

University of Canterbury

End-of-year Examinations 2008

Prescription Number(s): CHEM 324

Paper Title: Analytical & Environmental Chemistry

Time Allowed: Three hours

Number of pages: Seven

This paper is divided into THREE sections.

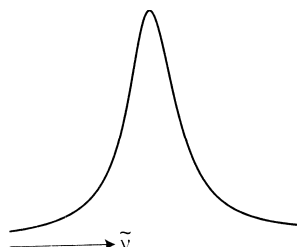
Answer **FIVE** questions out of SEVEN, including AT LEAST ONE question from each of sections A, B and C.

TURN OVER

SECTION A

(Answer **AT LEAST ONE** question from this section.)

1. Shown below is the profile of a weak absorption band with a Lorentzian profile.



- (a) Give two examples of the type of samples for which the shape of the bands in the infrared spectrum is Lorentzian. (2 marks)
- (b) A Lorentzian band centred at 1500 cm^{-1} has a peak absorbance of 0.1 absorbance units (AU) and a full-width at half-height (FWHH) of 0.2 cm^{-1} .
- (i) What type of sample do you think was being measured? Give a brief reason for your answer. (2 marks)
- (ii) Sketch (as accurately as you can, including the scales of both the absorbance and wavenumber axes) the shape of this band when it is measured under the following conditions:
- (A) using a monochromator having a triangular instrument line shape (ILS) function with a FWHH of 4 cm^{-1} ; (4 marks)
- (B) using a FT-IR spectrometer having a sinc ILS function with a FWHH of 4 cm^{-1} ; (4 marks)
- (C) using a FT-IR spectrometer having a sinc^2 ILS function with a FWHH of 4 cm^{-1} ; (4 marks)
- (D) using a high-resolution FT-IR spectrometer having a sinc ILS function with a FWHH of 0.01 cm^{-1} . (4 marks)

TURN OVER

2. (a) Describe the sampling technique for infrared spectroscopy that is known as attenuated total reflection (ATR). (6 marks)
- (b) Why has ATR become so much more popular than the time-honoured methods of sample preparation for solids such as the preparation of KBr disks or mineral oil mulls? (5 marks)
- (c) Name two *advantages* and two *disadvantages* of ATR compared to conventional transmission techniques. (4 marks)
- (d) Name three materials that are commonly used as internal reflection elements (IREs) in ATR spectroscopy. Of these materials, which gives the lowest depth of penetration into a typical polymer film and why? (5 marks)
3. (a) In conventional Raman spectroscopy, only about 1 photon in 10^{10} contributes to the spectrum; what happens to the others? (2 marks)
- (b) Calculate the absolute wavelength of the Stokes and anti-Stokes Raman bands of toluene that have a vibrational frequency of 1000 cm^{-1} when measured with a 785 nm laser. (4 marks)
- (c) Calculate the relative intensity of the Stokes and anti-Stokes bands in the spectrum of toluene at 1000 cm^{-1} ; *hint, $kT \sim 200\text{ cm}^{-1}$.* (2 marks)
- (d) What are the three components in modern bench-top Raman spectrometers that have led to the far greater popularity of Raman spectrometry today in comparison to the situation 30 years ago. Give a reason for each of your answers. (6 marks)
- (e) Give a brief description of *either* resonance Raman spectroscopy *or* surface-enhanced Raman spectroscopy. (4 marks)
- (f) The relative band intensities in resonance Raman spectra are quite different from those in conventional Raman spectroscopy; which bands are the strongest in resonance Raman spectra? (2 marks)

SECTION B

(Answer **AT LEAST ONE** question from this section.)

4. (a) Predict the relative intensities of the molecular ion peak (M), the M + 2 peak, and the M + 4 peak in the mass spectrum of CH₂Br₂. (2 marks)
- (b) Discuss briefly, the reasoning behind your prediction in Question (a) above. (5 marks)
- (c) In the electron ionization mass spectra of many compounds, molecular ion peaks are either very weak or completely absent. Explain how you might overcome this limitation. (5 marks)
- (d) Tandem mass spectrometry (MS/MS) has become a powerful tool in sample analysis. Briefly describe this technique and discuss why it has become so useful. (8 marks)
5. (20 marks)
- Hyphenated techniques have enhanced and extended the capabilities and applications of mass spectrometry. Discuss, in detail, *either* GCMS *or* LCMS. Make sure you evaluate the following points:
- (a) advantages;
- (b) limitations;
- (c) applications.

TURN OVER

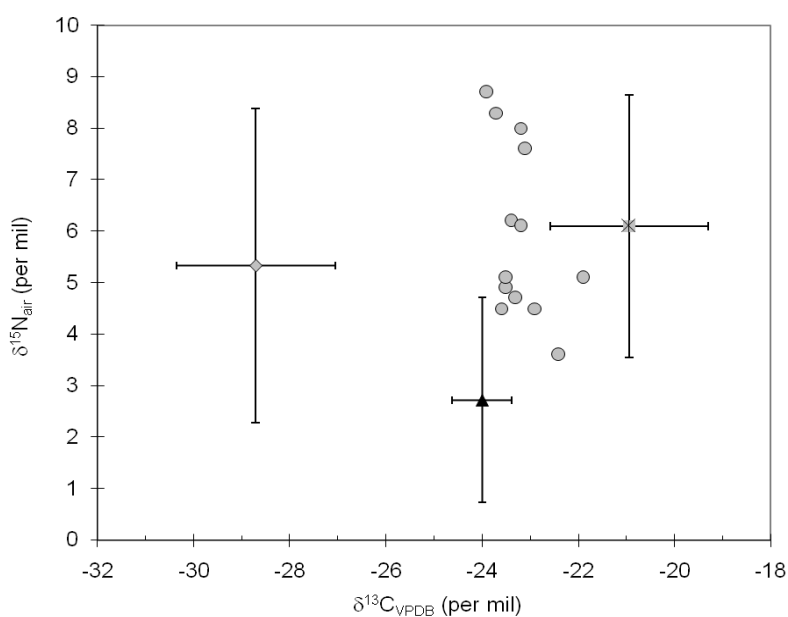
SECTION C

(Answer **AT LEAST ONE** question from this section.)

6. (a) The following scatter plot gives the isotopic enrichment of various elements of the biota on Adams Island, in the New Zealand sub-antarctic. Use the following information to answer the questions below.

- Snipe are insectivorous birds.
- Parakeets and bellbirds eat both insects and plant material.
- Rata is the dominant forest tree on the island, although the island is only sparsely forested.

- (i) Use the $\delta^{13}\text{C}$ data to compare the feeding location of snipe with parakeets, with respect to the forest canopy. (2 marks)
- (ii) Bellbirds have been seen feeding on insects associated with breeding seabirds, as well as within the forest. Briefly explain why the $\delta^{13}\text{C}$ data are consistent with this observation. (3 marks)
- (iii) The $\delta^{15}\text{N}$ of tree foliage (i.e., leaves) in cold temperate locations is usually negative. Briefly explain why rata foliage $\delta^{15}\text{N}$ is much higher than expected, and what this implies about the N source for vegetation on the island. (5 marks)



○ Snipe, Adams I. ▲ Parakeets, Adams I. ✱ Bellbirds, Adams I. ◆ Rata leaves, Adams I.

Question 6 continued on following page

Question 6 continued

- (b) Reactive N (Nr) is presently accumulating in the global environment. In recent decades, fossil fuel combustion has become a globally significant mechanism for the conversion of atmospheric N₂ to Nr. Briefly explain how this occurs, and why Nr is presently accumulating. (5 marks)
- (c) List four procedures that commercial laboratory client can use to maximise their confidence in sample results from the laboratory. Give a brief explanation of each procedure. (5 marks)
7. (a) Briefly explain the role of control charting (such as the use of Shewhart Charts) in the quality system of a laboratory. (5 marks)
- (b) The $\delta^{13}\text{C}$ of seaweed from the Canterbury coast is c. -13‰ whereas the $\delta^{15}\text{N}$ of the same seaweed is c. +7‰. By discussing the basis of δ scales, briefly explain how isotopic enrichment results can give either positive or negative values. (5 marks)
- (c) Atmospheric CO₂ concentrations measured at Mauna Loa in Hawai'i since 1958 show a clear annually repeating saw-tooth pattern superimposed over a slow but steady increase. Briefly explain both the saw-tooth pattern, and the slow but steady increase in the context of concentrations found in past glacial and interglacial cycles. (5 marks)
- (d) Of 170 Tg (1 Tg = 10¹² g) of reactive N (Nr) supplied to cropland to produce crops, 49 Tg is harvested annually in crops. Of 49 Tg of Nr harvested annually in crops, 16 Tg is directly consumed by humans and 33 Tg is diverted to animal feedlots to produce 5 Tg of animal protein for human consumption. Recycling of waste N from both human consumption and animal feedlot consumption back to crop production is negligible. Use this information to briefly discuss the consequence of crop consumption in animal feedlots for losses of Nr to soil, air, and water. (5 marks)

END OF PAPER