Mastership in Chemical Analysis

Part A Examination

Burlington House

30 April 2008

1300 – 1600

RSC | Advancing the Chemical Sciences

Instructions

Answer **five** questions out of eight.

The answers to each section must be returned in the examination script booklets provided. All examination scripts must be handed in at the end of the examination.

The marks allocated to each section are given in parentheses.

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1. (a) Describe what happens when electromagnetic (EM) radiation in each of the following regions of the EM spectrum is absorbed by atoms or molecules:

    (i) X-rays
    (ii) ultra-violet/visible light
    (iii) infra red radiation, and
    (iv) radio waves.

    (8 marks)

    (b) Explain how these interactions between radiation and matter are exploited in analytical chemistry, and describe the types of information obtained by spectroscopic techniques utilizing EM radiation in each of the above regions.

    (12 marks)

2. Discuss **four** of the following methods for extraction of analytes from samples. In each case, mention the type(s) of samples and analyte(s) for which the extraction method would be suitable.

    (i) Soxhlet extraction
    (ii) Headspace extraction
    (iii) Microwave-assisted leaching with hot *aqua regia*
    (iv) Solid phase extraction
    (v) Supercritical fluid extraction.

    (4 x 5 marks, total 20 marks)

3. (a) Describe the inductively-coupled plasma (ICP) as used in atomic spectrometry. Comment on how the plasma is formed and the analytes introduced.

(8 marks)

(b) Inductively-coupled plasma mass spectrometry (ICPMS) is now widely used for the measurement of trace metals in samples. What challenges are encountered in coupling a plasma to a mass spectrometer, and how are these overcome in modern instruments?

(8 marks)

(c) Mention **two** alternative techniques for measurement of trace metals, stating their advantages and disadvantages relative to ICPMS.

(4 marks)

4. (a) Describe the process of *electro-osmosis* (also called *cathodal drift*) and explain why it is important in capillary electrophoresis.

(8 marks)

(b) Outline the apparatus and procedure typically used for separation of analytes by gel electrophoresis.

(8 marks)

(c) Comment on the relative advantages and disadvantages of capillary and gel electrophoresis.

(4 marks)

5. (a) Describe the interactions that occur between analytes and stationary phase in ion chromatography. Include comments on the nature of the stationary phase in your answer.

(10 marks)

(b) Predict and explain the order of elution for chloride, fluoride, nitrate and sulfate ions when separated by an anion exchange chromatographic column.

(3 marks)

(c) Using sodium carbonate as an example, describe the suppression procedure that is used to reduce the contribution of the eluent to conductivity measurement in ion chromatography.

(7 marks)

6. (a) Describe the typical components of a uv/visible spectrophotometer, explaining the function of each part. Include a sketch in your answer.

(13 marks)

(b) An experiment is performed to determine the molar absorptivity (also called *molar extinction coefficient*) of copper sulfate. 0.25 g of $CuSO_4.6H_2O$ is dissolved in 50 ml distilled water, giving a blue solution. An aliquot of this solution is placed in a 1 cm cuvette and analysed by uv/visible spectrophotometry. An absorbance of 0.657 at the λ_{MAX} is obtained. Use the Beer-Lambert equation to calculate the molar absorptivity of the solution (A periodic table is provided).

(5 marks)

(c) The uv/visible spectrum of copper sulfate solution shows a single, broad absorption with a λ_{MAX} at around 800 nm. Comment on why this is consistent with the observed colour of the solution.

(2 marks)

7. A student analyst carries out an experiment to estimate the variable error associated with use of a 25 ml standard flask and a 25 ml pipette. Each piece of apparatus is filled to the mark ten times and the weight of water contained in the flask, or delivered by the pipette is recorded. The data obtained are converted from weight to volume by applying appropriate corrections for air temperature and atmospheric pressure, giving the results shown in Table 7.1.

Table 7.1 Volume of water contained or delivered (ml)

Replicate	Flask	Pipette
1	25.0039	25.0228
2	25.0439	25.0342
3	25.0252	25.0501
4	25.0078	25.0271
5	25.0395	25.0593
6	25.0271	25.0120
7	25.0271	25.0446
8	25.0271	25.0167
9	25.0339	25.0274
10	25.0334	25.0398

(a) Calculate the mean and standard deviation for the volume contained in the flask and delivered by the pipette.

(4 marks)

(b) Calculate the accuracy and precision obtained for the flask and for the pipette. Comment on the values obtained.

(5 marks)

(c) Use appropriate statistical tests to determine whether the volume of water contained in the flask, and delivered by the pipette, are the same within chance experiment error.

(8 marks)

(d) What are generally the largest sources of error in use of standard glassware?

(3 marks)

Statistical formulae and tables, ***some*** *of which* ***may*** *be required, are provided at the end of the examination paper*.

8. Discuss any **three** of the following, explaining their use in analytical chemistry

(a) The Raman effect

(b) Principal component analysis

(c) A control chart

(d) The polymerase chain reaction.

(equal marks for each part, total 20 marks)

END OF PAPER

Standard deviation

$$S \quad = \frac{\sum\left(x_i - \overline{x}\right)^2}{(n-1)}$$

Pooled standard deviation

$$S \quad = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{(n_1 + n_2 - 2)}}$$

The F test:

$$F_{calc} = \frac{s_1^2}{s_2^2}, \quad where\ s_1^2 > s_2^2$$

The t-test assuming equal variance

$$\left|t_{calc}\right| = \frac{\left(\overline{x_1} - \overline{x_2}\right)}{S\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

The t-test assuming unequal variance

$$\left|\mathrm{t_{calc}}\right| = \frac{\left|\overline{\mathrm{x}}_1 - \overline{\mathrm{x}}_2\right|}{\sqrt{\frac{\mathrm{s}_1^2}{\mathrm{n}_1} + \frac{\mathrm{s}_2^2}{\mathrm{n}_2}}}$$

Calculation of degrees of freedom

$$\nu = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{s_1^4}{n_1^2\,(n_1 - 1)} + \frac{s_2^4}{n_2^2\,(n_2 - 1)}}$$

TABLE A

Critical values of F at the 95 % confidence level

ν_2 (denom)	ν_1 (numerator)															
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**12**	**15**	**20**	**30**	**60**	**120**
1	648	800	864	900	922	937	948	957	963	969	977	985	993	1001	1010	1015
2	38.5	39.0	39.2	39.2	39.3	39.3	39.4	39.4	39.4	39.4.	39.4	39.4	39.4	39.5	39.5	39.5
3	17.4	16.0	15.4	15.1	14.9	14.7	14.6	14.5	14.5	14.4	14.3	14.3	14.2	14.1	14.0	13.9
4	12.2	10.6	10.0	9.60	9.36	9.20	9.07	8.98	8.90	8.84	8.75	8.66	8.56	8.46	8.36	8.31
5	10.0	8.43	7.76	7.39	7.15	6.98	6.85	6.76	6.68	6.62	6.52	6.43	6.33	6.23	6.12	6.07
6	8.81	7.26	6.60	6.23	5.99	5.82	5.70	5.60	5.52	5.46	5.37	5.27	5.17	5.07	4.96	4.90
7	8.07	6.54	5.89	5.52	5.29	5.12	4.99	4.90	4.82	4.76	4.67	4.57	4.47	4.36	4.25	4.20
8	7.57	6.06	5.42	5.05	4.82	4.65	4.53	4.43	4.36	4.30	4.20	4.10	4.00	3.89	3.78	3.73
9	7.21	5.71	5.08	4.72	4.48	4.32	4.20	4.10	4.03	3.96	3.87	3.77	3.67	3.56	3.45	3.39
10	6.94	5.46	4.83	4.47	4.24	4.07	3.95	3.83	3.78	3.72	3.62	3.52	3.42	3.31	3.20	3.14
12	6.55	5.10	4.47	4.12	3.89	3.73	3.61	3.51	3.44	3.37	3.28	3.18	3.07	2.96	2.85	2.79
15	6.20	4.77	4.15	3.80	3.58	3.41	3.29	3.20	3.12	3.06	2.96	2.86	2.76	2.64	2.52	2.46
20	5.87	4.46	3.86	3.51	3.29	3.13	3.01	2.91	2.84	2.77	2.68	2.57	2.46	2.35	2.22	2.16
30	5.57	4.18	3.59	3.25	3.03	2.87	2.75	2.65	2.57	2.51	2.41	2.31	2.20	2.07	1.94	1.87
60	5.29	3.93	3.34	3.01	2.79	2.63	2.51	2.41	2.33	2.27	2.17	2.06	1.94	1.82	1.67	1.58
120	5.15	3.80	3.23	2.89	2.67	2.52	2.39	2.30	2.22	2.16	2.05	1.94	1.82	1.69	1.53	1.48

TABLE B
Critical values of t at the 95 % confidence level

ν	**t**
1	12.7
2	4.30
3	3.18
4	2.78
5	2.57
6	2.45
7	2.36
8	2.31
9	2.26
10	2.23
11	2.20
12	2.18
13	2.16
14	2.14
15	2.13
16	2.12
17	2.11
18	2.10
19	2.09
20	2.09
21	2.08
22	2.07
23	2.07
24	2.06
25	2.06
26	2.06
27	2.05
28	2.05
29	2.05
30	2.04
∞	1.96