

CHUKA



UNIVERSITY

## UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF DOCTOR OF PHILOSOPHY  
IN CHEMISTRY

CHEM 942: ADVANCED SPECTAL TECHNIQUES

STREAMS: PhD CHEMISTRY

TIME: 3 HOURS

DAY/DATE: WEDNESDAY 18/12/2019

2.30 P.M. – 5.30 P.M.

## INSTRUCTIONS:

- Answer ALL questions.

## QUESTION ONE (20 MARKS)

1. (a) (i) Discuss the various efforts which has been made by researchers in increasing the sensitivity of NMR spectroscopy in liquids to enable it to be used for solving a variety of cutting-edge biological problems in solution, especially those that involve viscous samples, very large biomolecules or aggregation prone systems that need to be kept at low concentration.

(3 marks)

(ii) Compare the methods given below which are able to shift thermal nuclear polarization, polarization and polarization and overhauser dynamic nuclear polarization.

(8 marks)

(b) Briefly discuss on Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) and also suggests some of the modifications which can be done to increase its performance.

(4 marks)

(c) Analyze the various attempts which have been made by scientist in reduction of spinning side bands in proton NMR of biological tissue with slow high

resolution  
(5 marks) magic angle spinning.

**QUESTION TWO (20 MARKS)**

2. (a) Discuss using suitable examples the three dimensional electron diffraction as a complementary technique to powder x-ray diffraction for identification and structure solution of powders. (6 phase marks)
- (b) (i) Discuss the limitation of mid-IR spectroscopy in biological tissue analysis. (1 mark)
- (ii) Explain how the use of Fourier transform IR (FTIR) spectrometers, equipped with an attenuated total reflection (ATR) element can be used to overcome the problem in q (1b). (3 marks)
- (iii) Explain how attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy can be used to distinguish melanoma cells with a different metastatic potential. (3 marks)
- (c) (i) Discuss the advantages and drawbacks of diffuse reflectance infrared Fourier transform over conventional transmission reflection) FTIR method. (4 marks)
- (ii) Explain how to overcome some of the problems encountered while using diffuse reflectance infrared spectroscopy for analysis. (2 marks)

**QUESTION THREE (20 MARKS)**

3. (a) Briefly discuss the principles of the following techniques.
- (i) Fluorescence correlation spectroscopy (FCS). (4 marks)
- (ii) Fluorescence cross correlation spectroscopy. (3 marks)
- (b) Two samples are analyzed by fluorescence correlation spectroscopy. One sample contains an antibiotic peptide (molecular weight roughly 1200 Da) a covalently attached green-fluorescent probe group. The other labelled with

sample contains  
labelled with a red-

lipid vesicles (with a diameter of roughly 200 nm) that are  
fluorescent lipid probe.

- (i) The following autocorrelation functions  $G(t)$  are obtained for two samples. Assign with reasons the diagram corresponding to antibiotic peptide, lipid vesicles. (2

marks)

- (ii) A third sample is analyzed in which the peptide and the lipid vesicles are mixed. The following autocorrelation function is obtained by monitoring the (green) fluorescence.
- peptide

Briefly explain what these results (fig 3) indicates. (2 marks)

- (c) Suppose you have a protein that displays tryptophan fluorescence and you wish to determine if the protein binds to DNA or lipid bilayers. Describe how you could use the tryptophan fluorescence to detect binding. Be specific regarding spectral observables and expected results. Including the use of intrinsic fluorescence anisotropy and resonance energy transfer.
- the

(5 marks)

- (d) Discuss the new trends in derivative spectrophotometry. (3 marks)
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