University of Canterbury

End of Year Examinations 2005

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

Time Allowed:	THREE HOURS
Number of pages:	EIGHT

Answer **FIVE** questions.

All questions are of equal value.

TURN OVER

1. (a)As a recently appointed analytical/environmental chemist with a regional council you have been tasked by a non-scientist manager to advise the council on the measurement of trace CO and SO_2 in rural areas.

    (i) What questions, pertinent to this directive, would you put to the council before you were able to draft a business plan and commit resources?

    (ii) Suggest an instrumental method suitable for analysis of each of these trace gases (one for CO and one for SO_2). Give details of their operation, suitability and sensitivity.

    (b) Chlorofluorocarbons, CFCs, are efficient greenhouse gases and the major cause of stratospheric ozone depletion. Measurements of CFCs in the troposphere are routinely made using sample grab bags for GC analysis with an electron capture detector, ECD.

    Explain how the ECD works; compare the levels of CFCs in the troposphere with the detection limit of the ECD.

2. (a) Explain the term atmospheric aerosol under the headings:

    (i) size distribution and lifetimes in the atmosphere;

    (ii) origin, with particular emphasis on sulfate aerosols;

    (iii) radiative forcing.

    (b) Aerosol time-of-flight mass spectrometry (ATOFMS) is used to measure the size and composition of individual aerosol particles sampled directly from the atmosphere. Explain how ATOFMS measures size and composition by following a single aerosol particle through the instrument.

3. (a) Source waters used for drinking-water purposes fall into three general categories.

(i) Identify these categories and, where appropriate, any subcategories.

(ii) Describe the physical characteristics of each source type, the typical characteristics of the water quality derived from them (chemical and microbiological), and how these characteristics arise.

(b) Drinking water received by consumers is often chemically different from the water drawn from the source. The changes may be the result of the water treatment processes and other processes occurring in the reticulation network or individual plumbing systems. The table on page 5 records physico-chemical test results from water samples taken at three locations in a water supply:

- at the source;
- just after treatment;
- from a consumer's tap.

Identify which analytes have changed significantly between these locations. Explain why these changes are evident and suggest which treatment processes are likely to have been in use in this water supply.

Question 3 continued on following page

Question 3 continued

(units are in mg L^{-1} unless otherwise stated)

Analyte	Source	After treatment	Consumer's Tap
pH	7.9	8.0	8.0
Total alkalinity (to pH 4.5 as HCO_3^-)	42	42	42
Conductivity @ 20°C (mS m^{-1})	13	15	16
Turbidity (NTU)	1.2	3.0	1.5
Absorbance @ 270 nm	0.22	0.03	0.02
Nitrate-nitrogen	1.2	1.2	1.1
Sulfate	7.3	15	16
Calcium	5.6	9.7	9.7
Sodium	18	18	18
Chloroform (μg L^{-1})	<1	10	26
Arsenic	0.03	<0.01	<0.01
Boron	0.32	0.30	0.32
Reactive Aluminium	0.03	0.92	0.34
Reactive Silica as SiO_2	8.9	8.8	8.8
Zinc	<0.02	0.03	0.07
Copper	<0.02	<0.02	0.08

4. In May 2000, the drinking-water supply for the town of Walkerton in Canada became contaminated with *E.coli* O157:H7. Seven people died and more than 2,300 became ill when a heavy rain event washed farm manure into one of the water supply wells.

   Write an essay to explain why the incident happened, and how it could have been avoided. In your essay:

   (i) identify the different personnel and agencies involved, and describe how each contributed to the incident; and

   (ii) for **four** of the personnel and agencies you have identified, put yourself in their shoes and outline what you would have done differently to avoid the incident.

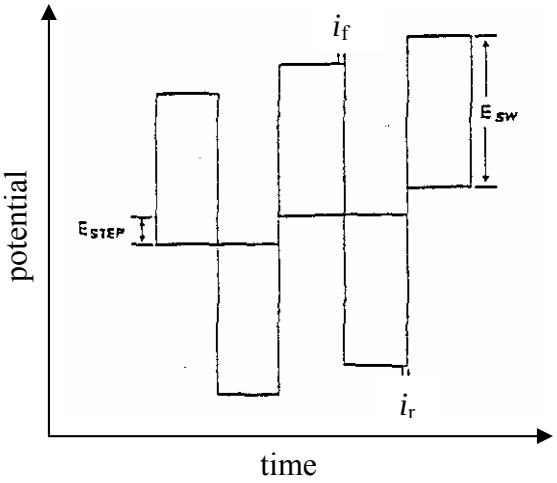
5. (a) The accessible potential range for a Hg electrode in 0.1 M HNO_3 is approximately 0.5 to –1.5 V *vs* SCE.

Explain the term **accessible potential range**. Describe the processes that determine the accessible potential range of a Hg electrode.

(b) In a voltammetric experiment, the total current is the sum of the Faradaic and charging currents, i_F and i_C, respectively.

(i) What processes do i_F and i_C arise from?

(ii) The diagram below shows the applied potential-time waveform during square-wave voltammetry. Explain why this waveform enhances the i_F:i_C ratio.



Potential-time waveform for square-wave voltammetry.

(c) By use of variable stirring rates, ASV (anodic stripping voltammetry) can be used to detect metal complexes of varying lability in natural waters.

Explain this statement.

6. The expression below may be helpful when answering this question.

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

(a) (i) Draw a diagram of a device used for the diffusive gradients in thin films (DGT) technique. Label all essential components of the device.

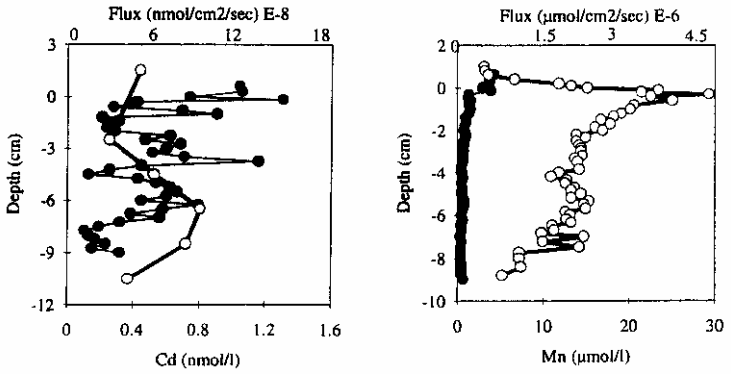
(ii) Describe the essential properties and function of the diffusive gel.

(iii) Using Chelex resin as an example, describe the essential properties of the binding material (the resin gel).

(b) (i) Briefly describe the steps involved in using a DGT device to determine the Cu(II) concentration in a stream over the period of one week.

(ii) Outline the advantages and limitations of the DGT technique for obtaining metal concentrations in waters.

(c) The figure below shows Cd and Mn concentrations measured in sediment pore waters, by using DGT devices (solid circles) and by extraction of sediment samples (open circles). What information do these data convey about pore water/sediment processes?



Mean flux and concentration profiles in surface sediments measured by DGT *in situ* insertion of a gel assembly (solid symbols). Comparative measurements on retrieved sediment cores, by porewater extraction shown using open symbols.

7. (a) The potential developed by an ion-selective electrode for ion i, in the presence of ion j, is given in the expression below. Explain each of the terms: E_{cell}, E', a_i, K_{ij}

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

(b) (i) A lithium ion-selective electrode was equilibrated in a solution of 5×10^{-5} M LiCl. The equilibrium potential was 89.5 mV. The electrode was then equilibrated in a separate solution of 1×10^{-3} M KCl. The equilibrium potential was 71.6 mV. Determine K_{Li^+,K^+} for the electrode, assuming the slope of the calibration curve is 60 mV per decade change in Li^+ concentration.

(ii) For the same electrode, K_{Li^+,Na^+} is 0.01. Which ion, K^+ or Na^+, interferes more strongly with the lithium ion-selective electrode?

(c) By considering the processes that occur at the membrane surfaces and within the membrane of a fluoride ion-selective electrode, explain how the electrode functions in the determination of fluoride ion activity. Assume that the membrane is a Eu^{2+}-doped single crystal of LaF_3.

(d) Outline the advantages and limitations of ion-selective electrode potentiometry for evironmental analyses. Consider factors related to the sample, analyte, concentration range, instrumentation, ease of use, and cost.

END OF PAPER