國立清華大學 100 學年度碩士班入學考試試題

系所班組別：生醫工程與環境科學系 乙組(環境分子科學組)

考試科目（代碼）：分析化學 2603

1. A silver chloride electrode is a type of reference electrode, commonly used in electrochemical measurements. For example, it is usually the internal reference electrode in pH meters. As another example, the silver chloride electrode is the most commonly used reference electrode for testing cathodic protection corrosion control systems in sea water environments. (10%)

   (1) The electrode functions as a redox electrode and the reaction is between the silver metal (Ag) and its salt — silver chloride (AgCl, also called silver(I) chloride). The overall electrode reaction can be written as:

   $AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-_{(aq)}$

   Please give the corresponding equations of this reaction.

   (2) The standard reduction potential of Ag^+ is 0.799 V. Please calculate the electrode potential of a silver electrode immersed in a 0.0500 M solution of NaCl.

2. Commercial pH electrodes used in pH meters consist of a H^+ selective membrane (which can be made made just of very thin glass), and internal and external reference electrodes, usually combined in one housing. Modern pH electrodes are usually of the "combination" type. Schematically, the total cell may be expressed as

   SCE||test solution ($[H_3O^+]=a_1$)|glass membrane|$[H_3O^+]=a_2$, Cl^-|AgCl(s)/Ag

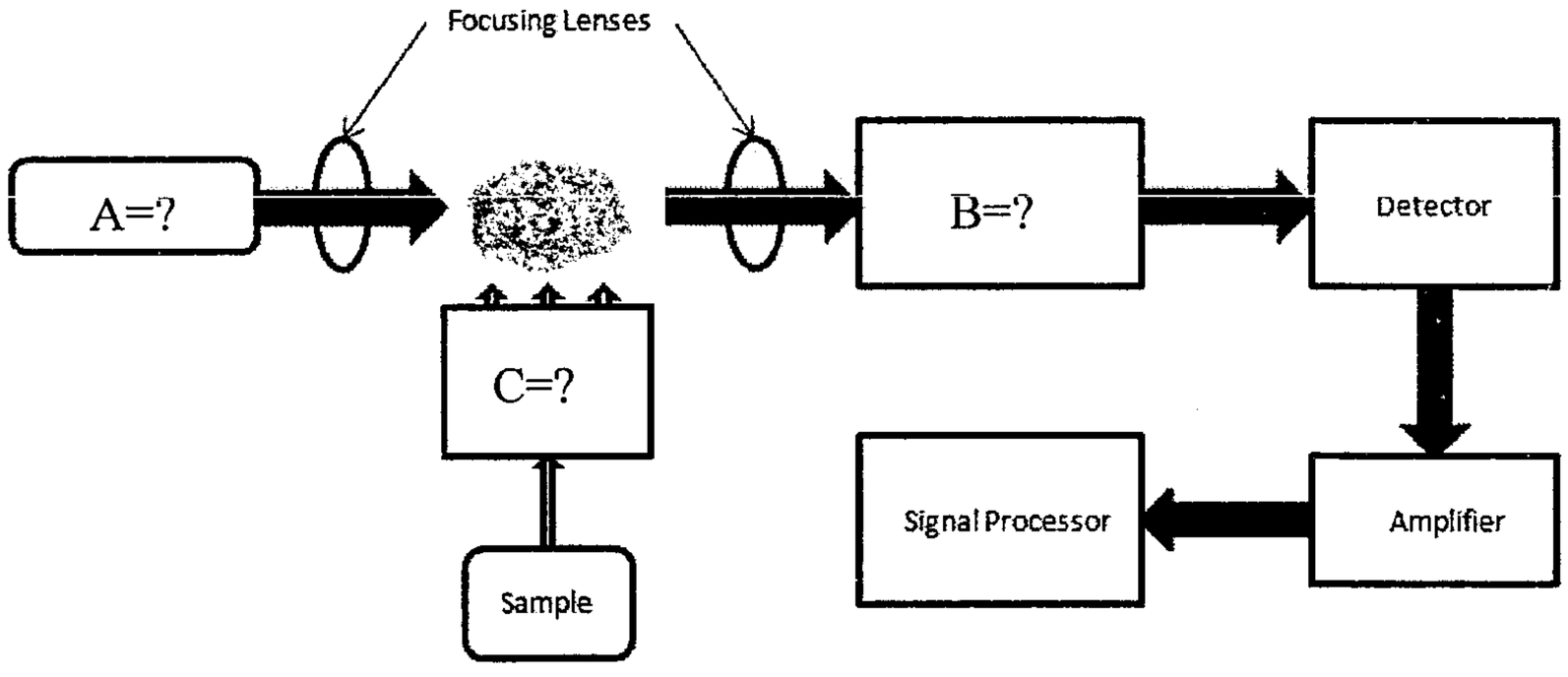
   (1) Please give the definition of boundary potential (E_b) and explain why E_b can be expressed as $0.0592 \log(a_1/a_2)$.

   (2) The potential of a combination pH electrode is due to the difference in activities of H^+ between the test solution (a_1) and reference solution (a_2) sides of the glass membrane. Please illustrate how we can keep the potential of internal reference electrode at a constant level.

   (3) What kind of error can be resulted in when the concentration of H^+ is very low and large amount of cations other than H^+ are present in solution.

3. Absorption spectroscopy refers to spectroscopic techniques that measure the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. The intensity of the absorption varies as a function of frequency, and this variation is the absorption spectrum. Absorption spectroscopy is employed as an analytical chemistry tool to determine the presence of a particular substance in a sample and, in many cases, to quantify the amount of the substance present.

(1) Following figure is the block diagram of atomic absorption spectrometer (AAS). Based on the principle of AAS, please fill the blanks in the block diagram with the correct name of the device.



(2) In the atomic absorption determination of uranium, a linear relationship is found between the absorption at 351.5 nm and the concentration in the range of 500 to 2000 ppm of U. Please explain why the relationship becomes nonlinear unless about 2000 ppm of an alkali metal salt re introduced at lower concentrations of U.

4. Evaluate the missing quantities in the accompanying Table. Where needed, use 200 for the molar mass of the analyte.

	A	%T	ε, L mol^{-1} cm^{-1}	A, cm^{-1} ppm^{-1}	B, cm	C, M	C, ppm
(a)	0.172		4.23×10^{3}		1.00		
(b)			3.73×10^{3}		0.100	1.71×10^{-3}	
(c)	0.179				1.00	7.19×10^{-5}	

5. Please state the principles of normal phase chromatography, reverse phase chromatography and ion-pairing chromatography.

6. A solution of $Ba(OH)_2$ was standardized against 0.1016 g of primary-standard-grade benzoic acid C_6H_5COOH (122.12 g/mol). An end point was observed after addition of 44.42 mL of base.

   (1) Calculate the molarity of the based.

   (2) Calculate the standard deviation of the molarity if the standard deviation for weighing was ± 0.2 mg and that for the volume measurement was ± 0.03 mL.

   (3) Assuming an error of – 0.3 mg in the weighing, calculate the absolute and relative systematic error in the molarity.

7. (1) Make a distinction between
   (a) activity and activity coefficient.
   (b) thermodynamic and concentration equilibrium constants.

   (2) Use activities to calculate the molar solubility of $Zn(OH)_2$ in the solution that results when you mix 20.0 mL of 0.250 M KOH with 80.0 mL of 0.0250 M $ZnCl_2$.

8. How would you prepare 1.00 L of a buffer with a pH of 7.00 from 0.200 M H_3PO_4 and 0.160 M NaOH?

Table 1. Acid dissociation constants at 25℃

Acid	**Formula**	K_1	K_2	K_3
Phosphoric acid	H_3PO_4	7.11×10^{-3}	6.32×10^{-8}	4.5×10^{-13}

9. A 0.5000-g sample containing $NaHCO_3$, Na_2CO_3, and H_2O was dissolved and diluted to 250.0 mL. A 25.00-mL aliquot was then boiled with 50.00 mL of 0.01255 M HCl. After cooling, the excess acid in the solution required 2.34 mL of 0.01063 M NaOH when titrated to a phenolphthalein end point. A second 25.00-mL aliquot was then treated with an excess of $BaCl_2$ and 25.00 mL of the base; precipitation of all the carbonate resulted, and 7.63 mL of the HCl were required to titrate the excess base. Calculate the composition of the mixture.

10. (1) What are the structural characteristics of a chelating agent?

(2) Calculate conditional constant for the formation of the EDTA complex of Fe^{2+} at pH 10.0.

Table 1. Formation constant for EDTA complex

Cation	K_{MY}	**Log** K_{MY}
Fe^{2+}	2.1×10^{14}	14.33

Table 2. Values for α_4 for EDTA at selected pH values

pH	α_4	**pH**	α_4
6.0	2.2×10^{-5}	9.0	5.2×10^{-2}
7.0	4.8×10^{-4}	10.0	3.5×10^{-1}
8.0	5.4×10^{-3}	11.0	8.5×10^{-1}