Second Semester Examination
Academic Session 2020/2021

July 2021

KAT349 – Analytical Chemistry II

Duration: 2 hours

Please check that this examination paper consists of **EIGHT (8)** pages of printed material before you begin the examination.

Answer **FOUR (4)** questions only.

SECTION A : Answer all the questions.

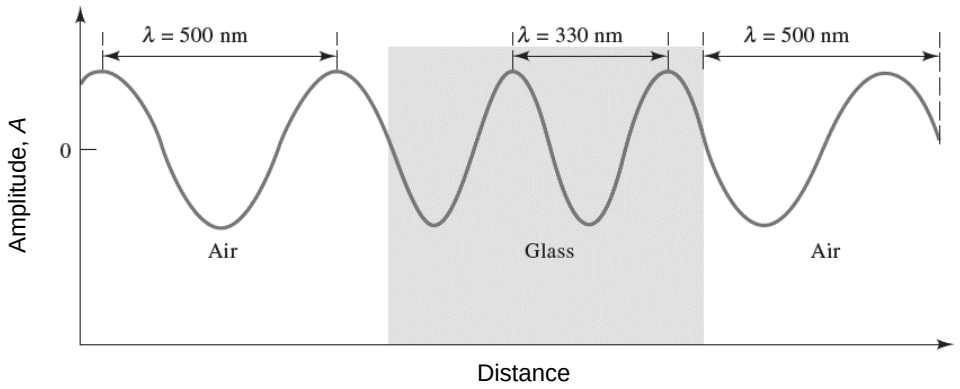
SECTION B : Select and answer only **ONE (1)** question.

Answer each question on a new page.

If a candidate answered more than four questions, only the first four questions in order of the arrangement in the received answer script will be marked.

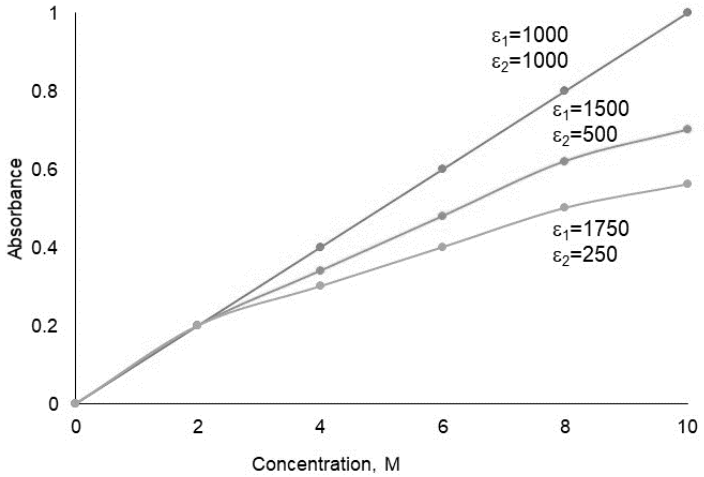
SECTION A

1 (a) The figure below shows the change in wavelength as radiation passes from air into a dense glass and back to air. Calculate the energy in joules of the radiation in the air and glass.



(6 marks)

(b) Figure below shows the relationship between absorbance and concentration is no longer linear when the molar absorptivities (ε) are varied.



(i) Briefly explain the reason for this situation

(ii) Suggest an approach to overcome the problem.

(4 marks)

(c) Justify the below statements either TRUE or FALSE.

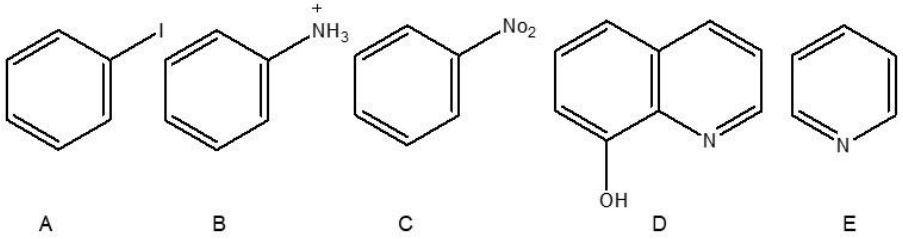
(i) Photomultiplier tubes unsuited for the detection of infrared radiation.

(ii) Iodine is introduced into a tungsten lamp to prolongs the life of the lamp.

(iii) Deuterium lamp produce a line spectrum rather than continuum in the ultraviolet.

(9 marks)

(d) (i) Identify the compounds that do not produced fluorescence.



A B C D E

(ii) Explain your answer in (i)

(6 marks)

2 (a) The distribution coefficient, K_D of 1.00 g benzoic acid between water and chloroform is 49. Calculate the weight of benzoic acid remained in 100 mL of water and extracted into 100 mL of chloroform.

(3 marks)

(b) A sample mixture was analysed using gas chromatography-flame ionisation detector (GC-FID) on a 30-m capillary column. The following data were obtained:

Compound	Retention time (min)	Peak width (min)
A	8.70	1.06
B	10.90	0.78
C	11.40	0.60

(i) Calculate the plate number and plate height of the column for compound A.
(ii) Calculate the resolutions for the peaks.
(iii) Explain the separation of the peaks based on the resolution by sketching the chromatogram.

(14 marks)

(c) The following proteins were separated using gel filtration chromatography (GFC): lysozyme (MW 14,400), ovalbumin (MW 45,000), phosphorylase B (MW 97,400), myosin (MW 212,000) and galactosidase (MW 116,000) on a 150 Å ZORBAX GF-250 column with a molecular weight range of 4,000-400,000.
(i) Briefly explain the principle for the separation using GFC.
(ii) Draw with label the chromatogram for the above analysis of proteins.
(iii) Suggest the suitable mobile phase used for the above separation.

(8 marks)

3 (a) Nernst equation can be connected to the standard potential (E^o) and the concentration of redox analyte. Discuss the reduction potential (E) for the potentiometric measurement and its relationship between the E^o and the concentration of the redox analyte.

(7 marks)

(b) An ion-selective electrode (ISE) can be defined as an electrode that can follow a Nernstian response in monitoring a single ion. Illustrate this approach.

(4 marks)

(c) A cation-sensitive electrode is used to determine the activity of the Ca^{2+} in the presence of Na^+. The potential of the electrode in 0.0100 M $CaCl_2$ measured against an SCE is 195.5 mV. In a solution containing 0.0100 M $CaCl_2$ and 0.0100 M NaCl, the potential is 201.8 mV. Calculate the activity of Ca^{2+} ion in an unknown solution if the potential of the electrode measured was 215.6 mV versus SCE and the Na^+ ion activity has been determined with a sodium ion-selective electrode was found to be 0.0120 M. Assume that your potentiometric measurement is following a Nernstian behavior.

(8 marks)

(d) Distinguish between:
(i) linear sweep voltammetry and cyclic voltammetry,
(ii) non-faradaic current and faradaic current.

(6 marks)

SECTION B

4 (a) Four standards of essential oils with boiling point range 170−300 °C were separated using gas chromatography (GC). Baseline separation were obtained for all essential oils using column temperature program as follows:
Initial temperature : 160 °C
Rate : 10 °C/min
Final temperature : 320 °C
Describe the expected peak obtained if the analysis is done isothermally at 200 °C.

(5 marks)

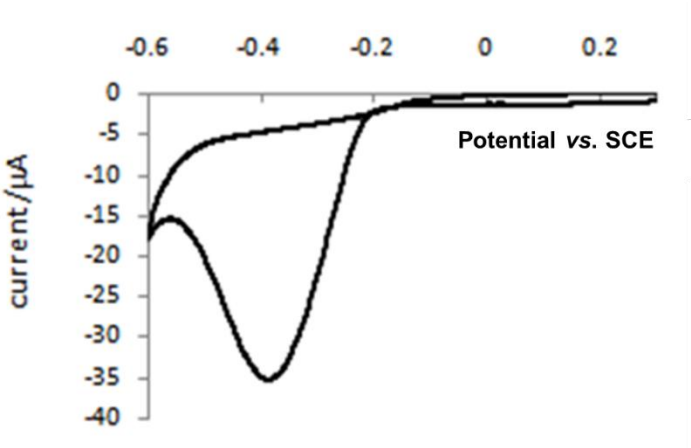
(b) A sample containing mixture of benzoic acid, hexanoic acid, 4-butylbenzoic acid, 2-nitrobenzyl alcohol and propanoic acid were analysed using high-performance liquid chromatography-ultraviolet (HPLC-UV) detector at a wavelength of 254 nm. From the analysis, only three peaks were observed which is benzoic acid, 4-butylbenzoic acid and 2-nirobenzyl alcohol. Describe an approach to improve the separation.

(3 marks)

(c) In flame atomic absorption spectroscopy (FAAS), the absorbance for calcium decreased in the presence of large concentration of phosphate ion.
(i) Explain the above observation.
(ii) Explain **TWO** possible methods to overcome the potential interference of phosphate in determination of calcium.

(8 marks)

(d) Shown below is a cyclic voltammogram (CV) of vanadium(IV) oxide sulphate hydrate in a buffer solution.



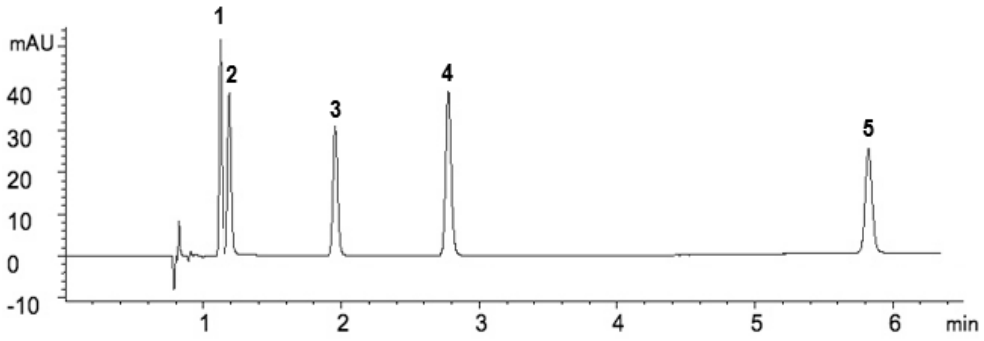
(i) Based on the figure above, identify whether the reactions are reversible, quasi-reversible or irreversible behaviour.

(ii) Briefly justify your answer in terms of Nernstian behaviour and electrode kinetics.

(iii) If you use linear voltametric and normal pulse voltametric techniques, illustrate the expected voltammograms for this compound.

(9 marks)

5 (a) Figure below shows the chromatogram for analysis of pharmaceutical compounds in wastewater using isocratic elution of methanol/water with a composition of 50/50 (v/v). Discuss an approach to separate compound 1 and 2 and to shorten the retention time of compound 5.



(5 marks)

(b) Briefly explain the effect of the diameter of the particle for packed column on the column efficiency.

(3 marks)

(c) Explain a fundamental difference of detectors for infrared (IR) and ultraviolet/visible (UV/VIS).

(4 marks)

(d) A solution containing 4.48 ppm $KMnO_4$ exhibits 85.9 %*T* in a 1.00-cm cell at 520 nm. Calculate the molar absorptivity of $KMnO_4$ at this wavelength. Given molecular weight $KMnO_4$ is 158.03 g mol^{-1}.

(5 marks)

(e) You are now analysing trace amounts of Ni and Co in a plating solution with a high Cu content.

(i) Identify the best polarographic technique you should use to get a well-defined polarogram.

(ii) Briefly explain your answer based on the selected technique.

(iii) Sketch the possible polarogram for this analysis. The redox couples (E° versus SCE) for the respective metals are Cu^{2+}/Cu (0.377 V), Ni^{2+}/Ni (-0.250 V), and Co^{2+}/Co (-0.31 V).

(8 marks)

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