注意：考試開始鈴響前，不得翻閱試題，
並不得書寫、畫記、作答。

國立清華大學 114 學年度碩士班考試入學試題

系所班組別：分析與環境科學研究所

科目代碼：3001

考試科目：分析化學

—作答注意事項—

1. 請核對答案卷（卡）上之准考證號、科目名稱是否正確。
2. 考試開始後，請於作答前先翻閱整份試題，是否有污損或試題印刷不清，得舉手請監試人員處理，但不得要求解釋題意。
3. 考生限在答案卷上標記「▼ 由此開始作答」區內作答，且不可書寫姓名、准考證號或與作答無關之其他文字或符號。
4. 答案卷用盡不得要求加頁。
5. 答案卷可用任何書寫工具作答，惟為方便閱卷辨識，請儘量使用藍色或黑色書寫；答案卡限用 2B 鉛筆畫記；如畫記不清（含未依範例畫記）致光學閱讀機無法辨識答案者，其後果一律由考生自行負責。
6. 其他應考規則、違規處理及扣分方式，請自行詳閱准考證明上「國立清華大學試場規則及違規處理辦法」，無法因本試題封面作答注意事項中未列明而稱未知悉。

國立清華大學 114 學年度碩士班考試入學試題

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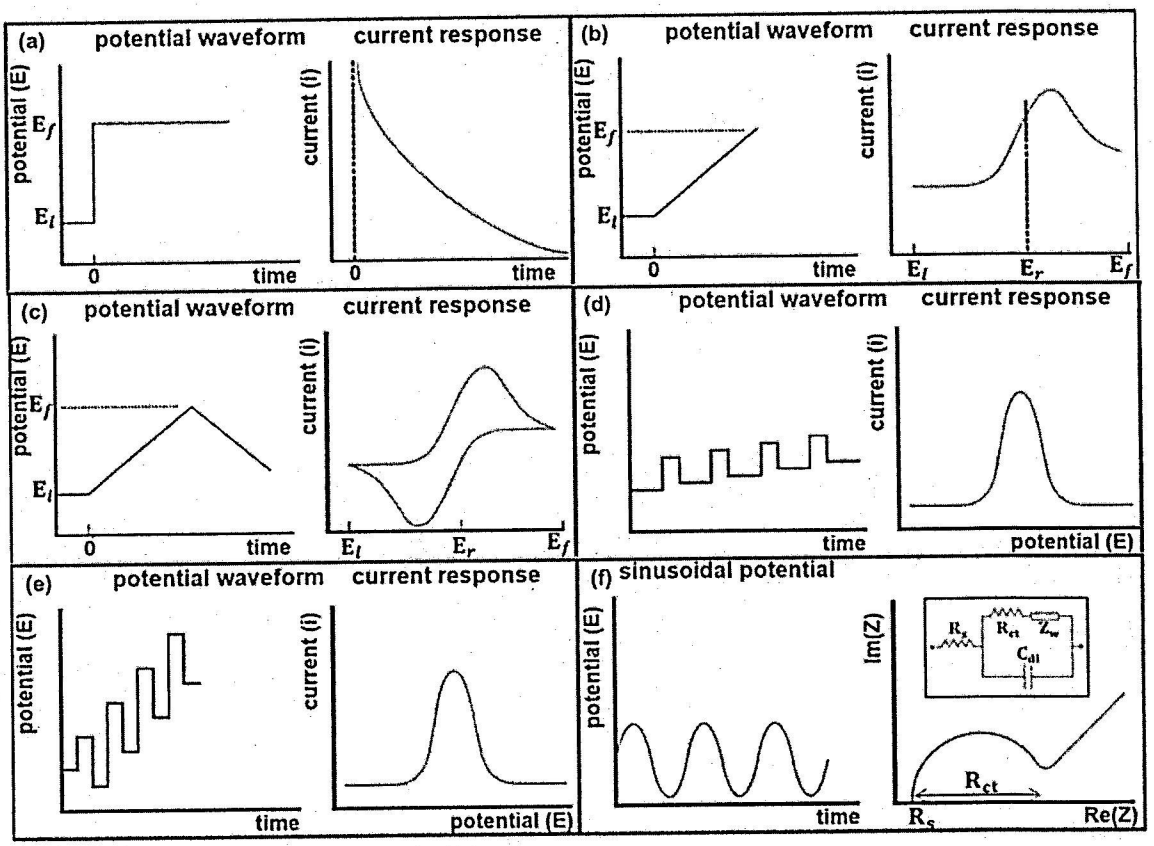
1. (4%) Water splitting, which involves the two half-reactions of proton reduction and water oxidation, has been extensively studied for clean hydrogen production. In theory, electrochemical water splitting requires a voltage of 1.23 V. However, in practice, over 1.6 V is needed to drive the overall water splitting reaction. Please explain the possible reasons behind this overpotential.

2. (12%) Please matches the following techniques: (i) cyclic voltammetry, (ii) differential pulse voltammetry, (iii) chronoamperometry, (iv) electrochemical impedance spectroscopy, (v) square-wave voltammetry, and (vi) linear sweep voltammetry with the corresponding electrochemical methods shown below.



3. (6%) In atomic absorption spectroscopy, flame, graphite furnace, hydride generation, and cold vapor are some representative atomization methods. Describe why electrothermic atomization, hydride generation and cold vapor can achieve higher sensitivity than flame atomization.

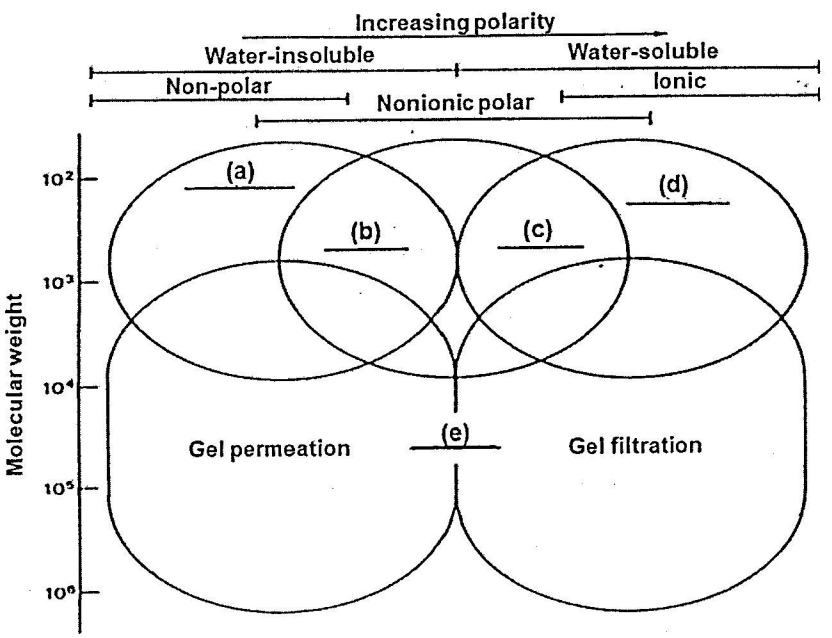
4. (3%) Why are detection limits in inductively coupled plasma mass spectrometry generally lower with double-focusing spectrometers than with quadrupole mass spectrometers?

5. (6%) Describe the key components and arrangement of an instrument used for fluorescence spectroscopic measurements.

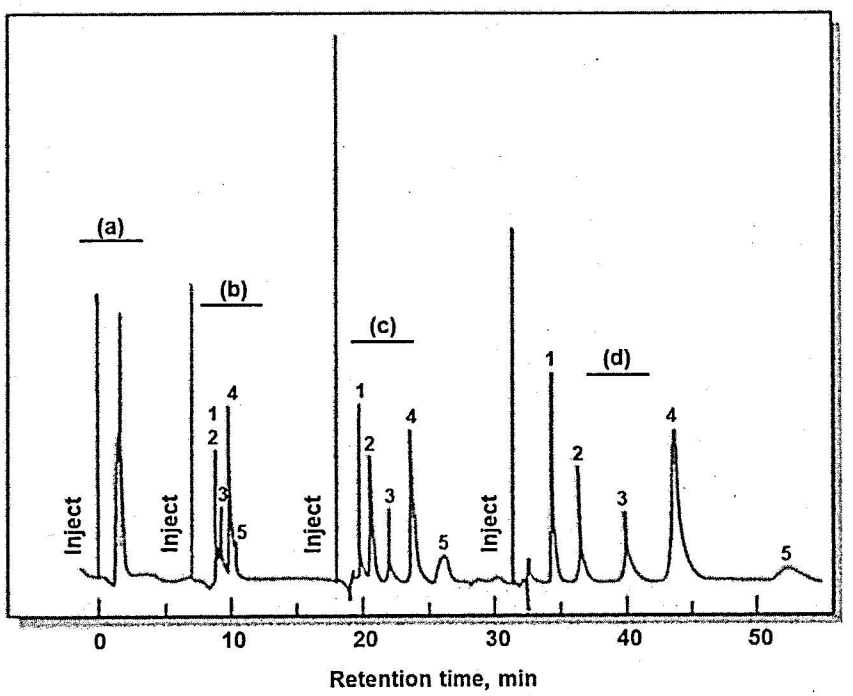
6. (6%) UV-vis absorbance for 1×10^{-4} M MnO_4^-, 1×10^{-4} M $Cr_2O_7^{2-}$, and an unknown mixture of both (all in a 1.0-cm cell) are given below. Find the concentration of each species in the mixture.

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

7. (10%) The five widely used types of high-performance liquid chromatography are listed below: (i) exclusion, (ii) adsorption, (iii) ion exchange, (iv) reversed-phase partition, and (v) normal-phase partition. Please match each type to the most suitable blank in the following figure.



8. (4%) The effect of solvent variation on chromatograms is shown in the following figure, illustrating the separation of analytes: (1) 9-10, anthraquinone; (2) 2-methyl-9,10-anthraquinone; (3) 2-ethyl-9,10-anthraquinone; (4) 1,4-dimethyl-9,10-antraquinone; (5) 2-*t*-butyl-9,10-anthraquinone. Please match the most suitable solvent composition from the list below to each blank: (i) 70% methanol/30% water, (ii) 60% methanol/40% water, (iii) 50% methanol/50% water, and (iv) 40% methanol/60% water.



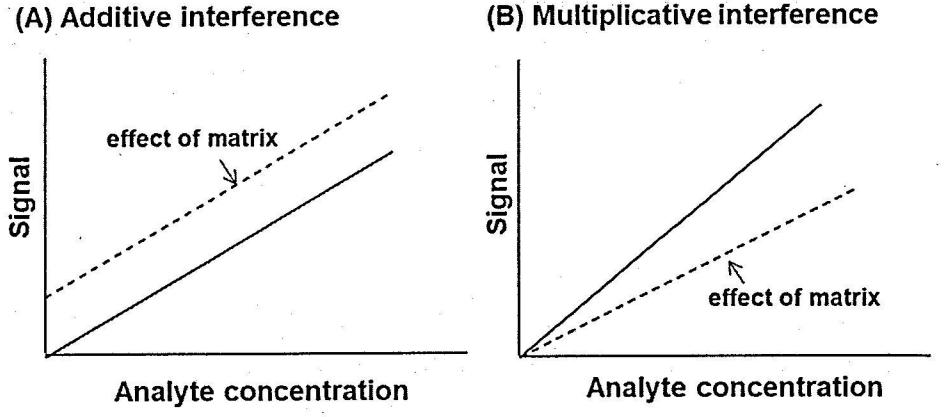
9. (6%) What are the differences between gas-liquid and gas-solid chromatography in terms of their separation mechanisms? Which technique is more suitable for separating permeant gases such as CO, CO_2, H_2 and methane?

10. (4%) Mass spectrometry is an extremely versatile detection system for gas chromatography (GC). Interfacing a high-performance liquid chromatography (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.

11. (6%) Consult the table below and select an appropriate acid/base pair to prepare a buffer with a pH of 7.4. Describe the procedure for preparing a 0.1 M buffer solution with a pH of 7.4.

Chemicals	Formula	K_1	K_2	K_3
Acetic acid	CH_3COOH	1.75×10^{-5}		
Phosphoric acid	H_3PO_4	7.11×10^{-3}	6.32×10^{-8}	4.5×10^{-13}
Tris	$(HOCH_2)_3CNH_2$	8.32×10^{-9}		

12. (6%) Plots (A) and (B) illustrate two common types of interference typically encountered in real sample detection. Can these interferences be corrected using the standard addition method? If so, how does the standard addition method work?



13. (6%) Calculate the formation constant K_f for $Ag(CN)_2^-$:

$Ag^+ + 2CN^- \rightleftharpoons Ag(CN)_2^-$

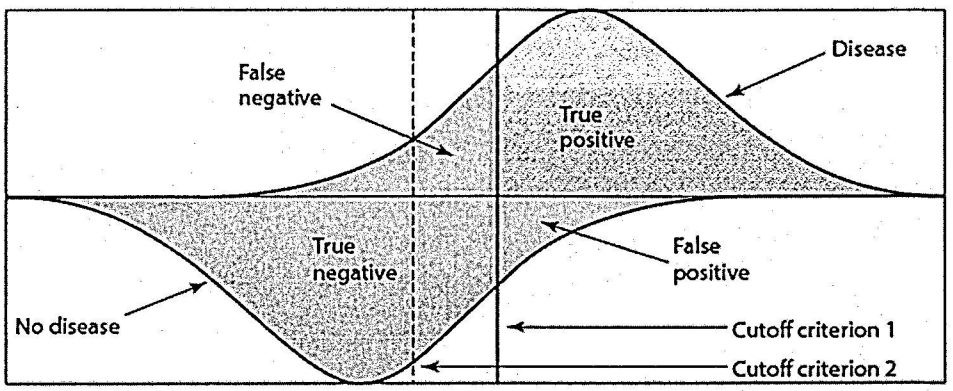
if the cell

$SCE \| Ag(CN)_2^-(7.5 \times 10^{-3}\ M), CN^-(0.025\ M) \mid Ag$ develops a potential of -0.625V.

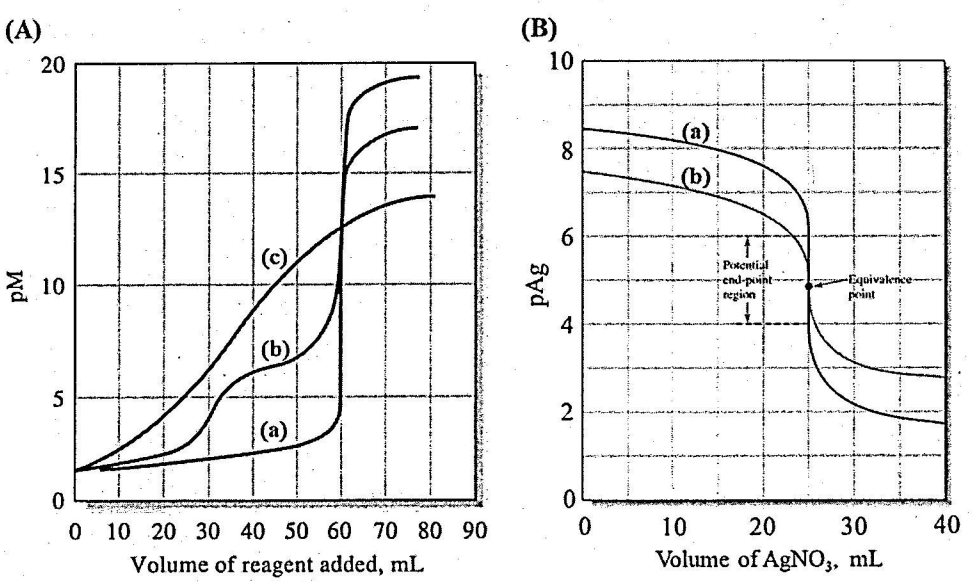
(The electrode potential of SCE is 0.244 V at 25°C)

$(Ag^+ + e^- \rightleftharpoons Ag_{(s)} \quad E^\circ = +0.799\ V)$

14. (4%) Moving the cutoff criterion line is known to affect sensitivity and specificity in opposing directions. In this case of improved sensitivity with reduced specificity, either Cutoff Criterion 1 or Cutoff Criterion 2 should be selected.



15. (5%) The two figures below illustrate the effects of (A) ligand coordination number and (B) analyte concentration on the shapes of complexometric and precipitation titration curves, respectively. For complexometric titration (Figure A), it should be noted that the overall formation constant for each product remains the same. Please match the most appropriate items from the list below to each label:
Figure A (a to c): (i) unidentate, (ii) bidentate, (iii) tetradentate ligands
Figure B (a, b): (i) high NaCl concentration, (ii) low NaCl concentration

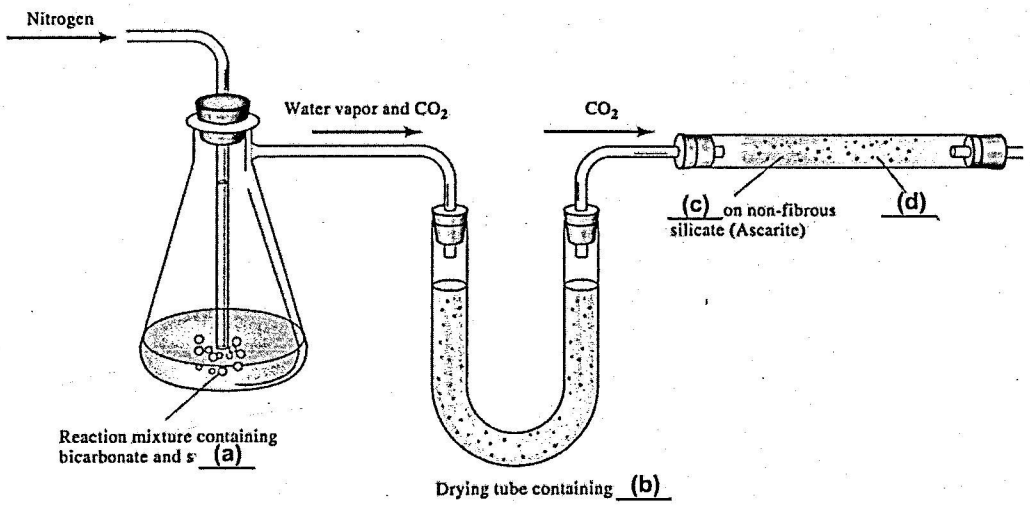


16. (8%) If you are tasked with determining the sodium hydrogen carbonate content of an antacid tablet, based on following equations and the principle of gravimetric volatilization procedure. Please fill in the blanks in the following figure.

$$NaHCO_{3(aq)} + H_2SO_{4(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + NaHSO_{4(aq)}$$

$$CaSO_4 + H_2O \rightarrow CaO + H_2SO_4$$

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$



17. (4%) The figure below illustrates the effect of electrolyte concentration on the thickness of the double layer surrounding a colloidal AgCl particle in a solution containing excess $AgNO_3$. Please fill in the blanks with: (i) high or (ii) low electrolyte concentration.