國立清華大學 107 學年度碩士班考試入學試題

系所班組別：生醫工程與環境科學系 乙組(環境與分子科學組)

考試科目（代碼）：分析化學(2601)

1. (10%) What is a buffer solution and what are its properties? Considering solutions prepared by (a) dissolving 8.0 mmol of NaOAc in 200 mL of 0.1 M HOAc. (b) adding 100 mL of 0.05 M NaOH to 100 mL of 0.175 M HOAc. (c) adding 40 mL of 0.12 M HCl to 160 mLof 0.042 M NaOAc. In what respects do these solutions resemble one another? How do they differ?

2. (10%) A 0.7121-g sample of a wheat flour was analyzed by the Kjeldahl method. The ammonia formed by addition of concentrated base after digestion with H_2SO_4 was distilled into 25 mL of 0.04977 M HCl. The excess HCl was then back-titrated with 3.97 mL of 0.04012 M NaOH. Calculate the percent protein in the flour. (Note: The nitrogen-to-protein conversion factor for cereals is 5.7)

3. (10%) Eriochrome Black T is a typical metal-ion indicator that is used in the titration of several common cations. When Eriochrome Black T complexes with Mg^{2+} ions, it produces a pink-red solution. The indicator is blue in the absence of metal ion as the pH is greater than 7.0. Determine the transition ranges for Eriochrome Black T in titration of Mg^{2+} at pH 10.0, giving (a) that the second acid dissociation constant of the indicator is 2.8×10^{-12} M and (b) that the formation constant for $MgIn^-$ is 1.0×10^7 M.

4. (10%) Calculate the potential required to initiate deposition of copper from a solution that is 0.01 M in $CuSO_4$ and contains sufficient H_2SO_4 to give a pH of 4.0.

$$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad E° = + 1.229 \text{ V}$$
$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E° = + 0.337 \text{ V}$$

5. (10%) Briefly distinguish between concentration polarization and kinetic polarization. What experimental variables affect concentration polarization and describe the conditions that favor kinetic polarization in an electrochemical cell.
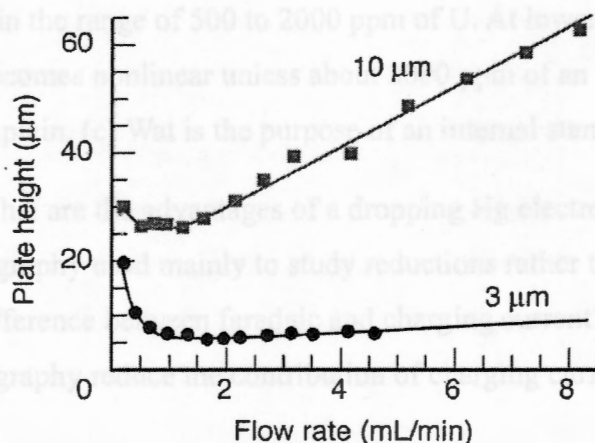
6. (10%) (a) Explain why plate height increases at (i) very low and (ii) very high flow rates in the following figure.

(b) Why is high pressure needed in high performance liquid chromatography (HPLC).

(c) When you try separating an unknown mixture by reversed-phase chromatography with 50% acetonitrile-50% water, the peaks are eluted between 1 and 3 min, and they are too close together to be well resolved for quantitative analysis. Should you use a higher or lower percentage of acetonitrile in the next run? Explain.

7. (4%) Mass spectrometry is an extremely versatile detection system for gas chromatography. Interfacing an HPLC system to a mass spectrometry is a much more difficult task, however. Describe the major reasons why it is more difficult to combine HPLC with mass spectrometry than it is to combine GC with mass spectrometry.

8. (6%) (a) Why is gas-solid chromatography not used nearly as extensively as gas-liquid chromatography? (b) Why do we use a makeup gas for some gas chromatography detectors?

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9. (10%) (a) Why is atomic emission more sensitive to flame instability than atomic absorption or fluorescence? (b) In the atomic absorption determination of uranium, a linear relationship is found between the absorbance at 351.5 nm and the concentration in the range of 500 to 2000 ppm of U. At lower concentrations, the relationship becomes nonlinear unless about 2000 ppm of an alkali metal salt are introduced. Explain. (c) Wat is the purpose of an internal standard in ICP-MS?

10. (10%) (a) What are the advantages of a dropping Hg electrode in polarography? Why is polarography used mainly to study reductions rather than oxidations? (b) What is the difference between faradaic and charging current? How does sampled current polarography reduce the contribution of charging current to the polarogram?

11. (5%) UV-vis absorbance for 1×10^{-4} M MnO_4^-, 1×10^{-4} M $Cr_2O_7^{2-}$, and an unknown mixture of both (all in a 1.0-cm cell) are given below. Find the concentration of each species in the mixture.

Wavelength (nm)	MnO_4^- standard	$Cr_2O_7^{2-}$ standard	Mixture
266	0.042	0.410	0.766
320	0.168	0.158	0.422

12. (5%) What processes lead to fluorescence and phosphorescence? Which coms at higher energy? Which is faster?