Name: CHEM382 TEST
10 October 2005

Time allowed: 90 minutes **Attempt all questions**

Question 1. (18 marks)

Part A (12 marks)

Answer the following questions concerning the determination of Cd^{2+} by anodic stripping voltammetry (ASV):

(a) Describe the processes that occur at the Hg drop electrode and/or in the solution (as relevant) during the following steps of an ASV experiment:

(i) A potential of -0.8 V vs Ag/AgCl is applied for 300 s while the solution is stirred;

(ii) An equilibration time of 5 s is applied;

(iii) A differential pulse scan is carried out between -0.8 V and 0 V.

(b) Explain why the solution in the electrochemical cell is flushed with nitrogen gas prior to analysis;

(c) The Cd^{2+} concentration in a seawater sample was determined by ASV, using the single spike method. The concentration of the Cd^{2+} standard solution used for the spike was 5×10^{-4}. From the data in the table below, calculate the concentration (mol L^{-1}) of Cd^{2+} in the seawater sample.

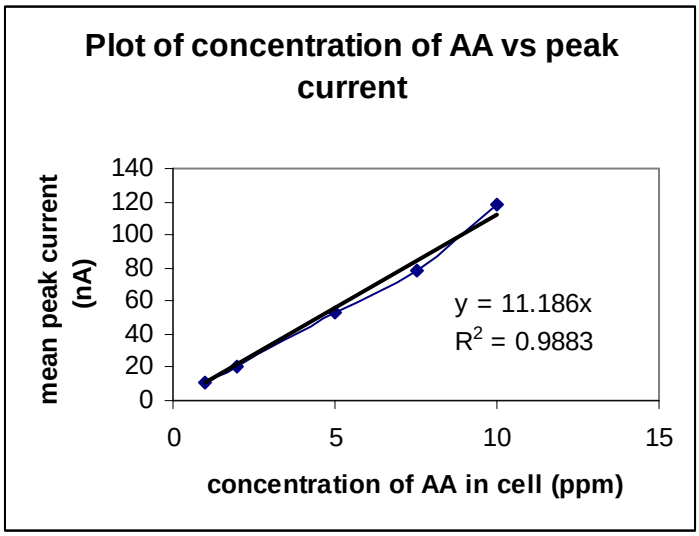
Solution (volume)	Deposition time (s)	Mean peak current (nA)
Seawater (10 mL)	300 s	3.76
Seawater (10 mL) plus standard (20 μL)	120 s	5.78

Question 1 Part B (6 marks)

Ascorbic acid (AA) concentration can be determined using differential pulse polarography at a dropping mercury electrode.

(a) The calibration curve shown below was obtained using the 'blank subtract' mode. To establish the detection limit, six repeat measurements of the 1 ppm solution were made giving peak currents (blank subtracted) of: 11.2, 9.8, 9.4, 10.3, 12.4 and 11.5 nA.

Use the data given to calculate the detection limit of AA.



(b) The standard additions method can be conveniently applied to the polarographic determination of AA. Comment, with brief explanation, whether you would use the standard additions method, or the calibration graph method, to obtain AA concentrations in:

(i) Three solutions containing only AA and the measurement buffer;

(ii) Three fruit juice samples.

Question 2. (18 marks)

(a) Using a diagram or diagrams, explain how a computer can be used to send an analogue voltage to an external instrument and how it can also be used to read an analogue voltage from an external instrument. (These functions may be either considered separately or combined.) Explain how handshaking is accomplished as part of your answer and note the specifications for the electronic chips used in your circuitry and the limitations imposed by the digital word size.

(b) A thermocouple delivers an output of 0 to 25.0 mV, corresponding to a temperature range of 0 – 200 °C.

(i) What is the gain required if the output of the thermocouple is to be read using a 5V ADC?
(ii) Sketch the circuit used to amplify the thermocouple voltage.
(ii) What is the smallest change in temperature that can be determined if the thermocouple is monitored by an 8-bit computer?

Question 3. (18 marks)

(a) Atomic absorption spectroscopy normally requires a flame or other heated "atom cell" for measurement of the atom concentration. For Hg determination, following treatment of the acidified sample with $NaBH_4$/NaOH, a cold atom cell (quartz tube) is used.

(i) Explain why, in the case of Hg, a hot "atom cell" is not required.
(ii) In general (not just for Hg), measurements using the quartz cell are much more sensitive than measurements using a flame or an electrically heated furnace. Explain.

(b) The determination of Cu in seawater by flame atomic absorption involves solvent extraction.

(i) Why is solvent extraction necessary?

(ii) What reagent (ligand) is used in the solvent extraction?

(iii) Is it necessary to buffer the seawater sample? Explain.

(iv) Ligands that are good complexing agents are likely to be contaminated with metal ions. How is a correction made for this in the determination of Cu in seawater?

Question 4. (18 marks)

In a viscometry experiment at 25˚C, an aqueous solution of poly(vinyl alcohol) of concentration 1.400 g dL^{-1} is found to have a flow-time of 432 s. When the concentration of the solution is halved, the flow-time is found to reduce to 248 s, while the flow-time of (pure) water under the same conditions is 137 s.

(a) Given that $[\eta] = 2.0 \times 10^{-4}$ dL g^{-1} $(\bar{M}_v$ / g $mol^{-1})^{0.76}$ for poly(vinyl alcohol) in water at 25˚C, **estimate** the average molecular weight of the poly(vinyl alcohol) of the above experiments.
[Useful information: $\eta_r = t/t_0$; $\eta_{sp} = \eta_r - 1$; $\eta_{red} = \eta_{sp}/c$; $\eta_{inh} = (\ln \eta_r)/c$.]

(b) What is another experimental technique that could be used to determine the molecular weight of the poly(vinyl alcohol)?

(c) In no more than two sentences, outline how this technique achieves measurement of polymer molecular weight.

Question 5. (18 marks)

In Experiment 10 you studied, by observing the emitted light intensity arising from N_2*, the termolecular reaction

(1) $N + N + N_2 \rightarrow N_2^* + N_2$

This experiment was carried in a flow tube under pseudo second-order conditions with $P_{N_2} >> P_N$. For this situation it may be shown that

(2) $1/P_N - 1/P_N^\circ = k't$

Here P_N° represents the initial partial pressure of N in the flow tube (in Torr), P_N is the partial pressure at time t. The pseudo second-order rate constant, k', is related to the termolecular rate constant for reaction (1), k, by the expression

$$k' = 2kP_{N_2}$$

A pair of students carried out an experiment under the conditions

$T = 22^\circ C$ $P_{N_2} = 3.65$ Torr

Using their data and equation (2), they determined $k' = 107$ Torr^{-1} s^{-1}.

What is the value of k (the termolecular rate constant) expressed in the more conventional units for a gas reaction, which in this case are cm^6 molecule^{-2} s^{-1}?

Data: $R = 8.314$ J mol^{-1} K^{-1} $N_A = 6.022 \times 10^{23}$ molecules mol^{-1}

1 Torr = 133.3 Pa

END OF PAPER