國立清華大學 103 學年度碩士班考試入學試題

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(2403)

1. (5%) In chemical analysis, matrix refers to the components of a sample other than the analyte of interest. The matrix can have a considerable effect on the way the analysis is conducted and the quality of the results obtained; such effects are called _____. For example, the ionic strength of the solution can have an effect on the _____ coefficients of the analytes. The most common approach for accounting for matrix effects is to build a _____ using standard samples with known analyte concentration and which try to approximate the matrix of the sample as much as possible. This is especially important for solid samples where there is a strong matrix influence. In cases with complex or unknown matrices, the _____ method can be used for the quantitative analysis approach. In this technique, the response of the sample is measured and recorded, for example, using an electrode selective for the analyte. Then, a small volume of standard solution is added and the response is measured again. The volume of standard solution should be small enough to disturb the matrix as little as possible.

2. (5%) Nine samples of illicit heroin preparations were analyzed in duplicate by a gas chromatographic method. The samples can be assumed to have been drawn randomly from the same population. Poll the following data to establish an estimate of pooled standard deviation for the procedure.

Sample	Heroin, %	Sample	Heroin, %
1	2.24, 2.27	6	1.07, 1.02
2	8.4, 8.7	7	14.4, 14.8
3	7.6, 7.5	8	21.9, 21.1
4	11.9, 12.6	9	8.8, 8.4
5	4.3, 4.2		

3. (10%) The homogeneity of the chloride level in a water sample from a lake was tested by analyzing portions drawn from the top and from near the bottom of the lake, with the following results in ppm Cl:

Top	Bottom
26.30	26.22
26.43	26.32
26.28	26.20
26.19	26.11
26.49	26.42

(a) Apply the *t* test at the 95% confidence level to determine if the means are different.

(b) Now use the paired *t* test and determine whether there is a significant difference between the top and bottom values at 95% confidence level.

(c) Why is a different conclusion drawn from using the paired *t* test than from just pooling the data and using the normal *t* test for differences in means?

TABLE 7-3

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
15	1.34	1.75	2.13	2.95	4.07
20	1.32	1.73	2.09	2.84	3.85
40	1.30	1.68	2.02	2.70	3.55
60	1.30	1.67	2.00	2.62	3.46
∞	1.28	1.64	1.96	2.58	3.29

4. (10%) Silver ion is being considered as a reagent for separating I^- from SCN^- in a solution that is 0.060 M in KI and 0.070 M in NaSCN.

   (a) What Ag^+ concentration is needed to lower the I^- concentration to 1×10^{-6} M?

   (b) What is the Ag^+ concentration of the solution when AgSCN begins to precipitate?

   (c) What is the ratio of SCN^- to I^- when AgSCN begins to precipitate?

   (d) What is the ratio of SCN^- to I^- when the Ag^+ concentration is 1.0×10^{-3} M?

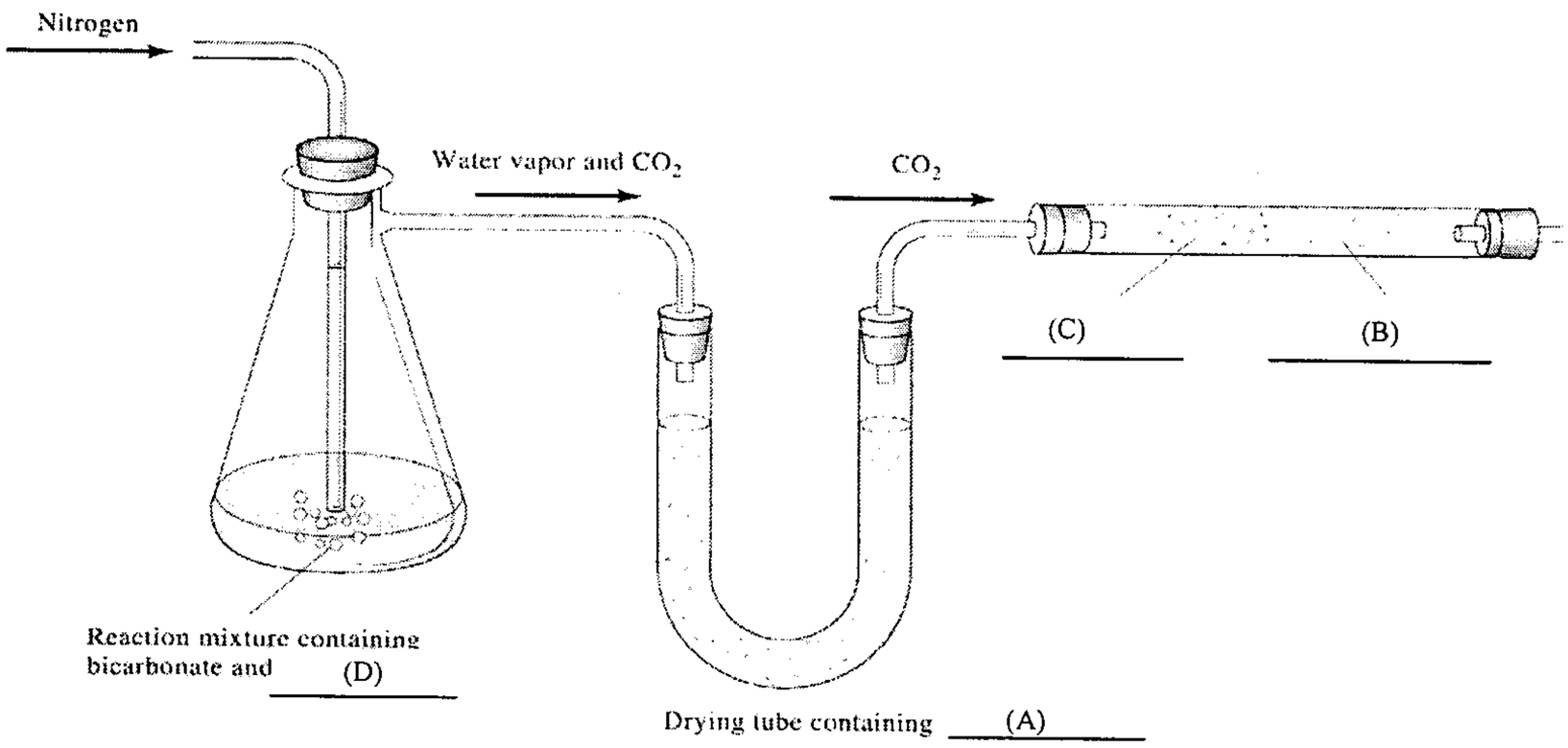
   (K_{sp} of AgI= 8.3×10^{-17} ; K_{sp} of AgSCN =1.1×10^{-12})

5. (10%) If you are assigned to determine the sodium hydrogen carbonate content of an antacid tablet. Based on following equations and the principle of gravimetric volatilization procedure, please fill up those blanks in following Figure.

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

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

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



6. (5%) In a titration of 50.00 mL of 0.05000 M formic acid (K_a=1.80 × 10^{-4}) with 0.1000 M KOH, the titration error must be smaller than 0.05 mL. What indicator can be chosen to realize this goal based on following Table?

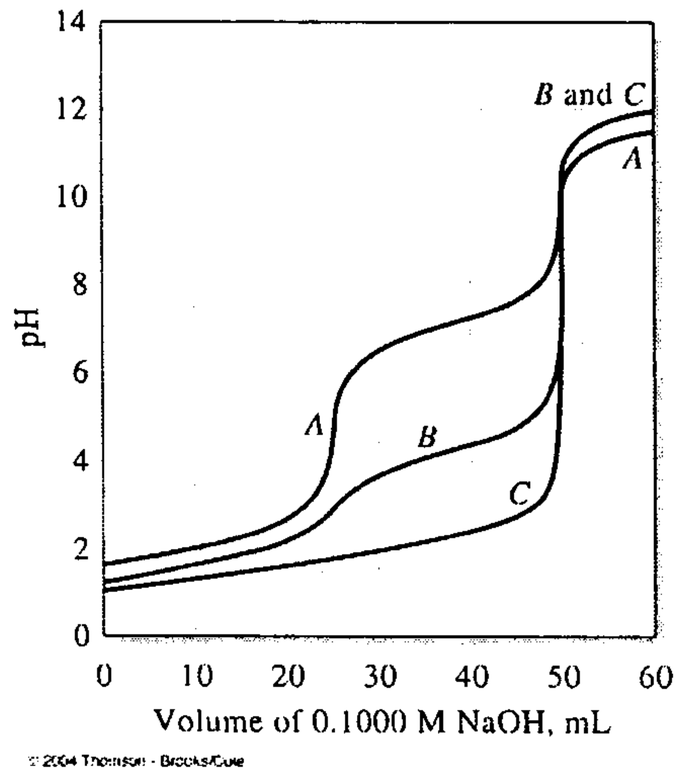
TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

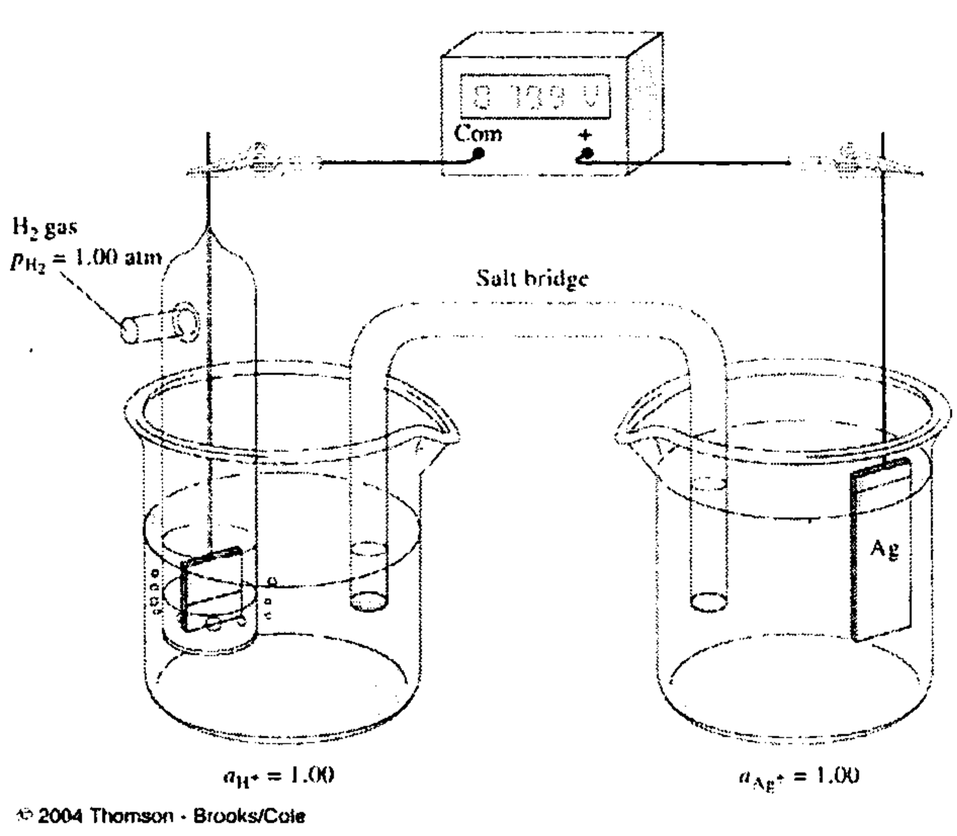
*At ionic strength of 0.1.
†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.
‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$.
§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$.

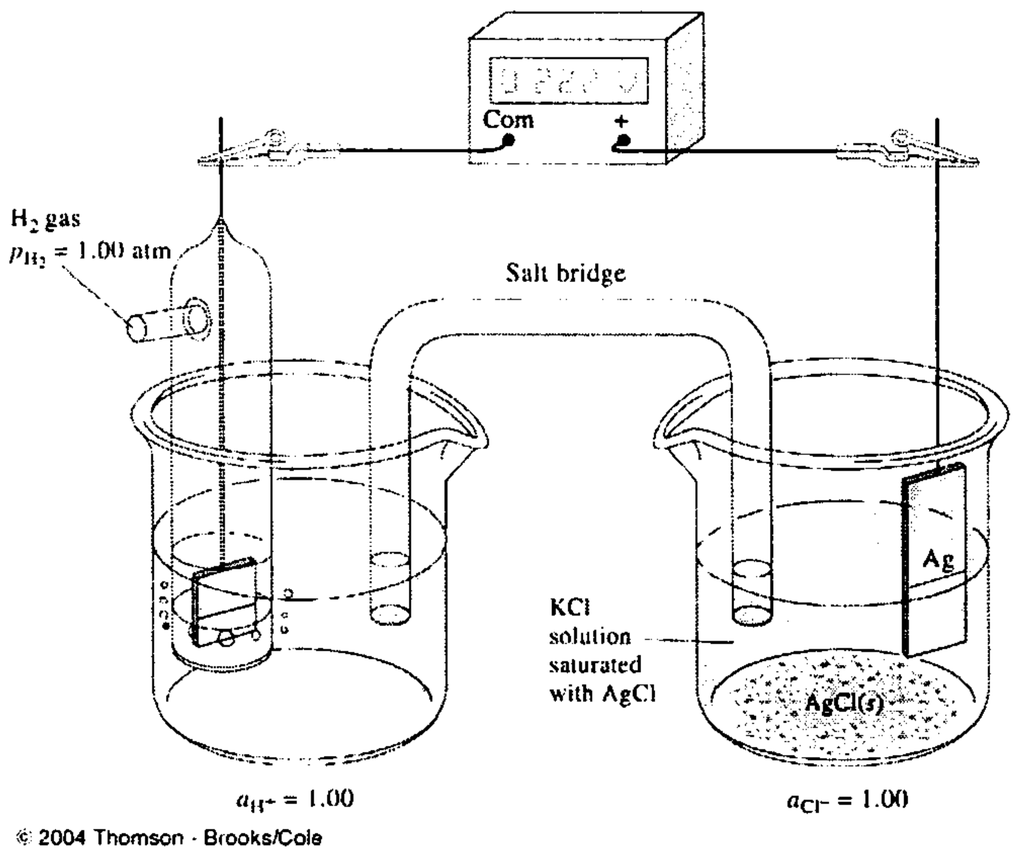
7. (5%) In following Figure, there are three titration curves of polyprotic acids. The values of K_a of each acid are listed below. Please indicate which curve (A, B, and C) is the theoretical curve for H_2SO_4 (K_{a2}=1.02×10^{-2}), H_3PO_4 (K_{a1}=7.11×10^{-3}, K_{a2}=6.32×10^{-8}, K_{a3}=4.5×10^{-13}), and $H_2C_2O_4$ (K_{a1}=5.60×10^{-2}, K_{a2}=5.42×10^{-5}).



8. (10%) As indicated in following equations and Figures, the standard potential for silver(I) is +0.799 V and the potential of a silver electrode in different environment (a_{Cl^-}=1.00) changes to +0.222 V. Please use Nernst equation and the solubility product of AgCl (=1.8×10^{-10}) to derive the potential of Ag/AgCl electrode and explain the reason causing the change in the potential of silver electrode.

- $Ag^+ + e^- \Leftrightarrow Ag$　　E^0 =+0.799 V
- $AgCl + e^- \Leftrightarrow Ag + Cl^-$　　E^0 =+0.222 V





9. (10%) Consider the following redox reactions:

$AgBr_{(s)} + V^{2+} \rightarrow Ag_{(s)} + V^{3+} + Br^-$

$Tl^{3+} + 2Fe(CN)_6^{4-} \rightarrow Tl^+ + 2Fe(CN)_6^{3-}$

$2V^{3+} + Zn_{(s)} \rightarrow 2V^{2+} + Zn^{2+}$

$Fe(CN)_6^{3-} + Ag_{(s)} + Br^- \rightarrow Fe(CN)_6^{4-} + AgBr_{(s)}$

$S_2O_8^{2-} + Tl^+ \rightarrow 2SO_4^{2-} + Tl^{3+}$

(a) Write each net process in terms of two balance half-reactions.

(b) Express each half-reaction as a reduction.

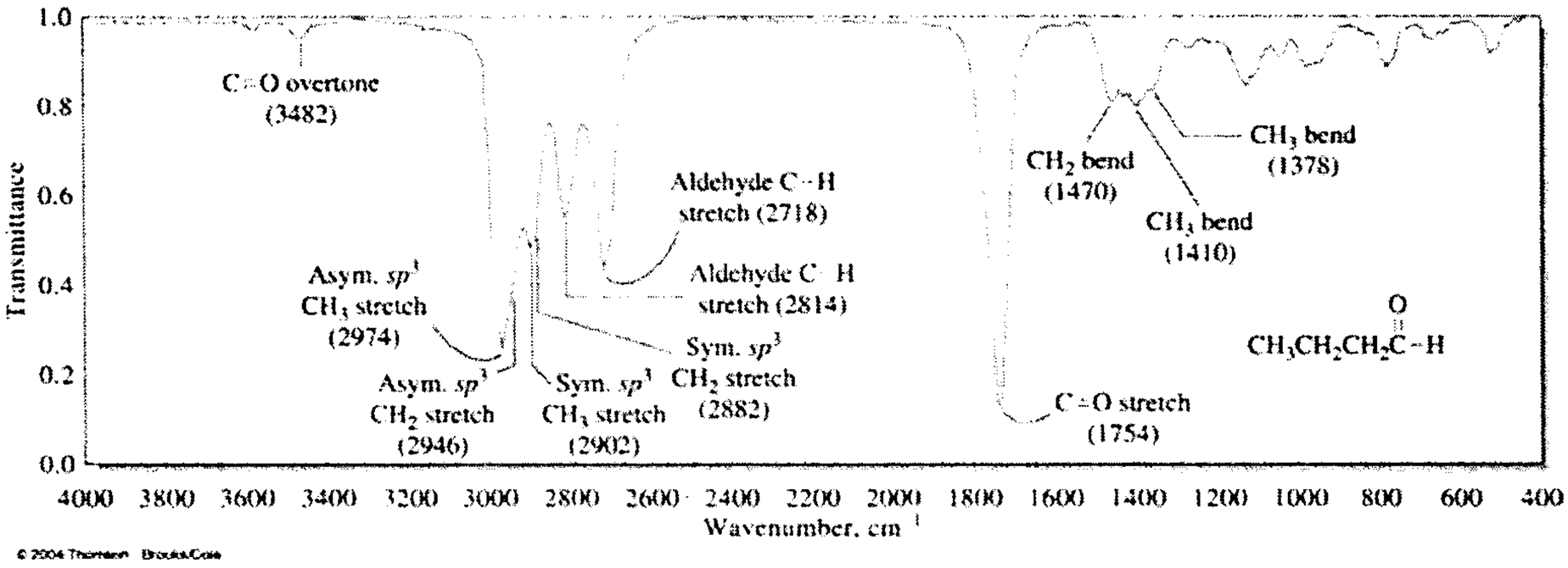
(c) Arrange the half-reaction in (b) in order of decreasing effectiveness as electron acceptors.

10. (10%) Please fill the blanks and give proper answers to following questions.

(a) The energy of infrared radiation can excite _____ and _____ transitions, but it is insufficient to excite_____ transitions.

(b) Based on following Figure, IR spectra exhibit narrow, closely spaced absorption bands resulting from transitions among the various _____ quantum levels.

Infrared spectrum for n-butanal (n-butyraldehyde)



(c) There are three types of IR instruments found in modern laboratories. Please give the names of instrument that is used for obtaining complete spectra for qualitative identification and is used for quantitative work.

(d) Please illustrate the advantages of Fourier-transform IR spectrometer for the qualitative identification work.

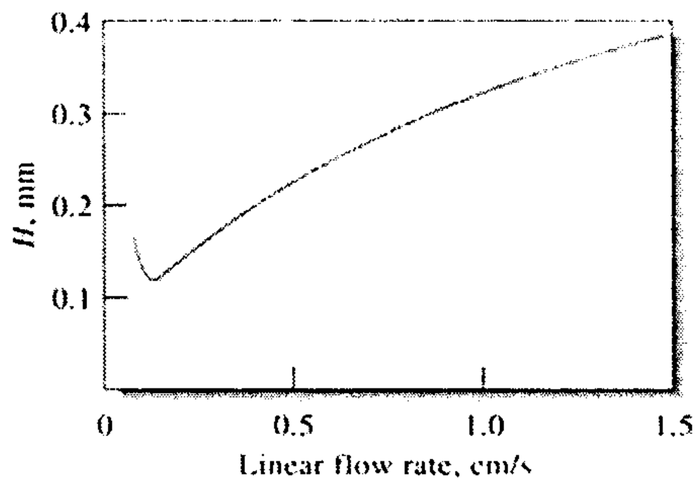
11. (10%) Mass spectrometry is an extremely versatile detection system for GC. Interfacing an HPLC system to a mass spectrometer is a much more difficult task, however. Describe the major reasons why it is more difficult to combine HPLC with mass spectrometry than it is to combine GC with mass spectrometry.

12. (10%) Following figure shows the contribution of various mass-transfer terms on the plate height.

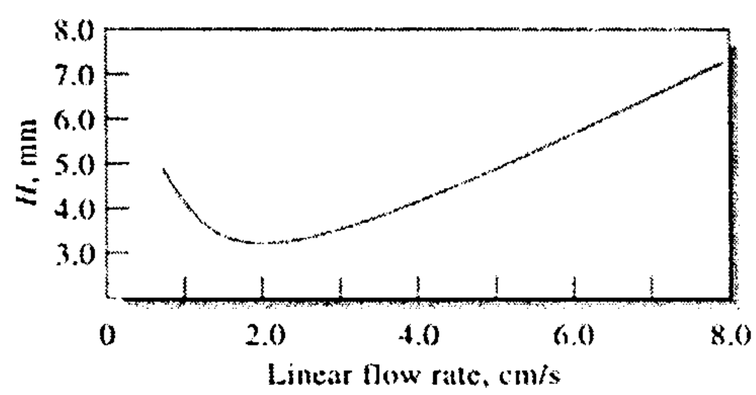
(a) Please define plate height and explain the relationship between plate height and column resolution.

(b) Please explain why the length of LC columns (~25 cm) are much shorter than GC capillary column (50 m).

(c) Based on following three figures, please indicate what kind of column can give better efficiency. Additionally, please give the reason why the column (GC or LC) you select can provide better separation efficiency.



(a) Liquid chromatography



(b) Gas-liquid chromatography