**NATIONAL UNIVERSITY OF SINGAPORE**

**CM2142– Analytical Chemistry 1**

(Semester 2：AY 2013/2014)

Time Allowed : 2 Hours

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**INSTRUCTIONS TO CANDIDATES**

1. Please write your student number only. **Do not write your name**.
2. This examination paper contains **FOUR** questions and comprises **SEVENTEEN** printed pages.
3. Answer **ALL** questions. Write your answer only in the space provided below each sub-question.
4. **The ENTIRE QUESTION PAPER SHOULD BE HANDED IN** at the end of the examination. Do not hand in any other papers.
5. This is a closed book examination, but two A4, double sided sheets of notes are allowed.
6. Statistical tables are provided at the back of this Question paper.
7. Non-programmable calculators are allowed.

| Matriculation No.: | | |
|---|---|---|
| Q1 | | 25 marks |
| Q2 | | 25 marks |
| Q3 | | 25 marks |
| Q4 | | 25 marks |
| Total | | 100 marks |

**Question 1**

(a) The concentrations of volatile organic compounds in the cabin of a car were measured during trips through the CTE tunnel and Ayer Rajah Expressway, when one drives from Ang Mo Kio to the National University of Singapore. The total concentrations (± standard deviations) of m- and p-xylene were:

Ayer Rajah Expressway: 32.4±29.8 μg/$m^3$ (31 measurements)

CTE tunnel: 51.9±29.7 μg/$m^3$ (31 measurements)

Do these results differ at the 95% confidence level? At the 99% confidence level?

(6 marks)

(b) You bought a Standard Reference Material from NIST. It is certified to contain 84.6 ppm of a particular compound. Your analysis of this material gives values of 83.7, 85.4, 87.3, 85.6 and 86.1 ppm. Do your results differ from the expected result at the 95% confidence level? If you make one more measurement and obtain a value of 84.6ppm, would your conclusion change?

(6 marks)

(c) You would like to sample a carload of lead ore containing galena (~86.6% Pb) and other particles with little or no lead. Explain how you can minimize the sampling error for this heterogeneous population.

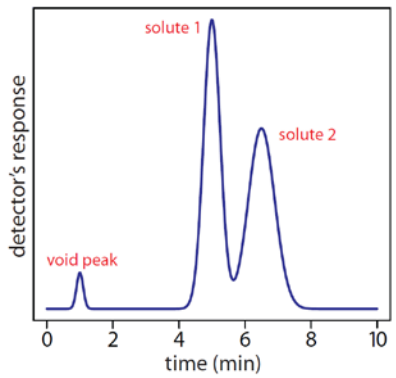
(5 marks)

(d) You have been requested to analyze the concentration of $Cd^{2+}$ ions in the water of a highly polluted lake. Briefly described the entire procedure you will undertake in order to achieve an accurate and precise determination.

(8 marks)

**Question 2**

(a) Two peaks belonging to solute 1 and 2 emerge from a HPLC column as sketched in the following illustration. Describe the measures which you can take to improve the resolution.




(10 marks)

(b) A standard solution containing $6.3\times10^{-8}$M iodoacetone and $2.0\times10^{-7}$M p-dichlorobenzene (an internal standard) gave peak areas of 396 and 786, respectively, in a gas chromatogram. 2.00 mL of an unknown solution of iodoacetone was treated with 0.100 mL of $1.6\times10^{-5}$M p-dichlorobenzene and the mixture was diluted to 10.00 mL. Gas chromatography gave peak areas of 623 and 525 for iodoacetone and p-dichlorobenzene, respectively. Find the concentration of iodoacetone in the 2.00 mL of original unknown.

(6 marks)

(c) Riboflavin (a neutral compound), niacinamide (a neutral compound), niacin (an anion), and thiamine (a cation) were separated by micellar electrokinetic chromatography in 15 mM borate buffer (pH 8.0) with 50 mM sodium dodecyl sulfate. The migration times measured were: niacinamide (8.0 min), riboflavin (13.1 min), niacin (14.2 min) and thiamine (22.0 min). What is the role of sodium dodecyl sulfate in the separation process? What would be the order in the absence of sodium dodecyl sulfate? Which compound is most soluble in the micelles? Explain your answers.

(9 marks)

**Question 3:**

(a) Explain the workings of an ion-selective electrode using any example of your choice.

(7 marks)

(b) The cell

$$SCE \| H^{+}(a = x) | glass\_electrode$$

has a potential of 0.2107 V when the solution in the right-hand compartment is a buffer of pH 4.016. The following cell potentials were recorded when the buffer is replaced with unknowns: (a) -0.2802 V and (b) +0.1341 V. Calculate the pH of each unknown. (c) Assuming an uncertainty of 0.002 V in the junction potential, what is the range of pH within which the true value might be expected to lie?

(8 marks)

(c) Sketch a working electrochemical cell that has no liquid junction potentials. Please indicate the type of electrolyte(s) and electrode(s) used.

(5 marks)

(d) A solution with an unknown concentration of $Cd^{2+}$ was analyzed polarographically by the method of standard additions. A 25.00 mL sample of the unknown solution produced a diffusion current of 2.10 µA. Following addition of a 2.00 mL aliquot of $2.50\times10^{-3}$M $Cd^{2+}$ standard solution to the unknown solution, a diffusion current of 8.31 µA was produced. Calculate the concentration of $Cd^{2+}$ in the unknown solution.

(5 marks)

**Question 4:**

(a) A solute with a partition coefficient of 5.0 is extracted from 10 mL of phase 1 into phase 2. What volume of phase 2 is needed to extract 99.99% of the solute in one extraction? What is the total volume of phase 2 needed to remove 99.99% of the solute in three equal extractions?

(5 marks)

(b) Acetonitrile and acetone are good solvents for organic compounds. However, they are never used as the organic phase for extracting organic compounds from an aqueous solution (via liquid-liquid extraction). Why is this so?

(4 marks)

(c) Discuss the reason behind this sample pretreatment and analysis method.

In the US Environmental Protection Agency (EPA) method 505, gas chromatography is used for the analysis of organohalide pesticides and commercial polychlorinated biphenyl products in drinking water following extraction of the original sample with hexane.

(8 marks)

(d) Discuss the reason behind this analysis method.

Headspace gas chromatography is used by a forensic laboratory for the determination of alcohol levels in blood.

(8 marks)

**END OF PAPER**

| Confidence Levels for Various Values of $z$ | |
|---|---|
| **Confidence Level, %** | $z$ |
| 50 | 0.67 |
| 68 | 1.00 |
| 80 | 1.28 |
| 90 | 1.64 |
| 95 | 1.96 |
| 95.4 | 2.00 |
| 99 | 2.58 |
| 99.7 | 3.00 |
| 99.9 | 3.29 |



| Values of $t$ for Various Levels of Probability | | | | | |
|---|---|---|---|---|---|
| **Degrees of Freedom** | **80%** | **90%** | **95%** | **99%** | **99.9%** |
| 1 | 3.08 | 6.31 | 12.7 | 63.7 | 637 |
| 2 | 1.89 | 2.92 | 4.30 | 9.92 | 31.6 |
| 3 | 1.64 | 2.35 | 3.18 | 5.84 | 12.9 |
| 4 | 1.53 | 2.13 | 2.78 | 4.60 | 8.61 |
| 5 | 1.48 | 2.02 | 2.57 | 4.03 | 6.87 |
| 6 | 1.44 | 1.94 | 2.45 | 3.71 | 5.96 |
| 7 | 1.42 | 1.90 | 2.36 | 3.50 | 5.41 |
| 8 | 1.40 | 1.86 | 2.31 | 3.36 | 5.04 |
| 9 | 1.38 | 1.83 | 2.26 | 3.25 | 4.78 |
| 10 | 1.37 | 1.81 | 2.23 | 3.17 | 4.59 |
| 15 | 1.34 | 1.75 | 2.13 | 2.95 | 4.07 |
| 20 | 1.32 | 1.73 | 2.09 | 2.84 | 3.85 |
| 40 | 1.30 | 1.68 | 2.02 | 2.70 | 3.55 |
| 60 | 1.30 | 1.67 | 2.00 | 2.62 | 3.46 |
| $\infty$ | 1.28 | 1.64 | 1.96 | 2.58 | 3.29 |