國 立 清 華 大 學 命 題 紙

99 學年度 生醫工程與環境科學(環境分子科學) 碩士班入學考試

科目 分析化學 科目代碼 2403 共 3 頁第 1 頁 *請在【答案卷卡】內作答]

1. (10%) In flame AA with a hydrogen/oxygen flame, the absorbance for iron decreased in the presence of large concentrations of sulfate ion.
   (a) Suggest an explanation for this observation.
   (b) Suggest three possible methods of overcoming the potential interference of sulfate in a quantitative determination of iron.

2. (10%) A portable photometer with a linear response to radiation registered 73.6 μA (micro-amper) with a blank solution in the light path. Replacement of the blank solution with an absorbing solution yielded a response of 24.9 μA. Calculate
   (a) The percent transmittance of the sample solution.
   (b) The absorbance of the sample solution.
   (c) The transmittance to be expected for a solution in which the concentration of the absorber is one-third that of the original sample solution.
   (d) The transmittance to be expected for a solution that has twice the concentration of the sample solution.

3. (15%) (a) What are the structural characteristics of a chelating agent?
   (b) Why does the charge on the surface of precipitate particles change sign at the equivalence point in a titration?
   (c) Why does the typical acid/base indicator exhibit its color change over a range of about 2 pH units?
   (d) Based on following table, please suggest an indicator that would give an end point for the titration of the first two protons in H_3PO_4.
   ($[HPO_4^{2-}] = 0.01$, $K_{a1} = 7.11\times10^{-3}$, $K_{a2} = 6.32\times10^{-8}$, $K_{a3} = 4.5\times10^{-13}$)
   (e) Why are multidentate ligands preferable to unidentate ligands for complexometric titration?

TABLE 14-1
Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

*At ionic strength of 0.1.
†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.
‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type; $In + H_2O \rightleftharpoons InH^+ + OH^-$.
§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$.

4. (10%) A solution of $HClO_4$ was standardized by dissolving 0.4125 g of primary-standard-grade HgO in a solution of KBr:

$$HgO(s) + 4Br^- + H_2O \rightarrow HgBr_4^{2-} + 2\,OH^-$$

The liberated OH^- consumed 46.51 mL of the acid. Calculate the molarity of the $HClO_4$.

($\mathcal{M}_{HgO} = 216.59 \frac{g}{mole}$)

5. (10%) A 0.6004-g sample of Ni/Cu condenser tubing was dissolved in acid and diluted to 100.0 mL in a volumetric flask. Titration of both cations in a 25.00-mL aliquot of this solution required 45.81 mL of 0.05285 M EDTA. Mercaptoacetic acid and NH_3 were then introduced; production of the Cu complex with the former resulted in the release of an equivalent amount of EDTA which required a 22.85-mL titration with 0.07238 M Mg^{2+}. Calculate the percent Cu and Ni in the alloy.
(Atomic weight of Ni and Cu are 58.963 and 63.546 g/mole, respectively.)

6. (10%) Electrolytically generated I_2 was used to determine the amount of H_2S (MW= 34.08 g/mole) in 100 mL of brackish water. Following addition of excess KI, titration required a constant current of 36.32 mA for 10.12 min. The reaction was

$$H_2S + I_2 \rightarrow S_{(s)} + 2H^+ + 2I^-$$

Express the results of the analysis in terms of ppm (mg/L) H_2S. (10%)

7. (10%) (a) In 1975, the problem created by the high conductance of eluents was solved by the introduction of an eluent suppressor column immediately following the ion-exchange column. Please describe how the conductance of eluent can be suppressed in the use of suppressor column.
(b) Indicate the order of elution of the following compounds from a reverse-phase packed HPLC column:
(1) benzene, diethyl ether, *n*-hexane
(2) dichloroethane, acetamide, acetone
(c) What is meant by temperature programming in gas chromatography? (5%)

8. (10%) A solution is 0.150 M in Co^{2+} and 0.0750 M in Cd^{2+}

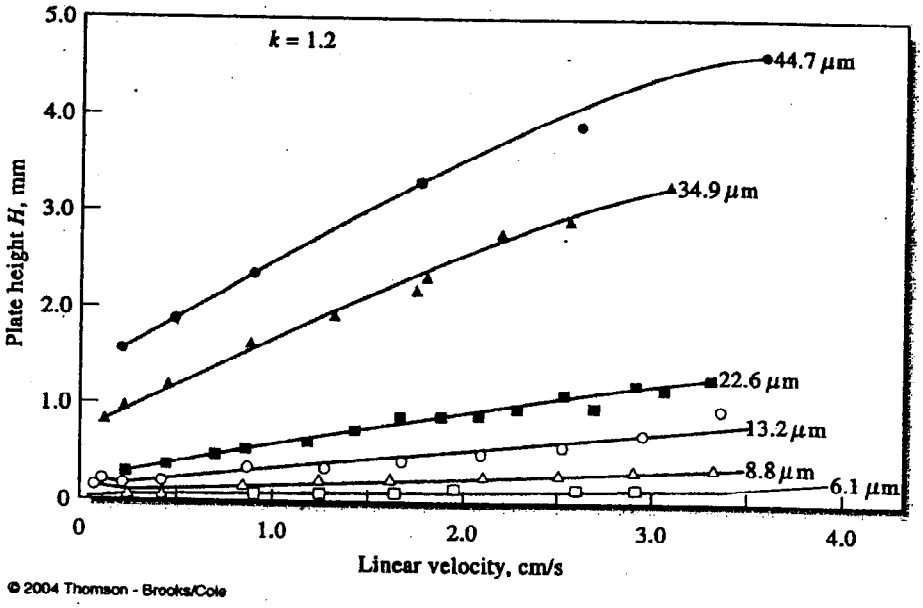
(a) Calculate the Co^{2+} concentration in the solution as the first cadmium starts to deposit.

(b) Calculate the cathode potential needed to lower the Co^{2+} concentration to 1.00×10^{-5} M.

(c) Based on (a) and (b) above, can Co^{2+} be quantitatively separated from Cd^{2+}?

($E^{o}_{Cd} = -0.403\,V$ $E^{o}_{Co} = -0.277V$)

9. (10%) Please refer to following figure and illustrate two parameters arbitrarily to explain their effects on the performance of HPLC.



10. (5%) Define following terms

(a) replicate samples and interferent

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

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