**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 109 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. 作答中如有發現試題印刷不清，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 109 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)



1. (6%) An aqueous solution contains $NaNO_3$ and KBr. The bromide ion is precipitated as AgBr by addition of $AgNO_3$. After an excess of the precipitating reagent has been added, (a) what is the charge on the surface of the coagulated colloidal particles? (b) what is the source of the charge? (c)what ions make up the counter-ion layer?

2. (10%) Tris(hydroxymethyl)aminomethane (TRIS) is one of the most commonly used buffers. Its acid dissociation constant, $K_a$, is $8.32 \times 10^{-9}$ M. You have available at your lab bench a 0.1 M solution of TRIS in its protonated form, 0.1 M solutions of HCl and NaOH, and distilled water. Describe the preparation of a 1 L solution of 0.02 M TRIS buffer, pH 7.8.

3. (10%) Two different analytical methods were used to determine residual chlorine in sewage effluents. Both methods were used on the same samples, but each sample came from various locations, with differing amounts of contact time with the effluent. The concentration of Cl in mg/L was determined by the two methods, and the following results were obtained:

| Sample | Method A | Method B |
|---|---|---|
| **1** | 0.39 | 0.36 |
| **2** | 0.84 | 1.35 |
| **3** | 1.76 | 2.56 |
| **4** | 3.35 | 3.92 |
| **5** | 4.69 | 5.35 |
| **6** | 7.70 | 8.33 |
| **7** | 10.52 | 10.70 |
| **8** | 10.92 | 10.91 |

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

(b) Do the two methods give different results? State and test the appropriate hypotheses.

(c) Does the conclusion depend on whether the 90%, 95%, or 99% confidence levels are used?

**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 |

4. (4%) Distinguish between the equivalence point and the end point of a titration.

5. (10%) Compute $E^0$ for the process

$$ZnY^{2-} + 2e^- \rightleftharpoons Zn(s) + Y^{4-}$$

where $Y^{4-}$ is the completely deprotonated anion of EDTA. The formation constant for $ZnY^{2-}$ is $3.2 \times 10^{16}$. ($E^0_{Zn2+/Zn} = -0.763$ V)

6. (10%) A solution contains $NaHCO_3$, $Na_2CO_3$, and NaOH, either alone or in permissible combination. Titration of a 50 mL portion to a phenolphthalein end point requires 22.1 mL of 0.1 M HCl. A second 50 mL aliquot requires 48.4 mL of the HCl when titrated to a bromocresol green end point. Deduce the composition, and calculate the molar solute concentrations of the original solution.

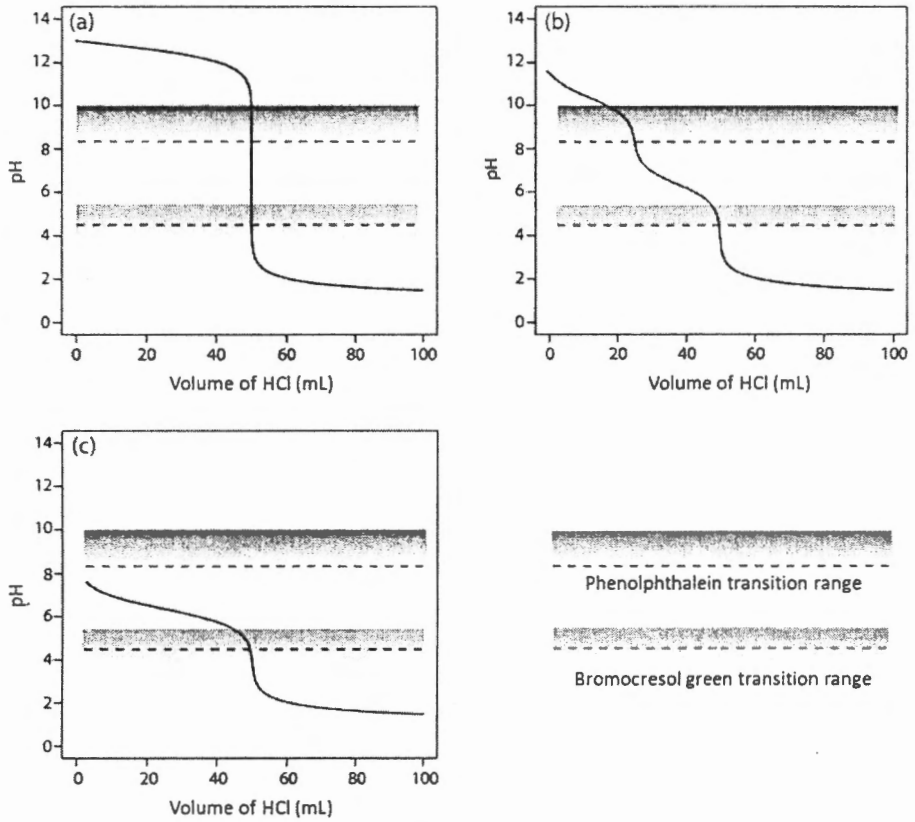



Figure 1. Titration curves and indicator transition ranges for the analysis of (a) NaOH, (b) $Na_2CO_3$, and (c) $NaHCO_3$.

7. (6%) (a) Describe the source of pH dependence in a glass membrane electrode and how does a glass electrode measure pH? (b) Describe the alkaline error in the measurement of pH. Under what circumstances is this error appreciable? How are pH data affected by alkaline error?

8. (4%) Make a comparison between two-electrode system and three-electrode system used for electrochemical analysis.

9. (6%) Please state the working principle of flame ionization detector (FID). Why FID is considered an almost universal detector for the measurement of organic compounds by GC?

10. (4%) Why are ionization interferences usually not as severe in the ICP as they are in flames?

11. (4%) In the atomic absorption determination of uranium (U), a linear relationship is found between the absorbance at 351.5 nm and the concentration in the rage of 500 to 2000 ppm of U. At lower concentrations, the relationship becomes nonlinear unless about 2000 ppm of an alkali metal salt are introduced. Explain.

12. (6%) Please fill in the blanks in the following table.

| Types of Transition | Absorption Spectroscopic Technique |
|---|---|
| Nuclear | Mossbauer spectroscopy |
| Inner electron | (a) _____ |
| Bonding electron | (b) _____ |
| Rotation/Vibration | (c) _____ |
| Rotation | Microwave |

13. (10%) List the variables that lead to zone broadening in chromatography. Please explain why the length of LC columns (~25 cm) are much shorter than GC capillary columns (50 m).

14. (10%) In spectrometry, the Beer-Lambert law, also known as Beer's law relates the absorption of light to the properties of the material through which the light is travelling. The diagram below shows a beam of monochromatic radiation of radiant power $I_0$, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power I. The absorbance of a sample can be related to the concentration of the absorbing species through Beer's law:

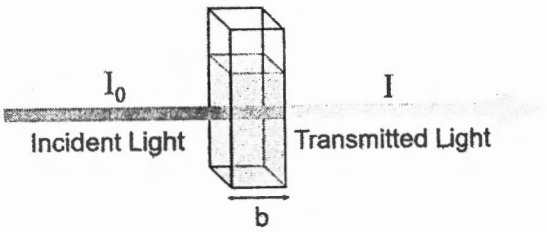
Transmittance, $T = I / I_0$

$A = \varepsilon bc$

Where A is absorbance (no units, since $A = log(I_0/I)$ )

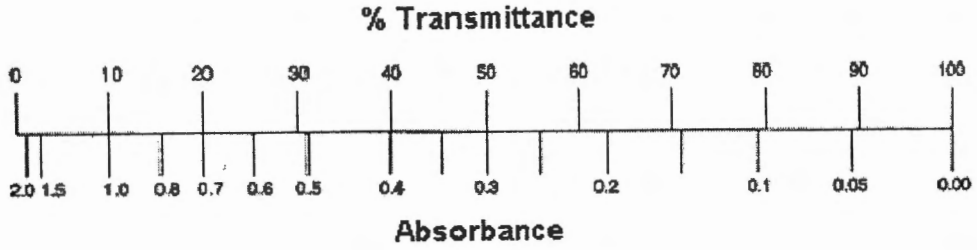
ε is the molar absorptivity with units of L $mol^{-1}$ $cm^{-1}$

b is the path length of the sample – that is, the path length of the cuvette in which the sample is contained. We will express this measurement in centimetres.




c is the concentration of the compound in solution, expressed in mol $L^{-1}$

(a) The relationship between absorbance and transmittance is illustrate in the following diagram:




Why do we prefer to express the Beer-Lambert law using absorbance as a measure of the absorption rather than % T.

(b) What is the significance of the molar absorptivity, ε?

(c) In the following figure, it shows the effect of polychromatic radiation on Beer's law. Consider a light beam consisting of just two wavelength, λ' and λ". Based on those equations given in this question, please derive an equation and describe the reason why the relationship between A and concertation is no longer linear when the molar absorptivities differ.

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