國　立　清　華　大　學　命　題　紙

97 學年度 生醫工程與環境科學 系（所） 環境分子科學 組碩士班入學考試

科目 分析化學 科目代碼 2603 共 4 頁第 1 頁 * 請在【答案卷卡】內作答

1. (30%) Please define following terms and explain the difference

(a) Gradient elution and isocratic elution in liquid chromatography

(b) Concentration polarization and kinetic polarization in voltammetry

(c) Activity and activity coefficient

(d) TD and TC marks on pipette, burette, volumetric flask

(e) Formation constant and conditional formation constant

(f) Mass-action effect and common-ion effect

(g) Standard electrode potential and half wave potential for a reversible reaction at a voltammetric electrode

(h) Chemical interference and releasing agent in atomic spectroscopy

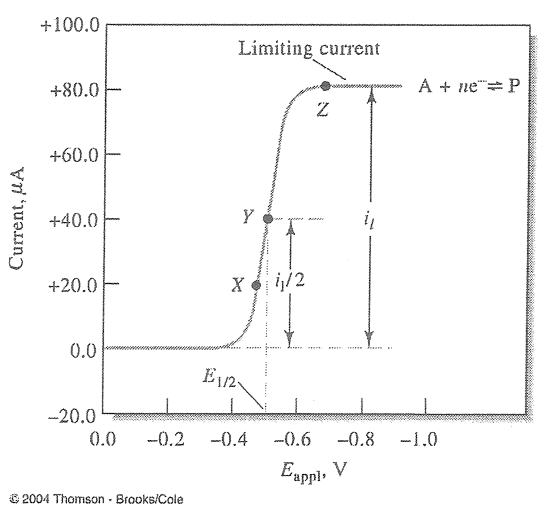
(i) Quantum yield of fluorescence and self-quenching

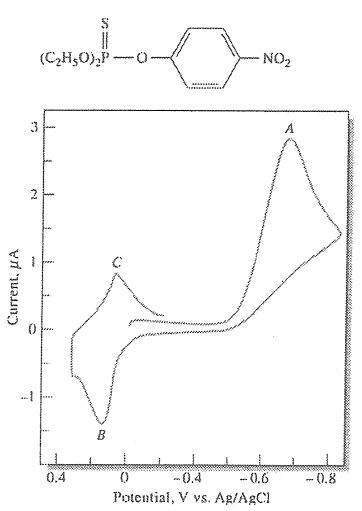
(j) Standard electrode potential and half wave potential for a reversible reaction at a voltammetric electrode

2. (10%) Following figures show two current-voltage plots obtained in linear-sweep and cyclic voltammetry.

(1) Please state what linear-sweep and cyclic voltammetry are.

(2) Please explain the reason resulting in the difference in the current-voltage plots.

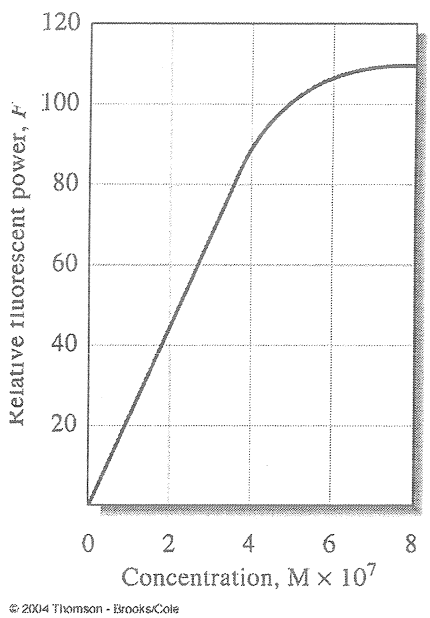




3. (10%) Following figure and equations show the relationships between the analyte concentration and the measured fluorescence intensity.

(1) Please explain the reason why we can enhance the analytical sensitivity by increase the power of the incident (excitation) beam.

(2) Please explain the reason why there is a departure from linearity in the relationship between measured fluorescence power and analyte concentration as the analyte concentration become greater than 4×10^{7} M.



F=K' (P_0-P)

F= power of fluorescent radiation

Po= power of the beam incident on the solution

P= power after traverses a length b of the medium

K' depends upon the q uantum efficiency of the fluorescence

$$\frac{P}{P_o} = 10^{-\varepsilon bc}$$

$$F = K'P_o(1-10^{-\varepsilon bc})$$

$$F = 2.3K'\varepsilon bcP_o$$

$$F = Kc$$

4. (5%) A cell consisting of a saturated calomel electrode and a lead ion electrode developed a potential of -0.4706 V when immersed in 50.00 mL of a sample. A 5.00-mL addition of a standard 0.0200 M lead solution caused the potential to shift to -0.4490 V. Calculate the molar concentration of lead in the sample.

$$For\ cations:\ E_{cell} = K - \frac{0.0592}{n}pX$$

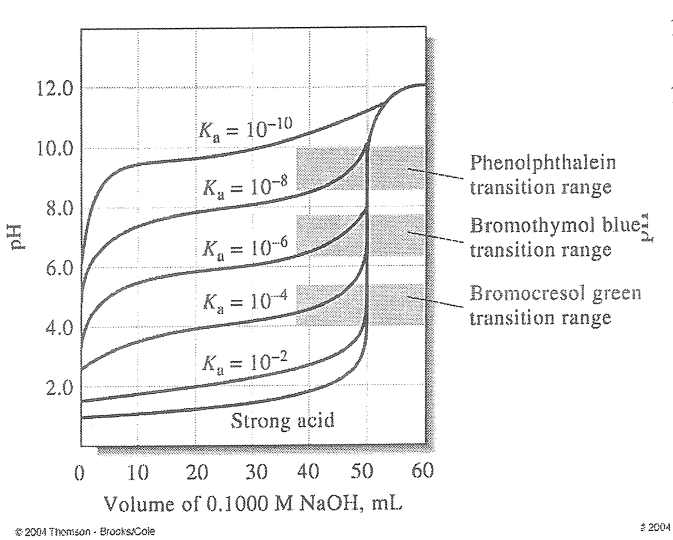
$$For\ anions:\ E_{cell} = K + \frac{0.0592}{n}pA$$

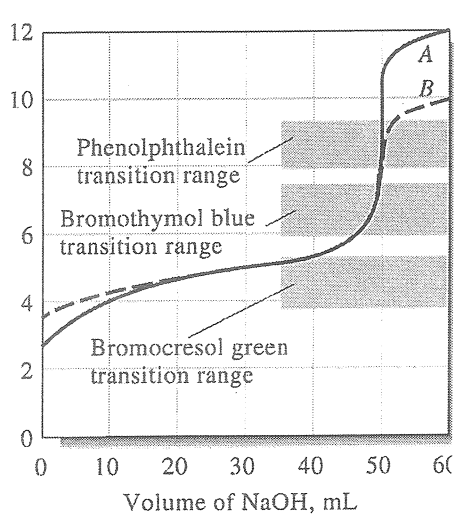
5. (10%) Which of the GC detectors in following table are suitable for HPLC? Why are some of these unsuitable for HPLC?

TABLE 31-1
Gas Chromatographic Detectors

Type	Applicable Samples	Typical Detection Limit
Flame ionization	Hydrocarbons	0.2 pg/s
Thermal conductivity	Universal detector	500 pg/mL
Electron capture	Halogenated compounds	5 fg/s
Mass spectrometer	Tunable for any species	0.25–100 pg
Thermionic	Nitrogen and phosphorous compounds	0.1 pg/s (P) 1 pg/s (N)
Electrolytic conductivity (Hall)	Compounds containing halogens, sulfur, or nitrogen	0.5 pg Cl/s 2 pg S/s 4 pg N/s
Photoionization	Compounds ionized by UV radiation	2 pg C/s
Fourier transform IR	Organic compounds	0.2 to 40 ng

6. (10%) Following two figures show the effects of concentration and reaction completeness on the shape of titration curves. Please illustrate the effects of analyte concentration and reaction completeness on the titration curve and applicability of titration method.





A: High Concentration

B: Low Concentration

7. (5%) A 5.00 g sample of a pesticide was decomposed with metallic sodium in alcohol, and the liberated chloride ion was precipitated as AgCl. Express the results of this analysis in terms of percent DDT ($C_{14}H_9Cl_5$) based on the recovery of 0.1606 g of AgCl. ($\mathcal{M}_{AgCl} = 143.37 \frac{g}{mole}$, $\mathcal{M}_{DDT} = 354.72 \frac{g}{mole}$)

8. (5%)What weight of sodium glycolate must be added to 300.0 mL of 1.00 M glycolic acid to produce a buffer solution that has a pH of 4.00?

($\mathcal{M}_{HOCH_2COONa} = 98.01 \frac{g}{mole}$, K_a of glycolic acid $=1.47\times10^{-4}$)

9. (5%) An analysis for borohydride ion is based on its reaction with Ag^+:

$$BH_4^- + 8Ag^+ + 8OH^- \rightarrow H_2BO_3^- + 8Ag + H_2O$$

The purity of a quantity of KBH_4 to be used in an organic synthesis was established by diluting 3.213 g of the material to exactly 500.0 mL, treating a 100.0 mL aliquot with 50.00 mL of 0.2221 M $AgNO_3$ and titrating the excess silver ion with 3.36 mL of 0.0397 M KSCN. Calculate the percent of the KBH_4 (53.941 g/mol).

10. (10%) A solution contains 1.694 mg of $CoSO_4$ (155.0 g.mol) per milliliter. Calculate

(a) The volume of 0.0864 M EDTA needed to titrate a 25.00-mL aliquot of this solution.

(b) The volume of 0.009450 M Zn^{2+} needed to titrate the excess reagent after addition of 50.00 mL of 0.008640 M EDTA to a 25.00-mL aliquot of this solution.

---- The end ----