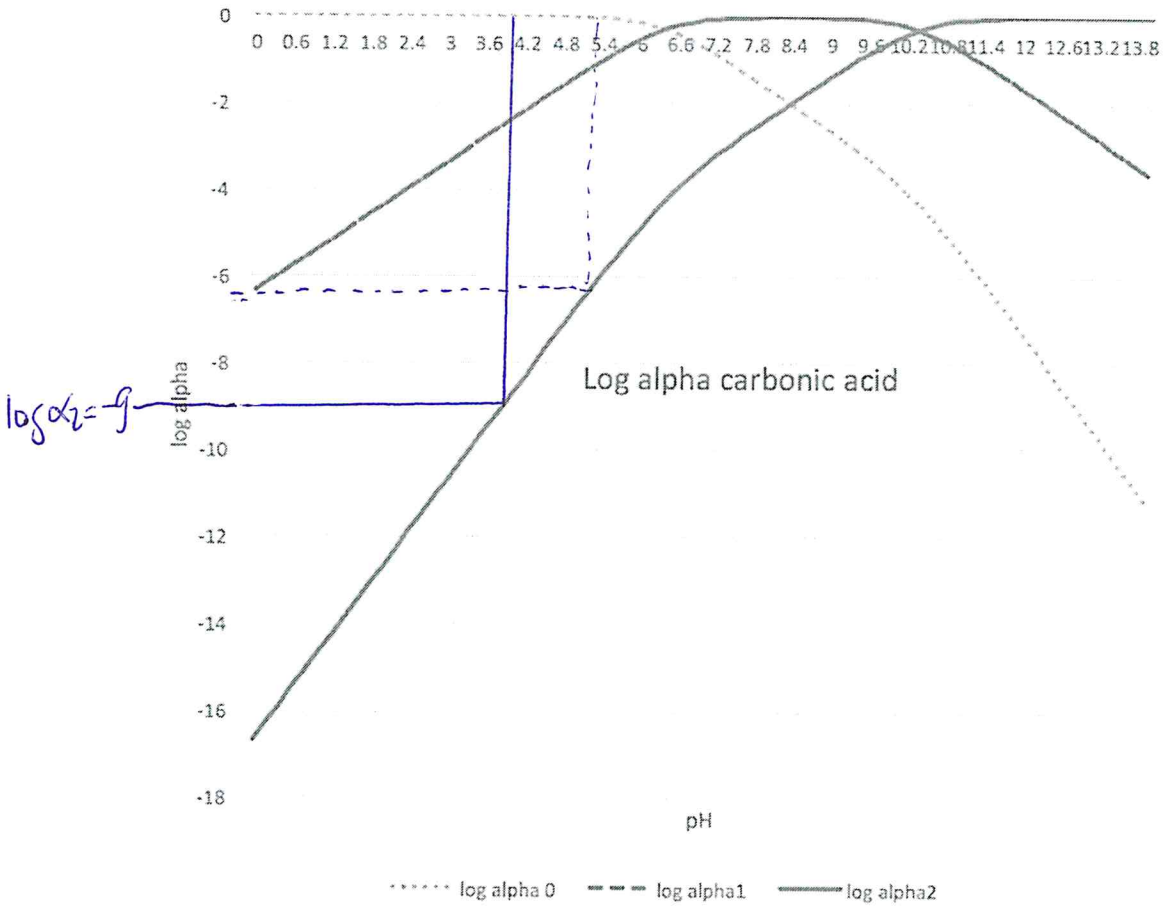
b) To select droplets by size from the nebuliser. Only the smallest droplets will reach the plasma.

c) In absorbance measurements, a mono λ light goes through a sample of known pathlength and transmittance is measured, along the axis of the incident light. In ICP OES, the torch is so intense that along the same axis it is impossible to detect a T change whether the sample is in or not. the sample is the light source in this experiment as emission is recorded.

5. A 10-g sample of lead carbonate ($PbCO_3$) is dropped into a 100-L beaker of water. The pH is adjusted to 4 with formic acid (HCOOH). The K_{sp} of lead carbonate is 7.4×10^{-14}.

   a) Calculate the Pb^{2+} concentration at equilibrium.

   b) Would it be possible to lower the pH enough to dissolve the whole sample?



$\log \alpha_2 = -9$

a) At pH 4, $\alpha_2 = 10^{-9}$ $[Pb^{2+}] = \sqrt{\frac{K_{sp}}{\alpha_2}} = \sqrt{\frac{7 \times 10^{-14}}{10^{-9}}} = 8.4 \times 10^{-3}$ M

b) Whole sample: $\frac{10\ g}{267\ g/mol} = 0.037$ mol Conc $Pb^{2+} = \frac{0.037\ mol}{100\ L} = 3.7 \times 10^{-4}$ M

The conc. is smaller than found in a) meaning that at pH 4 the whole sample is dissolved.

$\alpha_2 = \frac{K_{sp}}{[Pb^{2+}]^2} = \frac{7 \times 10^{-14}}{(3.7 \times 10^{-4})^2} = 5.1 \times 10^{-7}$, $\log \alpha_2 = -6.3$, $\Rightarrow$ pH ~ 5.2 is necessary to dissolve whole sample