

University of Canterbury

End-of-year Examinations 2008

Prescription Number(s): CHEM 404

Paper Title: Analytical & Environmental Chemistry

Time Allowed: TWO HOURS

Number of pages: SEVEN

This paper is divided in to **TWO** sections.

Answer **THREE** questions including **AT LEAST ONE** question from each section.

TURN OVER

SECTION A

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

Question 1 (30 marks)

- (a) Define the term bioavailability. As part of your answer explain what three criteria need to be met for a contaminant to be considered bioavailable.
- (b) Describe four types of chemical methods that can be used to assess the bioavailability of trace elements in soil. As part of your answer:
- outline the advantages of single extractant tests compared with bioassays; and
 - explain why these methods have only been partially successful at predicting bioavailability.
 - explain the differences in the extractable metal content in Table 1.

Table 1: Extractable cadmium content from agricultural soils using different extractants ($\mu\text{g/g}$ dry mass).^a

Soil	Total ^b	CaCl ₂	EDTA ^c
Ohura	0.31	0.018	0.130
Taupo	0.45	0.015	0.196
Tai Tapu	0.19	0.004	0.138

^a Adapted from Gray *et al.* (1999) Cadmium phytoavailability in some New Zealand soils. *Australian Journal of Soil Research* 37: 461–477.

^b Acid digest with HNO₃

^c Ethylenediaminetetraacetate

TURN OVER

Question 2 (30 marks)

- (a) With reference to the data in Table 2, explain the concept of aging of contaminants in soil. As part of your answer, explain the processes and key soil properties that contribute to the sequestration of hydrophobic organic contaminants in soil.

Table 2: Comparison of earthworm uptake and bacterial degradation of phenanthrene (from a silty clay loam soil of pH 6.4 and of organic matter content 4.5%) with increasing aging time^a

Aging time (days)	Earthworm uptake (%)	Bacterial degradation (%)
0	3.6	26.5
88	1.5	12.3
155	0.7	6.5

^a Adapted from Reid *et al.* (2000) Bioavailability of persistent organic pollutants in soils and sediments – a perspective on mechanisms, consequences and assessment. *Environmental Pollution* 108, 103-112.

- (b) Describe three types of chemical methods that can be used to assess the bioavailability of hydrophobic organic contaminants. As part of your answer explain why a “total” compound extraction may overestimate the bioavailability of a hydrophobic organic contaminant.
- (c) With reference to Table 1, explain the trend you would expect to observe in extractability of phenanthrene with time.

SECTION B

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

Question 3 (30 marks)

(a) (3 marks)

What is meant by an atmospheric window?

(b) (5 marks)

Why are rotational energy states important in considering the effect of greenhouse gases on global warming?

(c) (4 marks)

Name four molecules, other than water and carbon dioxide, that are important greenhouse gases?

(d) (18 marks)

How would you measure the concentration of at least two of the molecules you chose in (c) in the troposphere. Describe a fundamentally different instrumental technique for these two molecules. Give as much detail as you can.

TURN OVER

Question 4 (30 marks)

(a) (5 marks)

The frequency of the C=O stretching band of cyclohexanone is 1718 cm^{-1} ; give the absolute wavenumbers at which the Stokes and anti-Stokes bands of this mode are seen in the Raman spectrum when excited with a 532.0-nm laser.

(b) (5 marks)

What are the relative intensities of the two bands in (a) at room temperature, when $kT \sim 200\text{ cm}^{-1}$? What assumptions did you make in this calculation?

(c) (15 marks)

Twenty years ago, a Raman spectrometer would probably have consisted of an argon ion laser emitting at 488.0 nm and a double or triple monochromator, with detection using a photomultiplier tube with photon-counting electronics and analogue output. Draw a diagram of a modern bench-top Raman spectrometer and give the reasons why each of the components listed above were replaced by the components you drew.

(d) (3 marks)

How do the band intensities in resonance Raman spectra differ from those in standard (unenhanced) Raman spectra?

(e) (2 marks)

What are the two metals that are most commonly used to give surface-enhanced Raman spectra?

Question 5 (30 marks)

(a) (5 marks)

Most textbooks on analytical chemistry state that the limit of detection (LOD) when the noise is randomly distributed about a mean value of the signal is equal to 3σ , where σ is the standard deviation of the noise. Justify this definition and discuss where it breaks down.

(b) (5 marks)

The limit of quantification (LOQ) is frequently given as 10σ . Bearing in mind your previous answer, why is this definition even more inaccurate than the definition of LOD as 3σ ?

(c) (16 marks)

Describe at least four algorithms that are used to smooth noisy signals. (Give as much detail as you can.)

(d) (4 marks)

What is the common feature of all the smoothing algorithms you described in (c)?

END OF PAPER