國 立 清 華 大 學 命 題 紙

九十一學年度 原子科學 系（所） 乙 組碩士班研究生招生考試

科目 分析化學 科號 3302 共 2 頁第 1 頁 *請在試卷【答案卷】內作答

1. The chemical content of the tree rings presumably mirrors chemical changes in the environment. A combustion procedure was employed to measure Cl in the pine tree rings. Following combustion, 30 min was allowed for absorption of the products the solution. The element Cl was converted to chloride (Cl^-) in the oxidizing absorption solution. Currently, some conventional titration methods have been replaced by instrumental methods. However, conventional methods carried out by a skilled analyst are considered as reference methods available for producing high quality data. (15%)
   (a) Please illustrate a conventional titration method and an instrumental method, individually, for the determination of the concentration of Cl^- ion in the absorption solution. Meanwhile please compare the advantages and disadvantages of the methods you stated.
   (b) Please state the procedure for preparing a 7.2×10^{-4} M of silver standard solution from $AgNO_3$ (M.W.=169.9 g/mole) and a relevant titration method for the determination of the concentration of Cl^- ion in 25 mL of absorption solution. The equivalence point was reached when 37.38 mL of silver solution had been delivered.

2. NO_x and SO_x produced from automobiles and factories are the main causes of acid rain because they will convert into nitric acid and sulfuric acid after reacting with water and oxidizing agents in the atmosphere. (15%)
   (a) Please calculate the pH of a rain that is 5.0×10^{-5} M in HNO_3 and 1.0×10^{-5} M in H_2SO_4. (K_2 of H_2SO_4=0.01)
   (b) A 5.0×10^{-5} M of carbonate-free NaOH solution was prepared for the determination of acidity of aforementioned rain. If exactly 1.00 L of this solution was exposed to air for some time and absorbed 2.2×10^{-4} g of CO_2 (M.W.= 44.01 g/mole). Please calculate the relative carbonate error resulting from the dissolution of CO_2 into NaOH titrant.
   (c) Derive a curve for the titration of 25.00 mL of the acid rain with aforementioned carbonate-contaminated NaOH solution.

3. The hardness of water is always determined by EDTA-titration method. Please derive a curve (pCa as a function of volume of EDTA) for the titration of 50.0 mL of 0.00500 M Ca^{2+} with 0.0100 M EDTA in a solution buffered to a constant pH of
   (a) 6.0 ($K_{CaY}=5.0\times10^{10}$, $\alpha_4=2.2\times10^{-5}$)
   (b) 10.0 ($K_{CaY}=5.0\times10^{10}$, $\alpha_4=3.5\times10^{-1}$)
   (c) Determine the transition range for Eriochrome Black T in titration of Ca^{2+} at pH 10.0.
   ($HIn^{2-} + H_2O \Leftrightarrow In^{3-} + H_3O^+$ $K_2=2.8\times10^{-12}$)
   ($Ca^{2+} + In^{3-} \Leftrightarrow CaIn^-$ $K_f=2.5\times10^5$)
   (d) Please compare and make a comment on the titration curves obtained from aforementioned acidity.(15%)

4. Calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl using (10%)
   (a) $E^{\circ}_{Ag^+}$=0.779 V
   (b) E°_{AgCl}=0.222 V (K_{sp} of AgCl=1.82×10^{-10})

5. The cell
   SCE‖ HA (0.250 M), NaA (0.170 M) ‖H_2 (1 atm), Pt
   has a potential of –0.797 V. Calculate the dissociation constant of HA, neglecting the junction potential. (E_{SEC}=0.244 V) (10%)

6. Glass electrode is the most convenient and widely used tool for pH measurement. Generally, an internal Ag/AgCl electrode and 1.0 M KCl solution both can be found inside of glass electrode. (10%)
   (a) Please state the functions of Ag/AgCl electrode and 1.0 M KCl solution when a glass electrode is used for pH measurement.
   (b) Briefly describe (1) liquid-junction potential, (2) boundary potential and (3) asymmetry potential
   (c) Describe the alkaline error in the measurement of pH by a glass electrode.

7. According to the interaction mechanism between incident radiation (light or heat) and substances, absorption spectroscopic methods can be divided into atomic absorption spectroscopy, ultraviolet and visible molecular absorption spectroscopy, and infrared absorption spectroscopy. (10%)
   (a) Please state the difference among those spectrochemical methods.
   (b) Please describe the main application of aforementioned methods.
   (c) Please describe two common interferences encountered in the atomic absorption spectrometry.

8. Chromatography is the most powerful too for separating and measuring the components of a complex mixture. High-resolution capillary gas chromatography (capillary GC) and high-performance liquid chromatography (HPLC) are workhorses of the modern analytical chemistry laboratory. In order to reach a satisfactory analytical performance, reasonable working time, optimized separation resolution and proper detection sensitivity are the main factors should be taken into consideration for an analyst. (15%)
   (a) Please state the parameters that an analyst can adjust to achieve the optimized chromatographic separation.
   (b) Please illustrate two most widely used detectors and explain their application in HPLC separation.
   (c) Please illustrate two most widely used detectors and explain their application in capillary GC separation.