University of Canterbury

End of Year Examinations 2007

Prescription Number(s):	CHEM 224
Paper Title:	Analytical & Environmental Chemistry

Time Allowed:	TWO HOURS
Number of pages:	FIVE

Answer **ALL** questions

Total 60 marks

TURN OVER

1. (20 marks)

EITHER

Discuss the importance of chemical structure in determining toxicity;

OR

Describe the mechanisms of toxicity and the environmental impacts of two pollutants.

2. (15 marks)

An investigation at a childcare centre in central Christchurch found elevated concentrations of Pb in the soil. Blood samples collected from children attending the centre will be analysed by anodic stripping voltammetry (ASV).

(a) (i) Describe the significant anthropogenic and natural sources of Pb.

(ii) Discuss the uptake and retention of Pb by the body and its impact on human health.

(iii) Give details for an appropriate method for analysis of total Pb in urban soils.

(b) (i) Describe the essential steps in anodic stripping voltammetry

(ii) Explain why ASV measurements are done in the absence of O_2 and require the presence of an electrolyte in excess.

(iii) Explain how ASV could be used to measure total and bioavailable concentrations of a metal in a water sample.

3. (25 marks)

(a) Give an example of a primary standard that could be used to standardize **TWO** of the following:

(i) HCl;

(ii) $KMnO_4$;

(iii) EDTA.

For **one** primary standard chosen, explain why it is suitable.

(b) **EITHER**

Fe^{2+} is titrated with $KMnO_4$ in a potentiometric titration. From your knowledge of the Fe^{2+} *vs* Ce^{4+} potentiometric titration, explain how the cell voltage depends upon the concentrations of Fe^{2+}, Fe^{3+}, MnO_4^-, and Mn^{2+},

(i) before the equivalence point, and

(ii) after the equivalence point.

$E°(Fe^{3+}/Fe^{2+}) = +0.77$ V; $E°(MnO_4^-/Mn^{2+}) = +1.23$ V

OR

Explain how a fluoride electrode is constructed and how it functions.

(c) For phosphoric acid (H_3PO_4), the acid dissociation constants are:

$pK_{a1} = 2.12$, $pK_{a2} = 7.21$, $pK_{a3} = 12.44$.

Sketch the speciation diagram (relative concentrations *vs* pH) for phosphoric acid species. Label **all** curves. Ensure that curve crossings and maxima are at the correct pH.

Question 3 continued on following page

Question 3 continued

(d) A solution is formed by mixing 10.0 mL of 0.15 mol L^{-1} Na_2SO_3 and 20 mL of 0.10 mol L^{-1} HCl. What are the major sulfite species present? Calculate the pH of the solution.

$K_{a1}(H_2SO_3) = 1.7 \times 10^{-2}$; $K_{a2}(H_2SO_3) = 6.4 \times 10^{-8}$; $K_w = 1.0 \times 10^{-14}$

(e) Explain the difference between an ***open system*** and a ***closed system***, using the example of the equilibria involved in the dissolution of calcite ($CaCO_3$). What basic equilibrium constants (e.g. $K_s(CaCO_3)$) are required to model these two types of system?

END OF PAPER