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 112 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：2901

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 112 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

考試科目（代碼）：分析化學(2901)

　*請在【答案卷】作答

1. (5%) Describe the basic principle of voltammetry. Why are stripping methods more sensitive than other voltammetric procedures?

2. (6%) Describe the working principle and instrumentation of a pH meter.

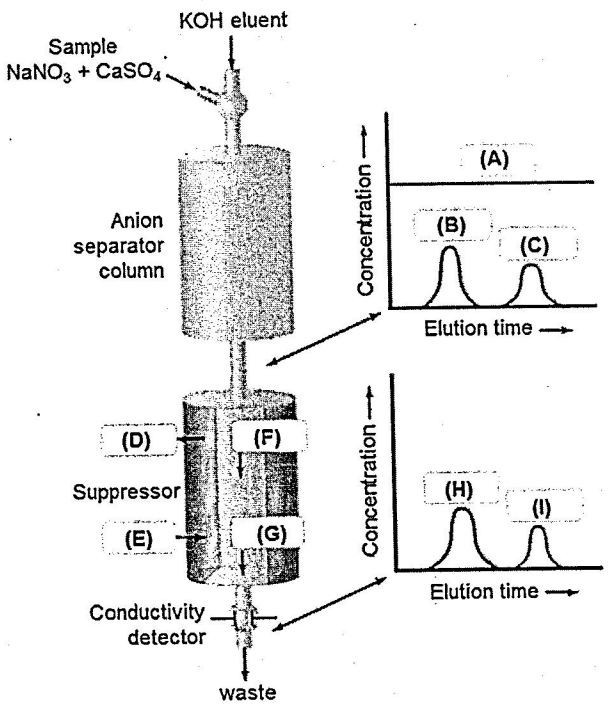
3. (3%) Distinguish between concentration polarization and kinetic polarization.

4. (6%) Why has inductively coupled plasma mass spectrometry (ICP-MS) become an important and widely used method for elemental analysis?

5. (3%) Please describe the basic principle of ion-pair chromatography.

6. (9%) In the Figure below, suppressed-ion anion chromatography is used to separate and detect NO_3^- and SO_4^{2-} in a sample containing $NaNO_3$ and $CaSO_4$. Fill in the blanks (A to I) with the species that are listed below.

   NO_3^-, SO_4^{2-}, KNO_3, K_2SO_4, HNO_3, H_2SO_4, KOH, H^+, K^+



7. (15%) The Table below lists the properties and characteristics of typical gas chromatography columns. Please (a) describe the physical differences between FSOT, WCOT, SCOT and packed columns. (b) Why the efficiency of SCOT columns is less than that of WCOT columns but significantly greater than that of packed columns? (c) What kinds of samples can be separated by PLOT columns?

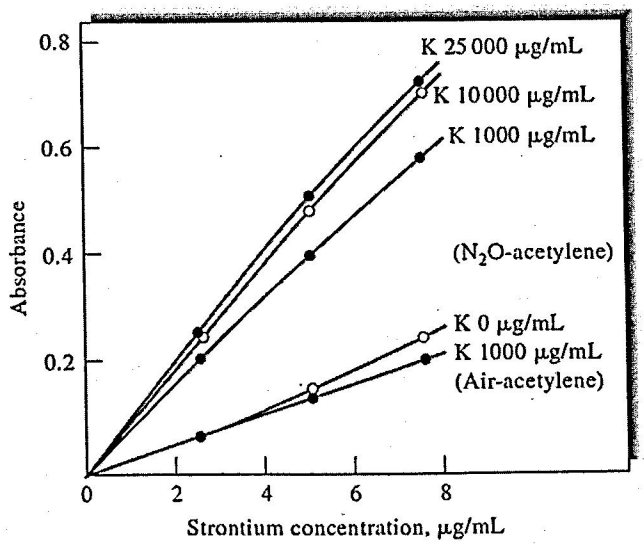
	FSOT*	WCOT§	SCOT#	Packed
Length, m	10-100	10-100	10-100	1-6
Inside diameter, m	0.1-0.3	0.25-0.75	0.5	2-4
Efficiency, plates/m	2000-4000	1000-4000	600-1200	500-1000
Sample size, ng	10-75	10-1000	10-1000	$10\text{-}10^6$
Relative pressure	Low	Low	Low	High
Relative speed	Fast	Fast	Fast	Slow

*Fused-silica open tubular column

§Wall-coated open tubular column

#Support-coated open tubular column (also called porous layer open tubular or PLOT)

8. (5%) The Figure below shows the effect of potassium concentration on the calibration curve for strontium determined by atomic absorption spectrometry (AAS). Please explain why the slope increases with (a) the use of nitrous oxide instead of air as the oxidant, and (b) increasing the concentration of potassium ions.

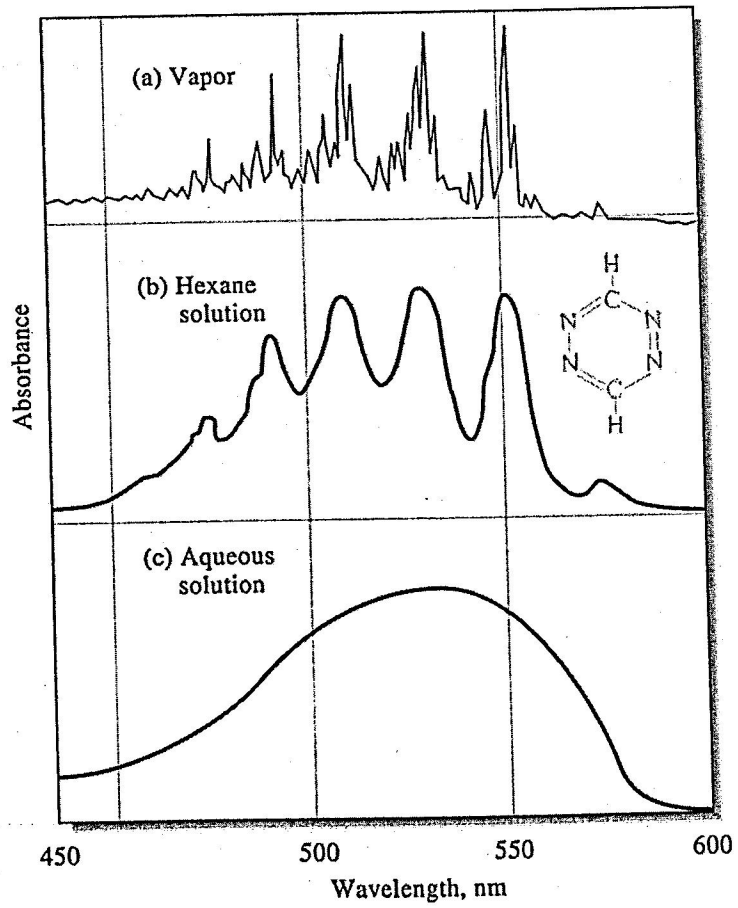


9. (6%) Please fill in the blanks in the following table.

Gas Chromatographic Detectors

Type	Applicable Samples	Typical Detection Limit
Flame ionization	(a) _____	0.2 pg/s
Thermal conductivity	(b) _____	500 pg/mL
Electron capture	(c) _____	5 fg/s
Mass spectrometer	Tunable for any species	0.25–100 pg

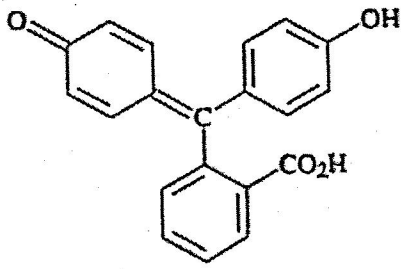
10. (4%) The Figure below shows the visible absorption spectra of 1,2,4,5-tetrazine. Please explain why the absorption profiles appear different in gas phase, hexane, and aqueous solution.



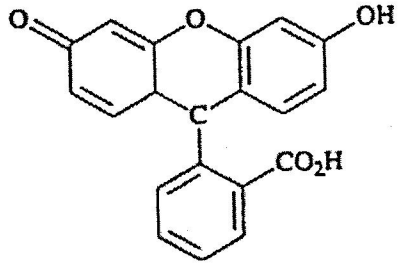
11. (6%) Describe the components and configuration of an ultraviolet and visible (UV-Vis) absorption spectroscopy.

12. (3%) Please explain why the complex ion $Cu(NH_3)_4^{2+}$ gives blue color in solution?

13. (3%) Which of the following compounds would have a greater fluorescence quantum yield? Explain.



phenolphthalein

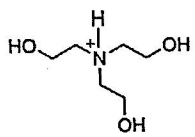


fluorescein

14. (6%) 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 was required to titrate the excess base. Calculate the composition of the mixture.

Phenolphthalein transition range: 8.3–10.0

15. (6%) The structure of triethanolamine in its fully protonated form is:



Its pK_a is 7.8. You have available at your lab bench 0.1 M solutions of HCl, NaOH, and the uncharged (free base) form of triethanolamine, as well as ample distilled water. Describe the preparation of a 0.5 L solution of 0.05 M triethanolamine buffer, pH 7.6.

16. (6%) Experiments show that the average observer can just detect the red color of $Fe(SCN)^{2+}$ when its concentration is 6.4×10^{-6} M. In the titration of 50.0 mL of 0.050 M Ag^+ with 0.100 M KSCN, what concentration of Fe^{3+} should be used to lower the titration error to near zero?

$$Ag^+ + SCN^- \rightleftharpoons Ag(SCN)_{(s)} \qquad K_{sp} = 1.1 \times 10^{-12}$$

$$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+} \qquad K_f = 1.05 \times 10^3$$

17. (8%) Calculate the potential required to initiate deposition of copper form a solution that is 0.010 M in $CuSO_4$ and contains sufficient H_2SO_4 to give a pH of 4.00.

Standard Electrode Potentials*

Reaction	E^0 at 25°C, V
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.359
$O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.087
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	+1.065
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.799
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771
$I_3^- + 2e^- \rightleftharpoons 3I^-$	+0.536
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.337
$UO_2^{2+} + 4H^+ + 2e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.334
$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-$	+0.268
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-$	+0.222
$Ag(S_2O_3)_2^{3-} + e^- \rightleftharpoons Ag(s) + 2S_2O_3^{2-}$	+0.017
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	**0.000**
$AgI(s) + e^- \rightleftharpoons Ag(s) + I^-$	−0.151
$PbSO_4 + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}$	−0.350
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.403
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	−0.763