University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 324
Paper Title:	Analytical & Environmental Chemistry

Time Allowed: Three hours

Number of pages: Eight

Answer **ALL** questions

Total marks: 180

1. (20 marks)

   (a) Briefly explain the challenges of mass spectrometric ion detectors. (5 marks)

   (b) In detail, describe and compare **TWO** examples of ion detectors that you might find in a mass spectrometer. You will need to address how the detectors overcome the challenges of detection you outlined above. (15 marks)

2. (20 marks)

   A major challenge in mass spectrometry of large molecules is the production of gas-phase ions. Describe in detail an ionization approach for large molecules, using proteins as an example. Include a discussion of the advantages and disadvantages of the technique described in your answer.

3. (10 marks)

   Answer **EITHER** (a) **OR** (b):

   Either

   (a) You are asked to develop a method for analysing polycyclic aromatic hydrocarbons (PAHs) in soil samples. Describe the types of extraction methods you could use. For each method outline the advantages and disadvantages.

   Or

   (b) (i) Outline how you would validate a new method for solid phase extraction of organic compounds from water samples.

   (ii) Describe **ONE** other extraction method that could be used for liquid samples.

4. Answer (a) (10 marks) and **TWO** of (b) – (d) (25 marks each).

(a) Briefly outline the general characteristics of analytical voltammetric techniques, considering the following aspects:

- Range of species that can be analysed;
- Detection limits;
- Capability for multi-analyte detection;
- Cost of instrumentation;
- Suitability for measurements in the field.

(Answer **TWO** of (b) – (d)):

(b) (i) Outline the factors that could lead an analyst to choose adsorptive stripping voltammetry (AdSV) to determine the concentration of a metal ion in an aqueous sample. You should assume that only voltammetric instruments are available for the analysis.

(ii) Ni(II) and Co(II) can be determined using AdSV and the ligand dimethylgyoxime (DMG). The peak potentials for reduction of the DMG complexes of Ni and Co are -0.92 and -1.08 V vs SCE, respectively.

Explain how you might carry out the analysis of Ni(II) and Co(II) by AdSV, suggesting suitable (approximate) potentials for the various steps in the procedure.

(iii) What additional measurements would you make to determine the concentration of each metal in the sample?

(iv) Explain why AdSV is characterised by a short linear working range.

(v) Explain why AdSV is the only electrochemical technique that can be used to determine the concentrations of Al(III) and Ca(II). What are the requirements of a ligand to be used in the analysis of these metals by AdSV?

Question 4 continued on following page

Question 4 continued

(c) Discuss the applications of diffusive gradients in thin films (DGT) for environmental analyses.

Your answer should note any limitations of the technique for these applications and should include a description of the DGT technique.

The expression below may be helpful when answering this question

$$C_b = C_r \Delta g \Delta r / Dt$$

(d) (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 described in (ii) is a reliable reference electrode.

Nernst equation: $E_{cell} = E^o + RT/nF$ [ln([O]/[R])

(iv) Hg, in the form of a drop or a thin film, is often used as the working electrode for analytical measurements. Outline the advantages and disadvantages of Hg electrodes, compared with Pt and carbon electrodes, for voltammetric analyses. Your answer should include mention of the technique of anodic stripping voltammetry, and should include a brief description of the principles of the technique.

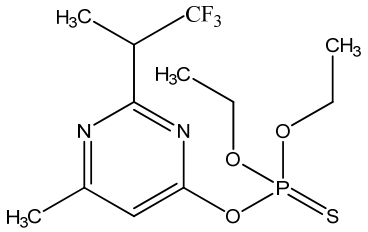
5. (15 marks)

Write descriptive notes on the environmental chemistry of arsenic

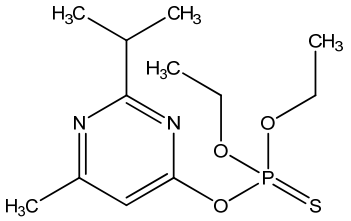
Your answer should cover anthropogenic and natural sources of arsenic, arsenic speciation in the environment, the toxicity of arsenic species and provide details for one method for analysis and speciation of arsenic in either food or water samples.

6. (55 marks)

A new pesticide (Registration Code IS32/6) for use as an aphicide in greenhouse lettuce production has the following molecular structure:



It is based on a commonly used pesticide, Diazinon, which has the following molecular structure:



The efficacy of IS32/6 was determined on the basis of aphid kill on lettuce in a controlled greenhouse environment. The LC_{50} [Diazinon, aphid] = 2.1 mg/L and the LC_{50} [IS32/6, aphid] = 0.32 mg/L.

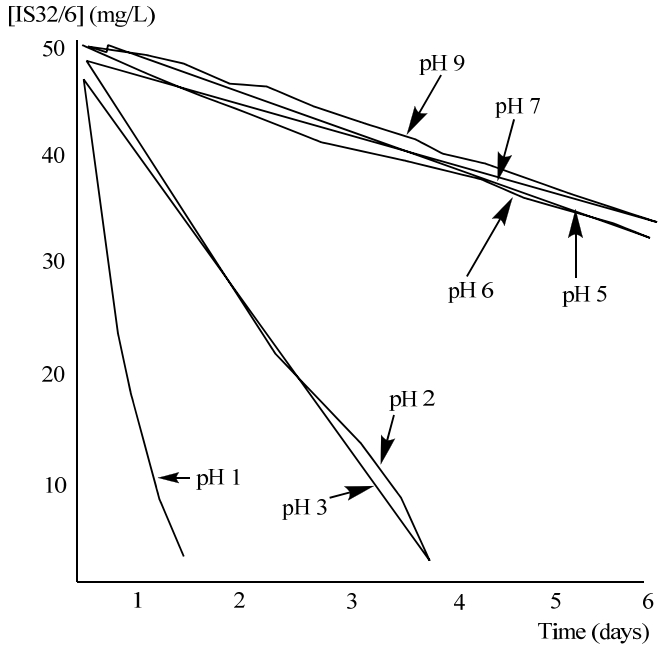
The following data were submitted to the Regulatory Authority as part of the approvals application dossier:

Parameter	Diazinon	IS32/6
Half life – *in vitro* in standard soil (Dark, 25ºC)	2.6 weeks	2.8 weeks
Half life – *in vitro* standard soil sterilized at 100ºC for 30 min (Dark, 25ºC)	4.5 weeks	5.2 weeks
Half life – in field test system (greenhouse, 25ºC)	2.0 weeks	2.5 weeks
EC_{50} [Chlorella]	135 mg/L	142 mg/L
EC_{50} [*Daphnia magna*]	12 mg/L	9.5 mg/L
EC_{50} [Trout]	2.3 mg/L	2.0 mg/L
NOAEL [oral, quail]	1.2 mg/kg body weight	1.8 mg/kg body weight
NOAEL [oral, rat]	150 mg/kg body weight	210 mg/kg body weight
NOAEL [oral, dog]	200 mg/kg body weight	240 mg/kg body weight
$LogP_{OW}$	2.2	3.2
K_d	3.8	2.9
K_{OC}	555	496
Mutagenicity [His^- *Salmonella typhimurium* reversion]	Negative	Negative

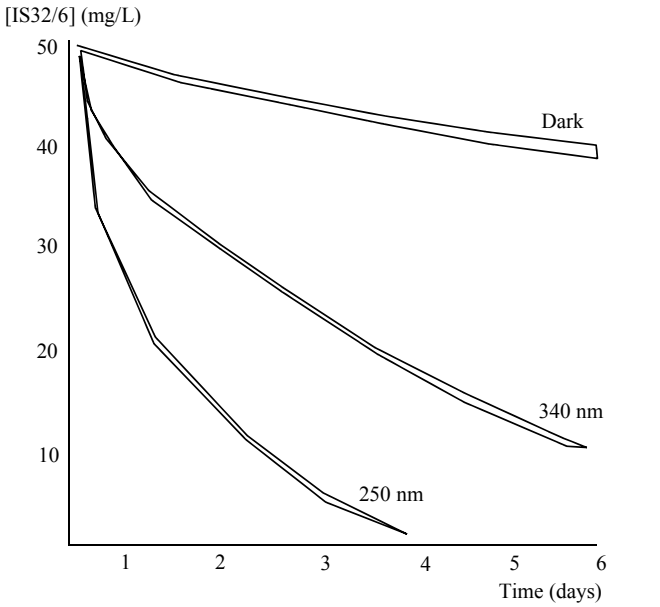
Question 6 continued on following page

Question 6 continued

In addition stability studies at varying pH and during *uv* exposure in aqueous solution were conducted with IS32/6, the results are as follows:



The stability of IS32/6 at different pHs in aqueous solution



The *uv* stability of IS32/6 at pH 7.0 in aqueous solution (duplicate results)

Residues in lettuce were determined by GC/MS following controlled greenhouse studies with IS32/6 at the proposed spray concentration. The results of these studies are as follows:

Time after spraying (days)	Residues level (mg/kg wet weight)
1	1,060
2	820
3	640
4	580
5	410
6	320
8	160
10	30
15	10
20	Not detected

The average consumption of lettuce from the New Zealand dietary survey is 5 g/day.

The proposed MRL for IS32/6 is 30 mg/kg for lettuce.

Question 6 continued on following page

Question 6 continued

You are the chair of the regulatory committee that must advise the government department whether or not IS32/6 should be granted approval for use as an aphicide for application to lettuce only. Carry out a structured risk assessment and write your report to the Minister including the decision with reasoning whether or not to approve IS32/6 for marketing. The report should be written under the following headings:

Background	(5 marks)
Efficacy	(2 marks)
Environmental fate and behaviour	(10 marks)
Environmental toxicity	(10 marks)
Operator toxicity	(3 marks)
Consumer exposure	(5 marks)
Comparison with an approved product	(5 marks)
Advice (to include proposed ADI and withdrawal period)	(5 marks)
	(TOTAL 55 marks)

END OF PAPER