Name Scan Index Number:

2411/305
INSTRUMENTAL METHODS OF ANALYSIS
Oct/Nov 2015
Time: 3 hours

Date:

Signature:

THE KENYA NATIONAL EXAMINATIONS COUNCIL

DIPLOMA IN ANALYTICAL CHEMISTRY

INSTRUMENTAL METHODS OF ANALYSIS

3 hours

INSTRUCTIONS TO CANDIDATES

Write your name and index number in the spaces provided above.
Sign and write the date of the examination in the spaces provided above.
You should have a scientific calculator (non-programmable) for this examination.
*This paper consists of **TWO** sections: **A** and **B**.*
*Answer **ALL** the questions in section **A** and any **THREE** questions from section **B** in the spaces provided in this question paper.*
*Each question in section **A** carries 4 marks while each question in section **B** carries 20 marks.*
Maximum marks for each part of a question are as indicated.
*Do **NOT** remove any pages from this booklet.*
Candidates should answer the questions in English.

For Examiner's Use only

Question	1	2	3	4	5	6	7	8	9	10	TOTAL SCORE
Candidate's Score											

Question	11	12	13	14	15	TOTAL SCORE
Candidate's Score						

GRAND TOTAL

This paper consists of 16 printed pages.

Candidates should check the question paper to ascertain that all the pages are printed as indicated and that no questions are missing.

Turn over

SECTION A: (40 marks)

*Answer **ALL** the questions in this section in the spaces provided.*

1. (a) State Beer-Lambert's Law. (1 marks)

(b) A 2.94g sample of $K_2Cr_2O_7$ (fw = 294) in a 500 cm^3 volumetric flask has an absorbance of 0.46; 25 cm^3 of this solution was pipetted into a 500 cm^3 volumetric flask and topped upto the mark with water. Calculate the absorbance of the diluted solution. (3 marks)

2. Outline the steps followed in estimating the amount of sodium in a water sample by flame photometry. (4 marks)

3. (a) Explain the meaning of the term "memory effects" as used in flame atomic spectroscopy.

(2 marks)

(b) Describe how memories are removed during analysis. (2 marks)

4. Outline the following aspects of HPLC.

(a) Qualitative analysis. (2 marks)

(b) Quantitative analysis. (2 marks)

5. Explain the disadvantages of using a photomultiplier tube as a detector. (4 marks)

6. Describe how the wave length of maximum absorption (λ_{max}) for sulphate ions may be determined using AR magnesium sulphate and AR sodium sulphate. (4 marks)

7. (a) Define the term overtone as used in IR spectroscopy. (1 mark)

(b) The frequency of the fourth overtone of an IR active bond is 5020 cm^{-1}. Calculate the frequency of the second harmonic. (3 marks)

8. Describe the preparation of 250 cm^3 solution of concentration 200 ppm with respect to phosphates using AR sodium phosphate.
(Na = 23, P = 31, O = 16) (4 marks)

9. (a) Explain the term instrumental sensitivity. (2 marks)

(b) A 50 ppm solution of calcium ions has an absorbance of 0.75.
Calculate the instrumental sensitivity for calcium ions. (2 marks)

10. (a) Explain why analytical instruments are optimized and calibrated before being used for analysis. (2 marks)

(b) List **two** ways of determining the accuracy of results during analysis of a sample by GLC. (2 marks)

SECTION B (60 marks)

*Answer any **THREE** questions from this section in the spaces provided after question 15.*

11. A metal ore is suspected to contain copper. Describe the procedure that can be used to:

(a) Confirm the presence or absence of copper in the ore using AAS. (15 marks)

(b) Estimate the amount of copper in the ore by AAS. (5 marks)

12. (a) (i) State the necessary conditions for analysis of a sample by colorimetry. (3 marks)

(ii) State the advantages of colorimetry as a method of analysis. (2 marks)

(b) The following is a description of the method used in the determination of iron in water and waste water.

Iron in the +2 oxidation state reacts with O- phenanthroline to form orange-red $Fe(O-Phen)_3^{2+}$ complex which absorbs at 510 nm. The intensity of the colour of the complex is independent of the acidity of the solution between pH 3 - 9. Due to a faster rate of complex formation in the none acidic solutions, the reaction is usually carried out within the pH range 3.0 - 3.5. Any iron present in the +3 oxidation state is reduced with hydroxylamine before adding the O-Phenanthroline. The most important interferants are strongly oxidizing agents such as polyphosphates and metal ions such as Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} interferences from oxidizing agents are minimized by adding excess hydroxylamine where as interferences from polyphosphates are minimised by boiling the sample in the presence of acid.

The absorbance of the samples and the standards is measured at 510 nm using 1 - cm cuvette. Ammonium acetate buffer is added to both the samples and the standards. Calibration standards, including a blank set at 100 % T are prepared using a stock solution containing a known amount of Fe^{2+}. Beer-Lambert's Law is obeyed for concentrations of iron within the range 0.2 - 4.0 ppm.

(i) Define the term stock solution. (1 mark)

(ii) Calculate the mass of AR iron (II) sulphate that must be dissolved in 250 cm^3 of solution so as to make a solution of concentration 50ppm with respect to Fe. (Fe = 56, S = 32; O = 16)

(2 marks)

(iii) Describe how a solution of 250 cm^3 of concentration 50 ppm with respect to Fe is prepared in a chemistry laboratory. (2 marks)

(iv) Describe the preparation of 250 cm^3 of concentration 4 ppm with respect to Fe from the solution prepared in (b) (iii) above. (2 marks)

(v) Explain why strong oxidizing agents interfere with this analysis and why excess hydroxylamine prevents such interferences from occurring. (2 marks)

(vi) The colour intensity of the complex is more stable between pH levels 3 and 9. State the possible complications at more basic pH levels. (1 mark)

(vii) Cadmium is an interference because it forms a precipitate with O-phenanthroline. Explain the effect that the formation of the precipitate would have on the determination of the amounts of iron in the sample. (3 marks)

(viii) Even high quality ammonium acetate contains significant amounts of iron. Explain why this source of iron does not cause a problem in the estimation of iron in a water/waste water sample. (2 marks)

13.

Figure 1 (a)

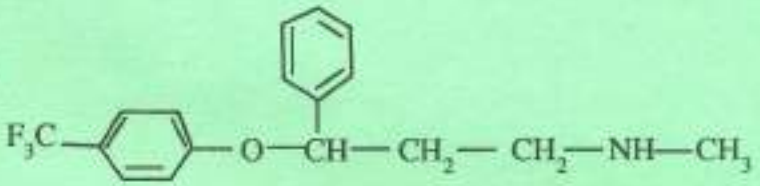
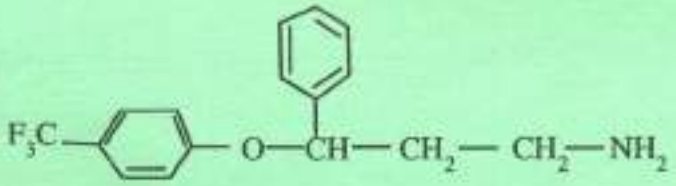


Figure 1 (b)



Fluoxetine, whose structure is shown in figure 1 (a) is another name for the antidepressant drug, prozac. The determination of fluoxetine and its metabolite norfluoxefine, figure 1 (b), in serum is an important part of monitoring its therapeutic use. The analysis is complicated by the complex matrix of the serum samples. A solid phase extraction followed by HPLC analysis using a UV-visible detector provides the necessary selectivity and detection limits. An isocratic mobile-phase mixture of water and acetonitrile is used to elute the sample using a column packed with C_8 - bonded stationery phase.

(a) Define the following terms as used in HPLC

(i) Selectivity (2 marks)
(ii) Detection limit (1 mark)
(iii) Isocratic elution (1 mark)
(iv) Resolution (2 marks)

(b) In the HPLC analysis of fluoxetine and its metabolic norfluoxetine, fluoxetine elutes with a retention time of 7.63 minutes and norfluoxetine elutes at 5.68 minutes with a void volume of 0.31 minutes.

Calculate:

(i) the capacity factor for fluoxetine. (2 marks)
(ii) the selectivity factor for fluoxetine and norfluoxetine. (2 marks)
(iii) resolution of the two components if their base widths are 1.46 and 1.65 minutes respectively. (2 marks)

(c) Explain the purpose of including an initial solid-phase extraction in this process. (4 marks)

(d) If the peaks for fluoxetine and norfluoxetine are insufficiently resolved, describe how the mobile-phase might be altered to improve their separation. (4 marks)

14. (a) Derive the equation for Beer-Lambert's law from first principles. (12 marks)

(b) A 50 ppm solution of potassium permanganate has a transmittance percent of 80% in a 1 cm - cuvette. A 50 cm^3 aliquot of the solution was pipetted and transferred into a 250 cm^3 volumetric flask and topped upto the mark with pure water.

Calculate the absorbance of the diluted solution. (K = 39, Mn = 55, 0 = 16) (8 marks)

15. (a) Derive the wave number equation as used in infrared spectroscopy. (10 marks)

(b) Use the equation derived in 15(a) above to calculate the following wave numbers.

(i) C - C bond in ethane
($K = 4.5 \times 10^5$ dynes /cm).
(3 marks)

(ii) C - C bond in benzene
($K = 7.6 \times 10^5$ dynes/ cm). (1 mark)

(iii) Comment on the values obtained in b(i) and b(ii). (2 marks)

(c) Describe the following sample preparation methods as used in infrared analysis.

(i) Pressed pellet technique.
2 marks)

(ii) Mull technique.
(2 marks)