

University of Canterbury

End of Year Examinations 2007

Prescription Number(s): CHEM 324

Paper Title: Analytical & Environmental Chemistry

Time Allowed: THREE HOURS

Number of pages: EIGHT

This paper is divided into **TWO** sections.

Section A: Answer **THREE** out of **FOUR** questions.

Section B: Answer **TWO** out of **THREE** questions

All questions are of equal value

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SECTION A

(Answer **THREE** questions from this section)

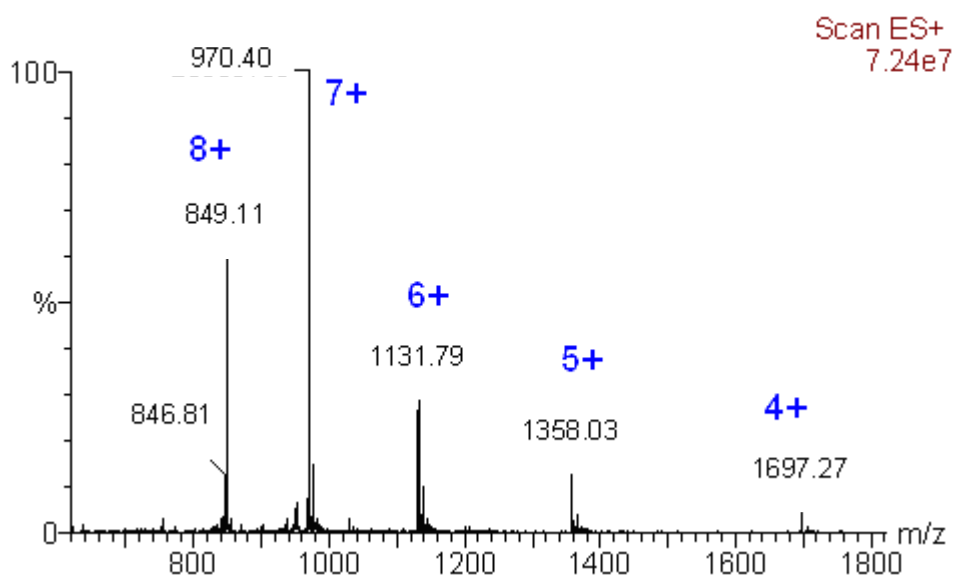
1. (a) (5 marks)

The **resolving power** of a mass analyser is a key characteristic of mass spectrometry. Define this characteristic and discuss how it is expressed. You may find drawing some diagrams useful in your answer.

(b) (7 marks)

Below is the electrospray spectrum of a purified protein from snake venom. The spectrum shows a characteristic ion envelope with the multiple charge states labelled.

- (i) Explain why this ion envelope is observed.
- (ii) Show, in detail, how you would calculate the molecular weight of this protein, and give its molecular weight.



(c) (8 marks)

How do mass spectra for electron impact (EI) and chemical ionisation (CI) sources differ from one another? Discuss briefly how these differences arise.

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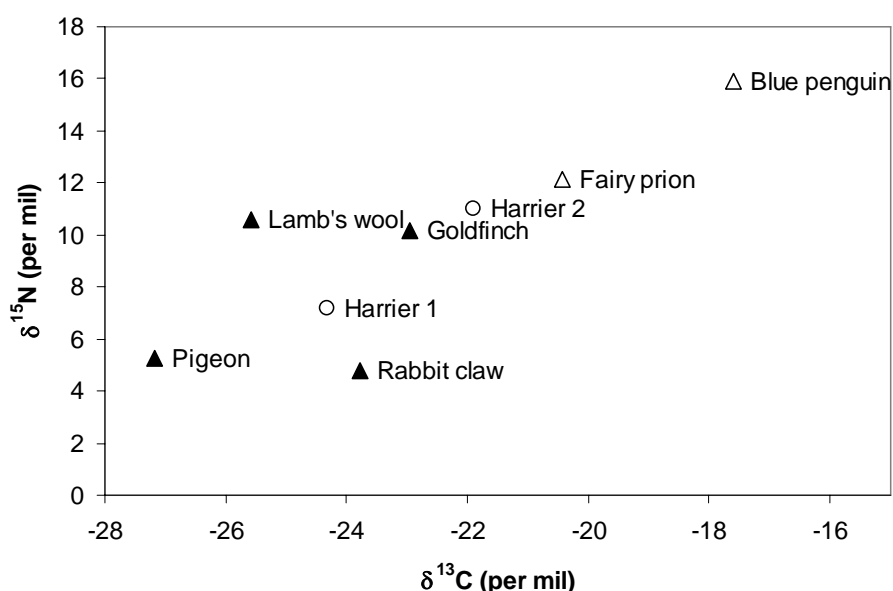
2. The isotopic data shown in the graph below were obtained from Motunau Island, a 3.4 ha island lying 1 km off the North Canterbury coast. Motunau Island hosts large numbers of breeding seabirds (especially fairy prions and blue penguins) as well as terrestrial birds such as pigeons and goldfinches. Consequently, Motunau Island may be a good model site for studying nutrient element flows in pre-human, post-glacial New Zealand.

The Australasian harrier is a native bird of prey, which feeds on carrion (dead animal material) from a wide range of items including birds, rabbits, and lambs. The fairy prion, blue penguin, pigeon, goldfinch, and lamb's wool data in the graph were obtained from a harrier nest on the island. The rabbit's claw was collected from road kill on the adjacent mainland.

Harrier 1 and Harrier 2 are data from two Australasian harrier feathers collected from the island.

- (a) (10 marks)

Qualitatively assess the relative contributions of marine and terrestrial C and N to each individual harrier, and hence discuss whether or not consumption of carrion by birds of prey, such as Australasian harriers, represents a route by which marine C and N can be incorporated into the terrestrial ecosystem.



Data source: redrawn from data in *Notornis* **52**, 158-162 (2005)

Question 2 continued on following page

Question 2 continued

(b) (5 marks)

The $\delta^{13}\text{C}$ of most New Zealand plant foliage falls within the range -22 to -34‰. Briefly explain how this value arises, and why there is such a broad range of values.

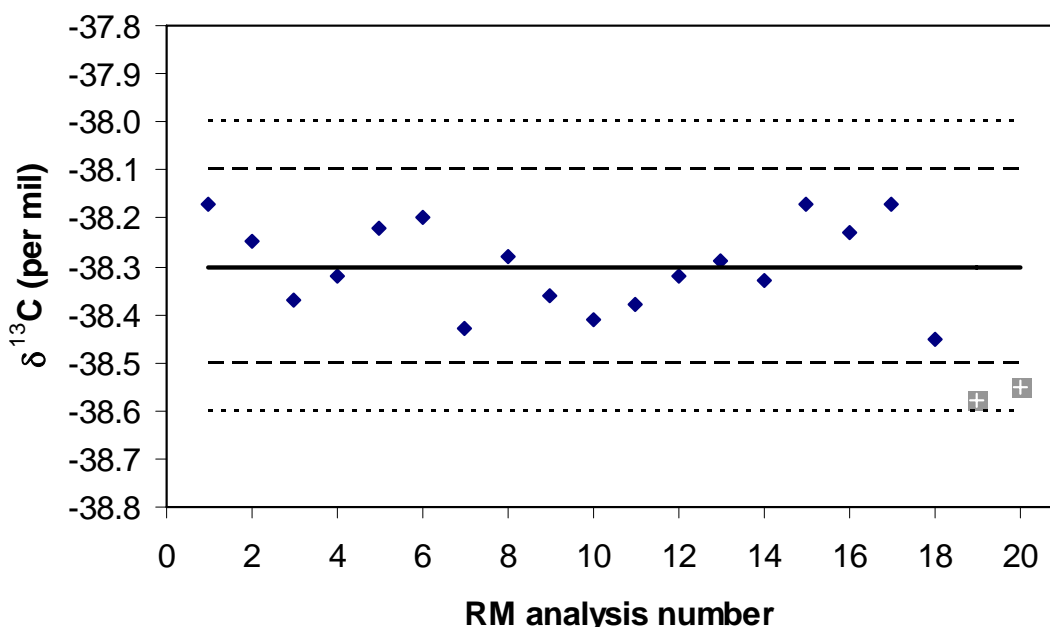
(c) (5 marks)

List FOUR procedures that a commercial laboratory client can use to maximise their confidence in their sample results from the laboratory. Give a brief explanation of each procedure.

3. Discuss, in detail, MALDI and ES ionisation sources. In particular, you should evaluate the following aspects that are critical in the selection of an ionisation technique:

- (a) advantages;
- (b) limitations;
- (c) applications.

4. The following Shewhart chart gives the analysis results of an EDTA quality control reference material (RM) during an IRMS analytical run. The solid line shows the mean value of the standard (-38.3‰); the *warning limits* are shown by the dashed lines, and the *action limits* by the dotted lines.



- (a) (5 marks)

Use probability theory, based on the normal distribution, to calculate the expected probability that two successive results (such as analysis numbers 19 and 20) will lie beyond the same warning limit (WL). The equations for upper warning limit (UWL) and lower warning limit (LWL) are, respectively:

$$\text{UWL} = \text{mean} + 2 \text{ standard deviations}$$

$$\text{LWL} = \text{mean} - 2 \text{ standard deviations}$$

- (b) (5 marks)

State the actions that should be taken if two successive results lie beyond the same warning limit.

- (c) (5 marks)

The $\delta^{13}\text{C}$ of atmospheric CO_2 is currently approximately -8.0‰. By discussing the basis of δ scales, briefly explain how isotopic enrichment results such as this can give negative values.

- (d) (5 marks)

Propose an IRMS-based method for detecting adulteration of honey with corn syrup. Explain the basis of your method, and any limitations.

SECTION B

(Answer **TWO** questions from this section)

5. (a) Discuss the following statement as it relates to polymers:
- “Chemists are very good at providing environmentally desirable solutions to social problems where society has expressed the will to change.”
- (b) (i) Using the deployment of DGT (‘diffusive gradients in thin films’) devices in a lake as an example, describe the purpose and functioning of the devices.
- (ii) Discuss the advantages and limitations of the DGT technique for environmental use.
6. (a) The accessible potential range for a Hg electrode in KNO_3 is approximately 0.15 to -1.8 V vs SCE.
- (i) Explain the expression **accessible potential range**.
- (ii) With respect to the accessible potential range, what is the advantage and disadvantage, for voltammetric analysis, of a Hg electrode compared with a Pt or carbon electrode?
- (b) Describe the essential features of anodic stripping voltammetry (ASV).
- (c) ‘By use of variable stirring rates, ASV can be used to detect metal complexes of varying lability in natural waters.’

Discuss the statement above. In your answer you should explain the effect of varying the stirring rate on ASV measurements, and consider how the technique can be applied to the detection of ‘free’ metal ions, and metal ions in somewhat labile and inert complexes.

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7. (a) (i) What is the essential property of a reference electrode?
- (ii) List the constituents of *either* the saturated calomel reference electrode (SCE) *or* the Ag/AgCl reference electrode and give the half-cell redox reaction for your selected electrode.
- (iii) With reference to the Nernst equation, explain why the electrode you describe in (ii) is a reliable reference electrode.

$$\text{Nernst equation: } E_{\text{cell}} = E^{\circ} - [RT/nF] \ln([R]^R/[O]^O)$$

- (b) For an ion-selective electrode,

$$E_{\text{cell}} = E^{\circ} + S \log(a_i + K_{ij} a_j^{n/z})$$

A chloride ion-selective electrode was equilibrated in 100 mL of 2.0×10^{-4} M LiCl at 25 °C. The equilibrium potential was 111.9 mV. After addition of 1 mL of 1.0 M LiBr, the equilibrium potential was 107.9 mV.

Determine $K_{\text{Cl}^-, \text{Br}^-}$, assuming that the slope of the chloride calibration curve is -59.2 mV and that ion activities are proportional to concentrations.

- (c) Explain, by briefly referring to the basic functioning of an ion-selective electrode, why only ionic species can be **directly** measured using an ion-selective electrode. Briefly explain the general strategy for determining non-ionic species using ion-selective electrodes.

END OF PAPER