

1.(3%) Give answers to the following calculations: (You do not need to show your calculations for *this* question. Pay attention to significant figures, as always.)

- a) $0.1000 + 1.000 + 10.000 + 100.00$
 b) $0.1000 \times 1.00 \times 10.00 \times 100.00$
 c) $\log(10.00)$

2.(6%) (a) Draw, with proper labeling, a schematic diagram which shows the arrangement of five main instrument components of a single-beam spectrophotometer for absorption measurements. (b) Name one device each that may be used as the (i) source and (ii) detector for uv-vis spectroscopy.

3.(8%) Distinguish between (a) calibration sensitivity and analytical sensitivity, (b) potentiometric selectivity coefficient vs. chromatographic selectivity factor.

4.(7%) A lot of biological samples are present in buffers, especially phosphate buffered saline (PBS), which contains disodium hydrogen phosphate (MW=141.96) and monopotassium phosphate (MW=136.086). How many grams of anhydrous disodium hydrogen phosphate and monopotassium phosphate should be added to 100.0 mL water and diluted to 1.00 L to prepare a buffer of pH 7.044 with a salt concentration of 0.0500 M? (For H_3PO_4 , $K_{a1} = 7.11 \times 10^{-3}$, $K_{a2} = 6.32 \times 10^{-8}$, $K_{a3} = 4.52 \times 10^{-13}$)

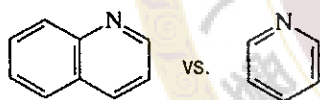
5.(8%) Sketch a diagram that shows, with proper labeling, all the essential components of a liquid-membrane electrode for Ca^{2+} and discuss how such an electrode can function as an ion selective electrode.

6.(6%) Which compound in each of the following pairs below has higher fluorescence intensity? Briefly explain each case.

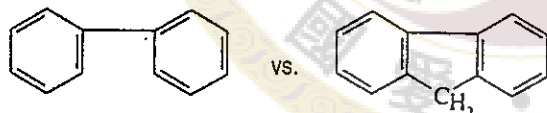
(a)



(b)



(c)



7.(7%) A solution was prepared by mixing 50.0 mL of 0.0200 M Pb^{2+} with 50.00 mL of 0.0400 M EDTA. The mixture was buffered to a pH of 3.00. Calculate the concentration of Pb^{2+} in the solution. (For PbY^{2-} , $K_f = 1.1 \times 10^{18}$; at pH 3.00, $\alpha_4 = 2.5 \times 10^{-11}$)

8.(18%) A news broke on Jan 9, 2014: 日本中部三重縣四日市一家化工廠發生爆炸，至少造成 5 人死亡。According to BBC (British Broadcasting Corporation) News, "The blast occurred in the afternoon at the plant run by Mitsubishi Materials in Yokkaichi city, Mie prefecture. Maintenance crews were cleaning out a heat exchanger used in the production of silicon products when the blast happened, officials said. Some reports suggest the cleaning water mixed with chemical residue inside the exchanger, producing a hydrogen blast. . . . A similar non-fatal accident happened at the same plant two years ago".

Suppose you are assigned to formulate a complete and rigorous analysis process to investigate the cause of the Jan 9 accident. Based on the analytical concepts and techniques learned in analytical chemistry, (a) draw a flow diagram showing the main steps in your analysis process, (b) discuss the main (i) analytical concepts and (ii) analysis logics/considerations behind each step of the analysis process.

Note: you should also include in the discussion your (1) start of the process, (2) initial experiment, and (3) at least two extension studies that are conducted in response to the possible challenges against the new experimental results you obtain, to confirm the cause.

For example, to properly answer (1) start of the process, you have to discuss the analytical concepts and logics that support how and why you start the process the way you have designed/selected.

9.(20%) Scientists are increasingly adopting mass spectrometry for food safety and environmental research. A range of ionization techniques have been developed in mass spectrometry to generate ions from analyte molecules. These techniques (and their abbreviations) include electron impact (EI), matrix-assisted desorption-ionization (MALDI), electrospray ionization (ESI), field ionization (FI), chemical ionization (CI), plasma desorption (PD), field desorption (FD), fast atom bombardment (FAB), secondary-ion mass spectrometry (SIMS), and thermospray ionization (TS). Use the technique abbreviation, when appropriate, to answer the questions below.

- (a) List all the techniques that belong to the categories of the (i) gas-phase and (ii) desorption ion sources, respectively? (Note: penalty will be applied for incorrect categorization.)
- (b) Describe the difference in sensitivity and the number of daughter ions displayed in the spectra taken using EI, CI, and FI.
- (c) Write down the most relevant ionization technique that mainly uses the following ionizing agent: (i) laser beam, (ii) reagent gaseous ions, (iii) energetic ion beam, (iv) fission fragments from ^{252}Cf .
- (d) Calculate the resolution required for separating the ions C_2H_6^+ ($M=30.0690$) and CH_2O^+ ($M=30.0260$).
- (e) The kinetic energy of an ion bearing a charge z under an accelerating voltage V is zeV , where e is the electronic charge. How long will a CH_2O^+ ion take to travel the 20.0 cm length of the rod assembly of a quadrupole mass spectrometer after the ion experiences 10.00 V accelerating voltage? Assume that the ion has a zero initial velocity in the rod direction and no fragmentation occurs during its traveling.

10.(17%) As shown below, a cyclic voltammogram is obtained from analyzing 0.0050 M $\text{K}_3\text{Fe}(\text{CN})_6$ in 1.0 M KNO_3 . (a) Describe the essential experimental condition/procedure with which a cyclic voltammogram of good quality may be obtained. (b) (i) Why is KNO_3 used in the experiment? (ii) What is the experimental requirement for KNO_3 to achieve the intended purpose of use? (c) Copy the figure in your answer book and properly label the y axis (d) (i) Write down the full names of E_{pc} , I_{pa} , $E_{p/2c}$, and $E_{1/2}$ and (ii) define each of them by drawing directly on your figure. (e) Use two examples to clearly show how such a plot can provide useful analytical information about the chemical system under study.

