

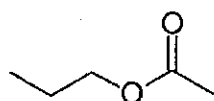
※ 考生請注意：本試題不可使用計算機。請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

I. Single or multiple choice questions (Each question has **one** or **more** answers.), 4 pts for each question.

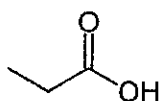
1. Which of the following diprotic acids a titration curve with 0.100 M NaOH will show just one equivalence point with 2:1 stoichiometry?

- (A) Resorcinol:  $pK_1$ : 9.30;  $pK_2$ : 11.06,
- (B) Leucine:  $pK_1$ : 2.33;  $pK_2$ : 9.74
- (C) Maleic acid:  $pK_1$ : 1.82;  $pK_2$ : 6.59
- (D) Salicylic acid:  $pK_1$ : 2.97;  $pK_2$ : 13.74
- (E) Tartaric acid:  $pK_1$ : 3.036;  $pK_2$ : 4.366

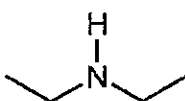
2. A student set up a normal phase partition HPLC separation of the following compounds:



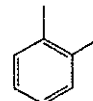
Propyl Acetate



Propionic Acid



Diethylamine

*o*-Xylene

What is the order of elution for these compounds?

- (A) Diethylamine > *o*-Xylene > Propionic Acid > Propyl Acetate
  - (B) Propyl Acetate > Propionic Acid > Diethylamine > *o*-Xylene
  - (C) *o*-Xylene > Diethylamine > Propyl Acetate > Propionic Acid
  - (D) Propionic Acid > *o*-Xylene > Propyl Acetate > Diethylamine
  - (E) Propyl Acetate > *o*-Xylene > Diethylamine > Propionic Acid
3. The most common composition of PBS buffer (1X) has the following components:

Salt	Concentration (mM)	Salt	Concentration (mM)
NaCl	137.	Na <sub>2</sub> HPO <sub>4</sub>	10.0
KCl	2.70	KH <sub>2</sub> PO <sub>4</sub>	1.80

What are the ionic strengths for HPO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup>, respectively?

- (A) 10.0 mM for HPO<sub>4</sub><sup>2-</sup>, 140. mM for Cl<sup>-</sup>
  - (B) 20.0 mM for HPO<sub>4</sub><sup>2-</sup>, 69.9 mM for Cl<sup>-</sup>
  - (C) 23.6 mM for HPO<sub>4</sub><sup>2-</sup>, 140. mM for Cl<sup>-</sup>
  - (D) 20.0 mM for HPO<sub>4</sub><sup>2-</sup>, 140. mM for Cl<sup>-</sup>
  - (E) 10.0 mM for HPO<sub>4</sub><sup>2-</sup>, 68.5 mM for Cl<sup>-</sup>
4. Which type of chromatography where the analyte ions in the mobile phase are attracted to the counter ions in the stationary phase?
- (A) Ion-pair chromatography
  - (B) Ion exclusion chromatography
  - (C) Ion-exchange chromatography
  - (D) Affinity chromatography
  - (E) Size exclusion chromatography

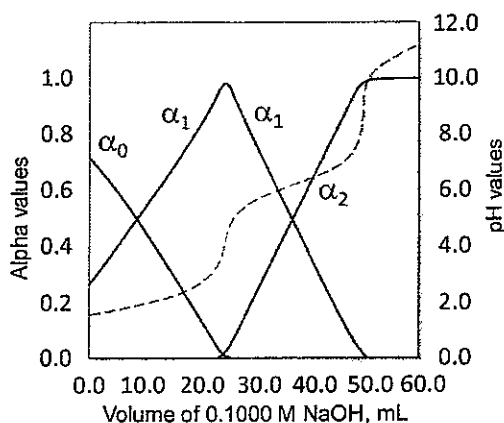
5. Which of the following statements about complexes formed by  $M^{n+}$  and EDTA in aqueous solutions is/are true?

- (A)  $M^{n+}$ -EDTA complexes have an equilibrium concentration that is dependent of pH.
- (B)  $M^{n+}$  ions and EDTA form complexes that are usually highly colored.
- (C)  $M^{n+}$ -EDTA complexes are often 1:1 in stoichiometry.
- (D)  $M^{n+}$ -EDTA complexes are less stable than corresponding metal-ammine complexes.
- (E) The presence of other ligands affects the equilibrium concentration of  $M^{n+}$ -EDTA complexes.

6. Which of the following statements about the advantage of an FT-IR spectrometer is/are correct?

- (A) The enhanced signal-to-noise ratio of an FT-IR spectrometer leads to longer acquisition time for good spectra.
- (B) The FT-IR spectrometer has signal-to-noise ratios that are better than those of a dispersive IR spectrometer.
- (C) A theoretical advantage of an FT-IR spectrometer is to provide a much lower energy throughput, which can reduce the noise and improve the sensitivity.
- (D) The interferometer in an FT-IR spectrometer is free from the problem of stray radiation because each IR frequency is chopped at a different frequency.
- (E) An FT-IR spectrometer can be used to study the compounds with strong absorption bands.

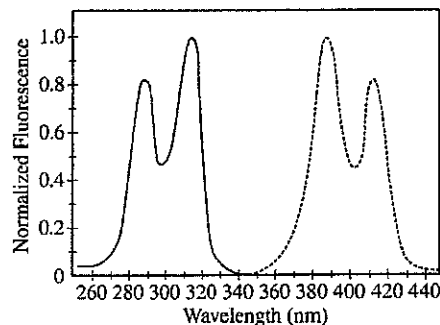
7. Which of the following statements about the titration curves below is/are correct?



- (A) The titration curve and alpha values plotted as a function of volume of sodium hydroxide indicate that the unknown species is a triprotic acid.
- (B) From the titration curves, one can conclude that the unknown species is a strong acid.
- (C) The intersection of  $\alpha_0 - \alpha_1$  and  $\alpha_1 - \alpha_2$  can represent the maximum of buffer capacity for corresponding each acid-base conjugates.
- (D) The second equivalence point shows up when  $\alpha_2$  becomes 1. The pH value at that equivalence point is the p-function of the dissociation constant of the unknown species.
- (E) When  $\alpha_0$  and  $\alpha_1$  values for each component are 0.5, it indicates the point at which chemically equivalent quantities of acid and base have been mixed. At this point, pH of the solution is equal to  $pK_a$ , which can be used to prepare a good buffer.

8. Based on the excitation and emission spectra for compound Z shown below, what appropriate excitation and emission wavelengths should be chosen to maximize the measured fluorescence intensity?

	Excitation $\lambda$ (nm)	Emission $\lambda$ (nm)
(A)	290	420
(B)	390	315
(C)	415	190
(D)	315	390
(E)	315	415



9. Which of the following methods can be used to characterize the surface morphology (structure) of a solid?
- Scanning electron microscopy (SEM)
  - Auger electron spectroscopy (AES)
  - Electron spectroscopy for chemical analysis (ESCA)
  - Scanning probe microscopy (SPM)
  - Secondary-ion mass spectrometry (SIMS)
10. Which of the following statements is/are true for signal-to-noise ratio enhancement?
- In spectroscopy, radiation sources are often modulated by mechanical devices, called chopper.
  - Boxcar averaging is a procedure for smoothing irregularities and enhancing the signal-to-noise ratio in a waveform, with the assumption that the noise irregularities are much smaller than signals.
  - High-pass filter reduces the drift effect and other high-frequency flicker noise.
  - Noise can be minimized through grounding and shielding, particularly in instruments that involve both analog and digital circuits.
  - Ensemble averaging can produce dramatic improvements in signal-to-noise ratios while successive sets of data stored in memory are collected and summed point-by-point for averaging.
11. Which of the following statements is/are not true for Raman scattering?
- Raman scattering requires a change in dipole moment.
  - Raman frequency shifts are independent of the frequency of excitation.
  - Raman scattering results in unequal shifts in frequency above and below the incident frequency.
  - Some Raman-active transitions are not infrared active.
  - Raman scattering requires a change in polarizability.
12. If 92.2 % of a compound X dissolved in 25.0 mL of water is extracted into 25.0 mL of dichloromethane, what is the distribution coefficient for the compound X between dichloromethane and the water?
- $7.05 \times 10^{-2}$
  - $8.46 \times 10^{-1}$
  - 7.80
  - $1.18 \times 10^1$
  - $1.42 \times 10^2$

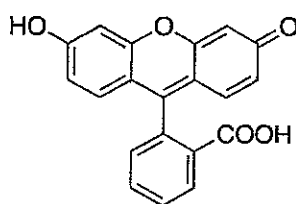
13. A 0.600 g sample of a pure, weak diprotic acid gives end points at 20.0 mL and 40.0 mL when it is titrated with 0.100 M NaOH. What is the molar mass of the weak acid?
- (A) 120 g/mole  
(B) 150 g/mole  
(C) 180 g/mole  
(D) 300 g/mole  
(E) 450 g/mole
14. A standard Y that is protonated should have a monoisotopic mass of 1234.1223 Da. When the compound Y is measured on time-of-flight mass analyzer, the recorded mass of the ion is 1234.1198 Da. What is the error in mass accuracy (ppm) for this measurement?
- (A) 2.03 ppm  
(B) 1.01 ppm  
(C) 0 ppm  
(D) -1.01 ppm  
(E) -2.03 ppm
15. The A term of the van Deemter equation is usually about zero in GC separations. Why?
- (A) Diffusion coefficients are much larger in the gas phase than in the liquid phase, so the longitudinal diffusion term is essentially zero.  
(B) Diffusion coefficients are much larger in the gas phase than in the liquid phase, so there is less efficient mass transfer between the mobile phase and the stationary phase.  
(C) The large particle sizes used in GC causes the differences in path lengths traveled by the solute molecules to be negligible.  
(D) Capillary columns are usually used in GC, and since there are no stationary phase particles, the differences in path lengths traveled by the solute molecules are negligible.  
(E) Eddy diffusion in GC column is so strong that there is efficient mass transfer.
16. Which of the following methods can be used to measure the size of gold nanoparticles?
- (A) Tunneling electron microscopy (TEM)  
(B) Dynamic light scattering (DLS)  
(C) Electrospray ionization mass spectrometry (ESI-MS)  
(D) Atomic force microscopy (AFM)  
(E) Size exclusion chromatography (SEC)
17. Which ion sources is/are commonly used for liquid chromatography-mass spectrometry (LC-MS)?
- (A) Matrix-assisted laser desorption ionization (MALDI)  
(B) Chemical ionization (CI)  
(C) Electrospray ionization (ESI)  
(D) Electron ionization (EI)  
(E) Atmospheric pressure chemical ionization (APCI)

18. The concentrations of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  in a mixture can be determined following their reaction with hexacyanoruthenate (II),  $\text{Ru}(\text{CN})_6^{4-}$ , which forms a purple-blue complex with  $\text{Fe}^{3+}$  ( $\lambda_{\text{max}} = 550 \text{ nm}$ ) and a pale-green complex with  $\text{Cu}^{2+}$  ( $\lambda_{\text{max}} = 396 \text{ nm}$ ). The molar absorptivities ( $\text{M}^{-1} \text{ cm}^{-1}$ ) for the metal complexes at the two wavelengths are summarized in the following table. When a sample containing  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  is analyzed in a cell with a pathlength of 1.00 cm, the absorbance at 550 nm is 0.183 and the absorbance at 396 nm is 0.109. What are the molar concentrations of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  in the sample?

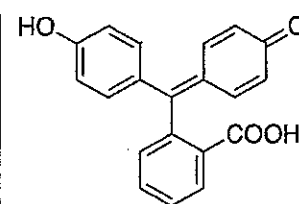
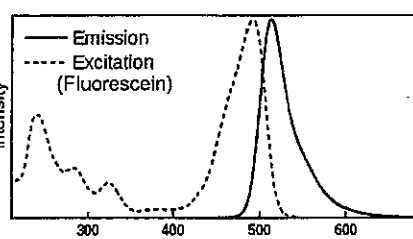
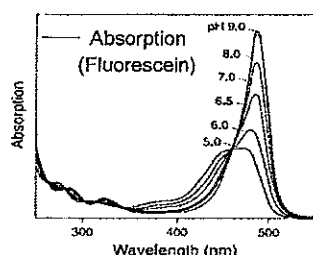
- (A)  $\text{Fe}^{3+}$  is  $1.43 \times 10^{-5} \text{ M}$ ;  $\text{Cu}^{2+}$  is  $1.86 \times 10^{-4} \text{ M}$   
 (B)  $\text{Fe}^{3+}$  is  $1.79 \times 10^{-5} \text{ M}$ ;  $\text{Cu}^{2+}$  is  $1.26 \times 10^{-4} \text{ M}$   
 (C)  $\text{Fe}^{3+}$  is  $1.26 \times 10^{-4} \text{ M}$ ;  $\text{Cu}^{2+}$  is  $1.79 \times 10^{-5} \text{ M}$   
 (D)  $\text{Fe}^{3+}$  is  $1.86 \times 10^{-4} \text{ M}$ ;  $\text{Cu}^{2+}$  is  $1.43 \times 10^{-5} \text{ M}$   
 (E)  $\text{Fe}^{3+}$  is  $2.52 \times 10^{-4} \text{ M}$ ;  $\text{Cu}^{2+}$  is  $3.58 \times 10^{-5} \text{ M}$

	$\epsilon_{550}$	$\epsilon_{396}$
$\text{Fe}^{3+}$	9970	84
$\text{Cu}^{2+}$	34	856

19 Which of the following statements about the spectroscopic properties of fluorescein below is/are correct?



Fluorescein



Phenolphthalein

- (A) Fluorescein has an absorption maximum at 494 nm and emission maximum of 512 nm (in water).  
 (B) Fluorescein has an isosbestic point at 460 nm for all pH values.  
 (C) The fluorescence of fluorescein is pH independent because the protonated and unprotonated forms of fluorescein switch too fast in water.  
 (D) Fluorescein has a greater fluorescence quantum yield than phenolphthalein because of its greater structural rigidity due to the bridging  $-\text{O}-$  groups.  
 (E) Fluorescein has higher fluorescence intensity because of its aromatic functional groups with  $\pi \rightarrow \pi^*$  and  $\sigma \rightarrow \pi^*$  transitions.
20. Which errors is/are commonly affecting pH measurements with glass electrode?
- (A) The alkaline error at pH value greater than 11 or 12.  
 (B) Significant errors, as much as 1~2 pH units, occur when the high-ionic-strength samples are measured with a glass electrode.  
 (C) Variation in the junction potential between standard and sample leads to an uncertainty in the measurement of pH that is not correctable.  
 (D) Hydration of the electrode may cause unstable performance and errors in pH measurements with glass electrode.  
 (E) The pH measurements with glass electrode must be made at 25°C. Otherwise, pH meter need adjustment to compensate for the change in nernstian response of the glass electrode.

II. Problem-solving and short answer questions, 5 pts for each question.

1. Why is glass better than fused silica as a prism construction material for a monochromator to be used in the region 400-800nm?
2. Explain how electroosmotic flow and differences in electrophoretic mobilities gives rise to separations in capillary zone electrophoresis.
3. At what wavelength in nm would the Stokes and anti-Stokes Raman lines for  $\text{CCl}_4$  appear ( $\Delta\nu = 790.0 \text{ cm}^{-1}$ ) using a He/Ne laser (632.8nm) and as excitation source?
4. The intensities of inductively coupled argon plasma emission are typically linear with concentration over a few orders of magnitude, whereas atomic absorption measurements are linear typically over a very limited range. Why?