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 113 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 ：2801

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 113 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(2801)

1. (5%) Gross error, systematic (or determinate) error, and random (or indeterminate) error are three types of errors that affect measurement precision and accuracy. How are systematic errors detected? In addition, which type of error cannot be eliminated, but it may be reduced by better technique.

2. (10%) Two different analytical methods were used to determine lead in river water. Both methods were used to the same samples, each collected from various locations. The concentration of Pb in parts per billion (ppb) was determined using the two methods, and the following results were obtained:

Sample	Method A	Method B
1	48.86	48.88
2	50.60	52.63
3	51.02	52.55
4	47.99	50.94
5	54.20	53.02
6	50.66	50.66
7	45.91	47.78
8	48.79	48.44
9	47.76	48.92
10	51.13	51.63

(a) What type of *t* test should be used to compare the two methods?

(b) Do the two methods give difference results at the 95% confidence level?

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Table 1. Values of *t* for Various Levels of Probability

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59

3. (4%) What is the molarity of K^+ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (329.3 g/mol)?

4. (4%) A 25.0-mL sample containing Cu^{2+} gave an instrument signal of 23.6 units. When 0.500 mL of 0.0287 M $Cu(NO_3)_2$ was added to the solution, the signal increased to 37.9 units. Calculate the molar concentration of Cu^{2+} assuming that the signal was directly proportional to the analyte concentration.

5. (7%) (a) What is the pH of a solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl. The acid dissociation constant K_a for NH_4^+ is 5.70×10^{-10}. (b) Calculate the pH change if we add 100 mL of 0.0500 M NaOH to 400 mL of the buffer solution that was described in (a)?

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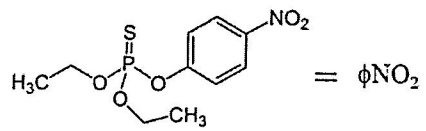
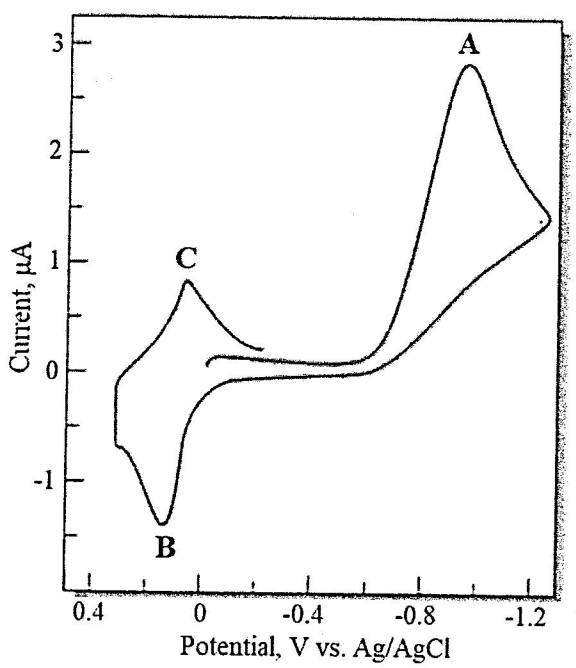
6. (5%) Calculate the potential of the following cell. If the cell is short circuited, indicate the direction of the spontaneous cell reaction.
   SHE: Standard Hydrogen Electrode
   Formic acid (HCOOH, $K_a = 1.8 \times 10^{-4}$)

   SHE || HCOOH(0.1302 M), $HCOO^-$(0.0764 M) | H_2(1.00 atm), Pt

7. (5%) The presented experimental results describe the electrochemical process of the insecticide parathion in 0.5 M pH 5 sodium acetate buffer in 50% ethanol. Please specify the instrument used and the chemical reactions resulted in peaks A, B, and C.
   Rxn 1: $\phi NO_2 + 2e^- + 2H^+ \rightarrow \phi NHOH$
   Rxn 3: $\phi NHOH \rightarrow \phi NO_2 + 2e^- + 2H^+$



= ϕNO_2

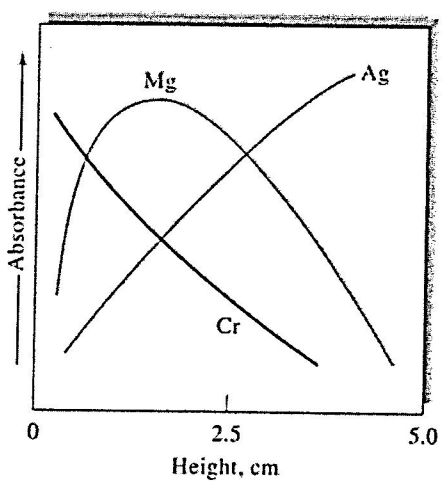


8. (6%) Ion-selective electrodes (ISEs) are widely used in the analysis of anions like bromide, chloride, and fluoride, or cations such as potassium, sodium, and calcium in various samples, including environmental, industrial, and clinical samples. Please explain the working principle of ISEs.

9. (6%) Compounds of Cu(II) are generally colored, but compounds of Cu(I) are not. Explain. The complex formed between Cu ion and 1,10-phenanthroline has a molar absorptivity of 7000 L cm^{-1} mol^{-1} at 435 nm, the wavelength of maximum absorption. Calculate the percent transmittance of a 6.77×10^{-5} M solution of the complex when measured in a 1.00-cm cell at 435 nm.

10. (4%) Select the spectroscopy technique below that is most significantly affected by atomization temperature.
    (A) Atomic absorption spectroscopy
    (B) Atomic emission spectroscopy
    (C) Atomic fluorescence spectroscopy
    (D) X-ray absorption spectroscopy

11. (5%) The presented figure illustrates the flame absorbance profiles for three elements: Cr, Mg, and Ag. Please explain the effects that give rise to the three distinct absorbance profiles.



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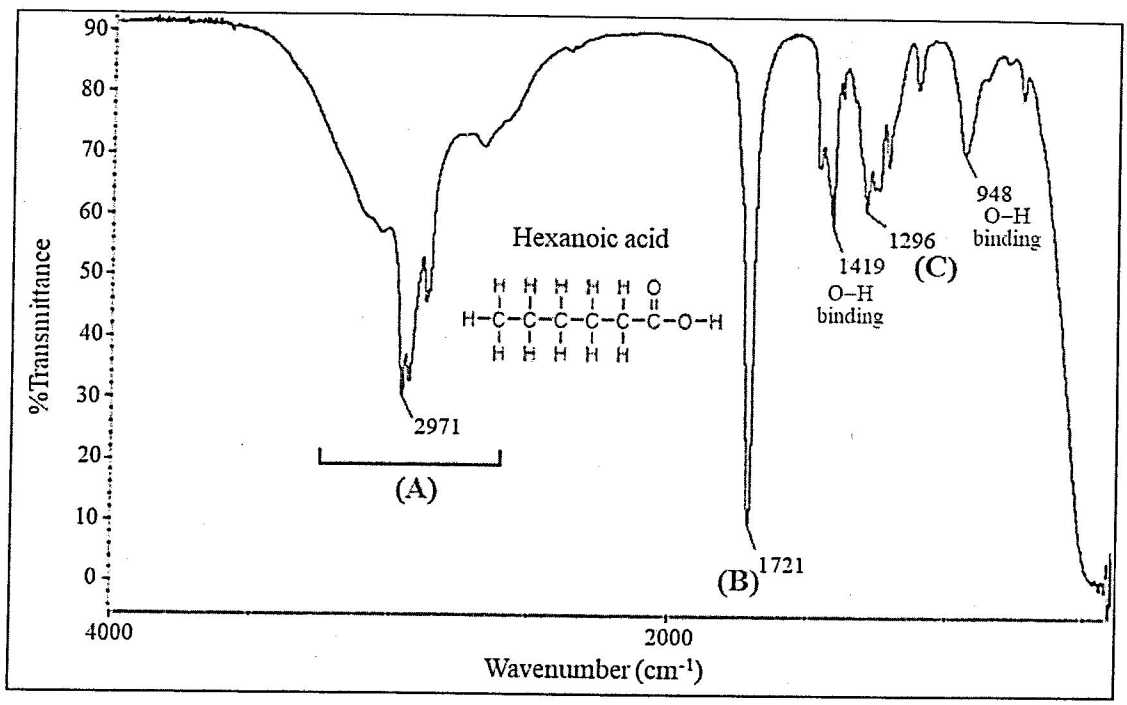
12. (6%) What types of mass spectrometer are used in inductively coupled plasma mass spectrometry (ICP-MS)? How do they differ from one another?

13. (6%) The presented spectrum illustrates the IR absorption of hexanoic acid. Please specify the potential stretching vibrations accountable for peaks A, B, and C.

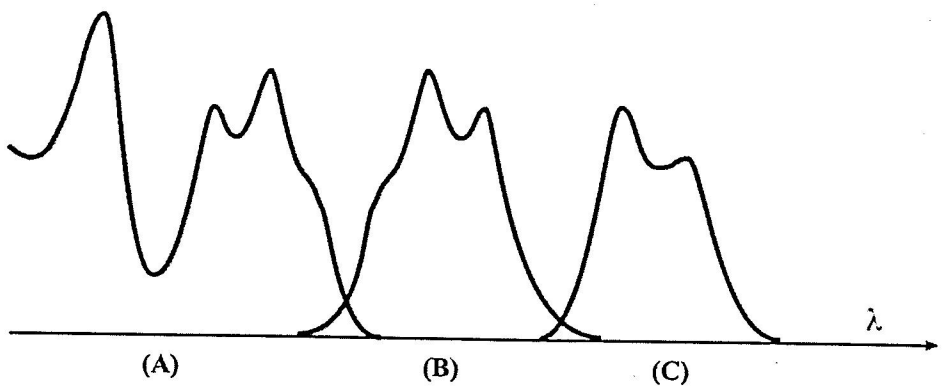
C–O stretching

C=O stretching

O–H stretching (and C–H stretching)



14. (10%) Below are typical optical spectra of an organic compound. Please identify the spectra of (A), (B) and (C) for the different radiative transitions between electronic states. In addition, explain why spectrum (A) and spectrum (B) are almost mirror images of each other. Explain why spectrum (C) has a longer wavelength than (B).



15. (8%) Please match the most applicable substance type list below to each of the chromatographic methods: (i) gas-liquid, (ii) ion-pair, (iii) liquid-liquid (partition), (iv) ion exchange, (v) gel permeation, (vi) gel filtration, (vii) gas-solid; and (viii) liquid adsorption.

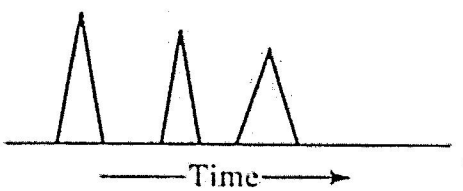
    Types of substances: (a) low molecular weight gases, (b) volatile, thermal stable substances; (c) ionic species, (d) ionic species using hydrophobic or nonpolar stationary phases, (e) non-volatile, thermal unstable compounds of low to moderate molecular weights, (f) high molecular weight polar compounds, (g) high molecular weight non-polar compounds, (h) low to moderate polarity solutes of low to moderate molecular weight.

16. (4%) Please select the most suitable detector listed below for gas chromatography (GC) analysis of organic pollutants such as (i) polycyclic aromatic hydrocarbons (PAHs) and (ii) polychlorinated biphenyls (PCBs), as well as (iii) permanent gas such as CO, CO_2, CH_4 and H_2, and (iv) organophosphorus pesticides.

    Types of detectors: (a) thermionic, (b) flame ionization, (c) thermal conductivity, and (d) electron capture.

17. (5%) The polarity order of the three compounds is A > B > C. Please predict the elution order of them in the reversed-phase chromatography illustrated below. In addition, how does the polarity of the mobile phase effect on the elution time? Please fill in the blanks (a) and (b) with "high" or "medium".

(a) polarity mobile phase



(b) polarity mobile phase