First Semester Examination
Academic Session 2020/2021

January 2021

KAT349 – Analytical Chemistry II
[Kimia Analisis II]

Duration : 2 hours
[Masa : 2 jam]

Please check that this examination paper consists of **NINE (9)** 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.

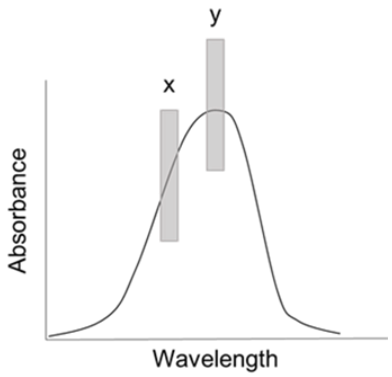
Answer each question on a new page. You may answer the questions either in Bahasa Malaysia or in English.

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

Answer **ALL** question

1. (a) The following figure shows an absorption spectrum of a compound using UV/Vis spectrophotometer.

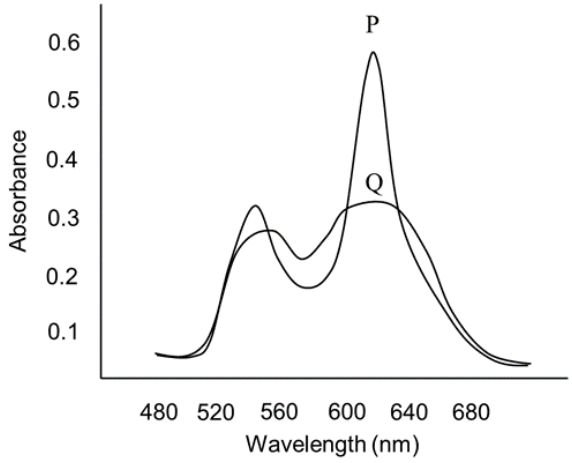


(i) Provide **THREE** reasons for an absorption measurement must be taken at wavelength of maximum absorbance (λ_{max}).

(ii) Explain the effect of selecting band x and y on Beer's Law.

(5 marks)

(b) Figure below shows the spectra obtained for reduced cytochrome *c* with 2 spectral bandwidths: 1 nm (P) and 10 nm (Q). A quantitative and qualitative analyses often require different monochromator slit widths. From the figure below, describe suitable absorption band to be used in qualitative and quantitative analyses.



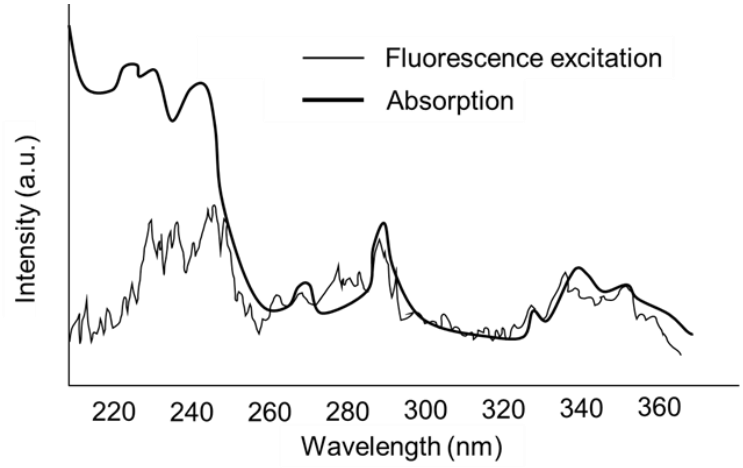
(4 marks)

...3/-

(c) NADH is a reduced form of nicotinamide adenine dinucleotide (NAD), a cofactor found in all living cells. A 0.725 mL aqueous solution of NADH shows an absorbance of 0.257 at 340 nm in 1.0-cm cuvettes. Calculate the concentration of NaDH (in nmol units) contained in the sample. Given, molar absorptivity of the sample is 6290 L mol^{-1} cm^{-1}.

(4 marks)

(d) The following figure shows the absorption and fluorescence excitation spectra of an organic compound. It can be observed that there is a difference in the relative intensities of absorption and fluorescence excitation spectra at maximum wavelength (λmax) below 250 nm. Using a Jablonski energy diagram, explain the process that can give rise to this observed situation.



(7 marks)

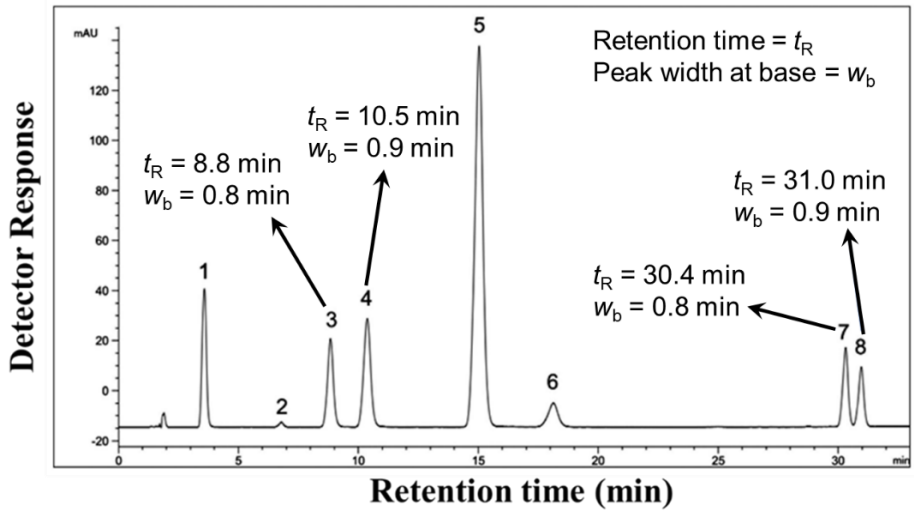
(e) In the analysis of barium in a groundwater sample by atomic absorption spectrometer (AAS), the presence of high amounts of calcium gives rise to a molecular interference due to the presence of a broad molecular band of calcium hydroxide.

(i) Explain solution to overcome this problem.

(ii) In a separate analysis of barium in the same groundwater sample (assume there are no calcium interferences in the sample), the absorption band for barium is increased in the presence of large amount of potassium. Analyse this observation.

(5 marks)

2. The following figure indicated the separation of phenolic compounds using reversed-phase high performance liquid chromatography (RP-HPLC) on a C18 column (4.6 mm inner diameter and 15 cm length) at a flow rate of 1.0 mL min^{-1}.



Chromatogram indicating RP-HPLC separation of phenolic compounds. Peak 1, hydroquinone (HQ); Peak 2, benzoquinone (BQ); Peak 3, catechol (CTL); Peak 4, *p*-hydroxybenzoic acid (HBA); Peak 5, *p*-hydroxybenzaldehyde (BZL); Peak 6, phenol (Ph); Peak 7, *p*-cresol (*p*Cr); Peak 8, *o*-cresol (*o*Cr).

(a) (i) Predict the order of polarity of the analysed phenolic compounds.

(ii) Justify your answers in (i).

(6 marks)

(b) Explain the features of RP-HPLC and normal-phase liquid chromatography approaches.

(4 marks)

(c) Explain the effects to retention time of the phenolic compounds if the:

(i) column was 10 cm.

(ii) flow rate was 0.50 mL min^{-1}.

(iii) mobile phase polarity was decreased.

(9 marks)

...5/-

(d) Calculate the resolutions of (i) CTL and HBA; and (ii) *p*Cr and *o*Cr.

(4 marks)

(e) Comment on the resolution factors obtained in (d).

(2 marks)

3. (a) The glass membrane electrode is one of the types of ion-selective electrodes (ISEs) and it is a commonly used method to measure the pH of a solution.

(i) Sketch a schematic diagram for the cell scheme of a conventional pH glass electrode.

(ii) Commonly, any pH ≥ 10 measured by a pH glass electrode is always erratic. Explain this problem.

(7 marks)

(b) Discuss the selectivity coefficient (*k*) for the ISEs and its relationship between the *k* to Nernstian response in determining of a single ion.

(4 marks)

(c) The following cell was found to have a voltage of 0.2150 V when the solution in the left compartment was a buffer of pH 7.00. Given $E^{o}_{Hg2Cl2/2Hg}$ = +0.268 V.

Glass electrode | H^+ || $KCl_{(saturated)}$, Hg_2Cl_2 | Hg

(i) Calculate the pH of the unknown solution for which the voltage reading was 0.5230 V.

(ii) Calculate the measured voltage in a 1.00 M acetic acid solution (assume a_{H+}= $[H^+]$ = 1.34×10^{-3} M).

(8 marks)

(d) Distinguish between:

(i) Limiting current and diffusion current.

(ii) Cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

(6 marks)

SECTION B

Answer at least **ONE (1)** question from this section.

4. (a) Distinguish single-beam and double-beam UV/Visible spectrophotometer.

(4 marks)

(b) Flame emission is more sensitive to flame instability than atomic absorption. Explain this statement.

(4 marks)

(c) Describe the importance of the following in gas chromatography:

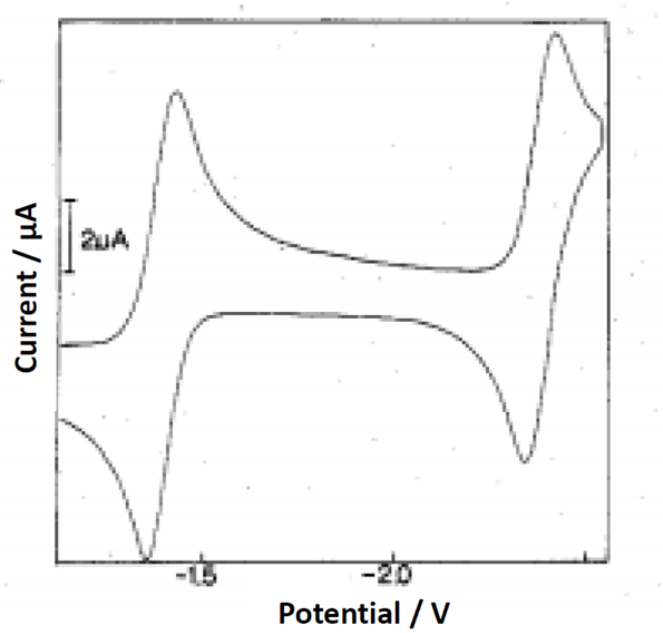
(i) split/splitless injection methods.

(ii) isothermal and temperature-programmed analysis.

(iii) non-polar versus polar stationary phases.

(8 marks)

(d) Shown below is a cyclic voltammogram (CV) of $(B_9C_2H_{11})_2Co^-$ complex ion in 1,2-dimethoxyethane solution. The table shows the information on the mid potential ($E_{1/2}$), and current ratio (i_{pa}/i_{pc}).



$E_{1/2}$ (V, versus SCE)	i_{pa}/i_{pc}
-1.38	1.01
-2.38	1.00

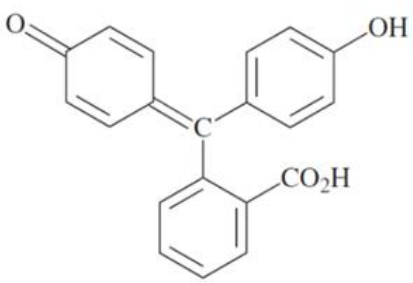
(i) Based on the table above, justify whether the reactions are reversible or quasi-reversible. Explain your answer.

(ii) If you use linear voltammetric and differential pulse voltammetric techniques, illustrate the voltammograms expected for this compound.

(9 marks)

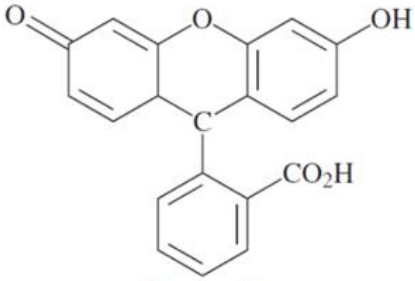
5. (a) From each pair of compounds listed below, explain the compound that you expect to have a greater fluorescence quantum yield.

(i)



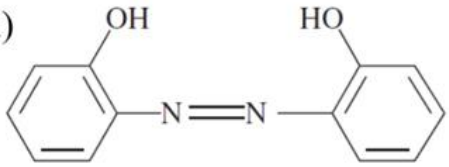
phenolphthalein

or



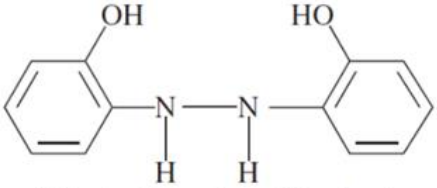
fluorescein

(ii)



o,*o*′-dihydroxyazobenzene

or



bis(*o*-hydroxyphenyl) hydrazine

(4 marks)

(b) Describe **FOUR** characteristics of inductively coupled plasma that make them suitable for atomic emission spectrometry.

(4 marks)

(c) A chemist intends to apply a solventless extraction technique for the analysis of floral volatile organic compounds.

(i) Explain a suitable extraction approach for the stated analysis.

(ii) Discuss the operating principles for the suggested extraction approach in (i).

(iii) Describe a suitable chromatography method for the analysis of the extracted volatile organic compounds. Provide explanations to your answer.

(9 marks)

(d) Describe the formation of flux that occurs at the electrode/electrolyte interface during voltammetric measurements by using a sketched diagram.

(4 marks)

(e) Essentially, there are three different steps in anodic stripping processes. Explain each step of the process.

(4 marks)