

UNIVERSITI SAINS MALAYSIA

Second Semester Examination  
Academic Session 2002/2003

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**KAA 505 – Separation Methods**

Time: 3 hours

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Please make sure this paper consists of **FOUR** typed pages before answering the questions.

Answer **FIVE** questions. Only the first five questions answered by the candidate will be marked.

1. (a) Draw and label a schematic diagram of a typical ion chromatographic unit that would be suitable for ultra-trace anion analysis. List the major capabilities and limitations of the ion chromatographic detector.

(10 marks)
- (b) Discuss the types of interactions between solutes and active sites of chromatographic stationary phases.

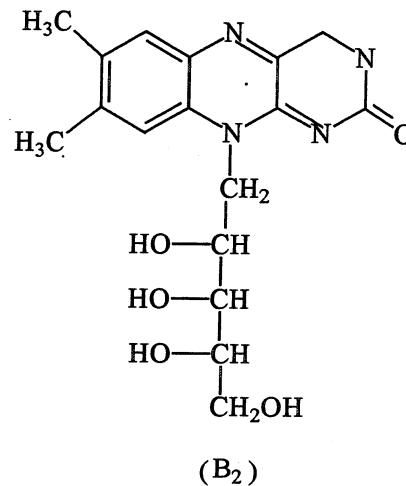
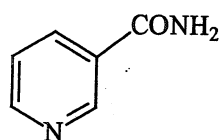
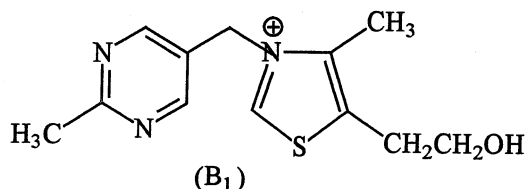
(10 marks)
2. (a) Discuss the effective strategies that can be implemented to yield satisfactory chromatographic quality.

(12 marks)
- (b) Describe the function of the following chromatographic components:
  - (i) Restrictor in supercritical fluid chromatography.
  - (ii) Guard column in liquid chromatography.
  - (iii) Suppressor column in ion chromatography.
  - (iv) Split injection in capillary gas chromatography.

(8 marks)

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3. The water-soluble vitamins B1 (thiamine hydrochloride), B2 (riboflavin), and B3 (niacinamide) may be determined by capillary zone electrophoresis (CZE) using a pH 9 sodium tetraborate/sodium dihydrogen phosphate buffer or by micellar electrokinetic capillary chromatography (MECC) using the same buffer with the addition of sodium dodecyl sulphate. Detection is by UV absorption at 200 nm. A 40 kV/m electric field is used to effect both the CZE and MECC separations. Methanol, which elutes at 4.69 min, is included as a neutral species. When using standard solutions of each vitamin, CZE peaks were found at 3.41 min, 4.69 min, and 8.31 min. Structures of the vitamins are shown below :

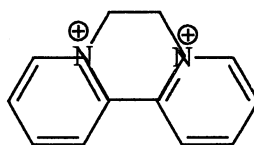


- (i) Why is methanol added to the electrolyte?
- (ii) Determine the order in which the vitamins elute. Offer justifications for the order as indicated.
- (iii) If the order of elution when using MECC is vitamin B3 (5.58 min), vitamin B2 (8.81 min), and vitamin B1 (11.21 min), what conclusions can you make about the relative hydrophobicity of the B vitamins in the micelles?
- (iv) Discuss the advantages of the MECC separations as compared to CZE method.
- (v) Suggest three strategies that can be done to increase the sensitivity of the detection.

(20 marks)

4. (a) For successful LC-MS interfaces, discuss the followings :
- Major technical difficulties that must be overcome.
  - Operating principles of the currently most popular interface.
  - Pros and cons of the major interfaces.
- (14 marks)
- (b) Explain the following statements :
- Band broadening in supercritical fluid chromatography is less than that in gas chromatography.
  - Capillary electrophoresis provides higher separation efficiencies when compared to liquid chromatography.
- (6 marks)
5. (a) Draw a schematic diagram of the liquid-liquid inter-phase for the extraction of lithium ion by 12-crown-4 ligand. Show the major equilibria involved in the extraction process.
- (4 marks)
- (b) Briefly describe how you would perform the following determinations:
- Indoor air quality.
  - Traces of fumigants in spice samples.
  - Stoichiometry of a metal-ligand complex.
  - Trace diquat in river samples. Structure of diquat is shown below.

(16 marks)



Diquat

6. For what kind of analytes would the analysis using the following techniques be particularly advantageous?

Provide short descriptions and offer specific examples to all answers.

- (a) Supercritical fluid chromatography. (4 marks)
- (b) Ion-pair chromatography. (4 marks)
- (c) Normal phase liquid chromatography. (3 marks)
- (d) Pyrolysis gas chromatography. (3 marks)
- (e) Solid phase microextraction. (3 marks)
- (f) Post-column derivatization in HPLC (3 marks)

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