ROYAL SOCIETY OF CHEMISTRY

Mastership in Chemical Analysis

Part A Examination

Online

20 April 2022

1000 - 1300

Instructions

Answer **five** questions out of eight questions.

All questions carry equal marks.

The marks allocated to each section are given in the brackets.

The answers to each section must be returned in the examination envelope provided. All examination scripts must be mailed to the RSC at the end of the examination.

There are several data tables at the back of the exam script, which can be used at any point during the exam.

Non-programmable calculators are permitted.

Graph paper is allowed.

Question 1. Answer **ALL** parts

In developing a method for the determination of an antibiotic in whey protein powder the following results (mg/g) were obtained: 14.06, 13.76, 13.99, 13.94, 13.95, 13.96, 14.17, 14.20, and 13.86 when method A was used. The reported mean and standard deviation (n =5) when an independent method B was used for the same analysis are as follows (mg/g): 13.85 and 0.05, respectively.

(a) Calculate the mean, variance, and standard deviation of the results for method A.
(9 marks)

(b) Calculate the 95% confidence interval of the mean for method A.
(4 marks)

(c) Are the results obtained by both methods A and B significantly different?
(5 marks)

(d) Comment on the results of your calculations.
(2 marks)

[Note Statistical information is presented at the end of the examination paper.]

Question 2. Answer **ALL** parts

(a) The organochlorine pesticide, lindane, has been identified in the run-off from an agricultural site and analysed by gas chromatography-mass spectrometry (GC-MS). The sample was extracted by placing 10 ml of the water sample in a separating funnel with 3 x 2 ml of dichloromethane. The final extraction volume (30 ml) was then evaporated to dryness and reconstituted in 100 µl of the solvent prior to analysis.

A calibration plot was generated by diluting a 1000 ppm stock solution of lindane as follows: 0.1 ml of the stock solution was placed in a 10 ml volumetric flask and made up to the mark with dichloromethane (working solution). This solution was diluted to make the following standard solutions:

Flask	lindane working solution(ml)	final volume (ml)	GC-MS signal (counts s^{-1})
1	0	10	0
2	0.1	10	15000
3	0.2	10	29000
4	0.3	10	43500
5	0.5	10	73000
diluted sample	-	-	1900

What is the concentration of lindane, in units of mg l^{-1}, in the original run-off sample?

(10 marks)

(b) Using a diagram describe a procedure for solvent evaporation after liquid-liquid extraction (LLE). Why is solvent evaporation sometimes required after LLE?

(3+3 marks)

(c) If the linear regression equation had been Y = 1845x + 1.7 (with a correlation coefficient, R2 of 0.9994) what would the final concentration in part (a) now be in units of mg l^{-1}.

(4 marks)

Question 3. Answer **ALL** parts

(a) Draw and label an isocratic HPLC system. Include in your answer a brief description of the components and their function.

(8 marks)

(b) Define and explain the importance of the following terms:

(i) Dead time (t_o)
(ii) Retention time (t_R)
(iii) Capacity factor (k')
(iv) Separation factor (α)

(4 marks)

(c) Compounds A and B have retention times of 3.60 and 5.45 minutes, respectively on a 30 cm column. If the peak width of A is 1.09 and for B is 1.15 minutes, calculate:

(i) Column Resolution
(ii) Average number of theoretical plates in the column (column efficiency, N)
(iii) Plate height (HETP) in mm.

(3+3+2 marks)

Question 4. Answer **ALL** parts

(a) Identify and explain, using a diagram, the key components of an inductively coupled plasma torch. Indicate typical gas flow rates, input power levels, normal frequency of operation and viewing height. The plasma is a self-sustaining ionized gas. Comment on its formation and nature.

(6 marks)

(b) Explain, with illustrations, the processes by which a liquid sample is converted to a fine aerosol suitable for introduction into an inductively coupled plasma.

(4 marks)

(c) Inductively coupled plasma mass spectrometry (ICP-MS), based on a quadrupole analyser is resolution limited (unit mass resolution only). Identify, with examples, the types of interference that can lead to detection errors.

(6 marks)

(d) The inherent sensitivity of ICP-MS is made possible by the efficiency of the instrument interface. Explain, with suitable diagrams, the construction and operation of such an interface.

(4 marks)

Question 5. Answer **ALL** parts

(a) Explain why a hollow cathode lamp is important as a light source in analytical atomic absorption spectroscopy. Include in your answer the principal mode of operation of a hollow cathode lamp.

(5 marks)

(b) A flame atomic absorption instrument is to be used for the determination of caesium in an industrial sample containing elevated concentrations of sodium, phosphate, and a silicate mineral. The detection limit for the instrument is quoted as 0.8 μg ml^{-1}. Explain the procedures to be adopted in carrying out this analysis, and for ensuring that the results are carefully validated.

(10 marks)

(c) Compare and contrast, using diagrams, the mode of operation of an electron multiplier tube, as used in mass spectrometry, and a photomultiplier tube, as used in atomic spectroscopy.

(5 marks)

Question 6. Answer **ALL** parts

(a) Describe the process, using diagrams, giving rise to the emission of Kα and Kβ fluorescent X-rays from a sample exposed to an incident beam of X-rays. **(8 marks)**

(b) Discuss the analytical advantages of X-ray fluorescence (XRF) spectroscopy.

(8 marks)

(c) Outline the preparation of pressed pellet for XRF analysis of powder samples.

(4 marks)

Question 7. Answer **ALL** parts

(a) Explain concisely the differences in the electroanalytical techniques of *potentiometry, coulometry,* and *voltammetry* in terms of:

(i) the type of measurement,
(ii) the fate of the analyte, and
(iii) the type of indicator electrode or working electrode used.

(3+3+2 marks)

(b) Explain the terms in the following equation for linear scan voltammetry. What is the qualitative and quantitative information that can be obtained from the application of the equation?

$$E_{applied} = E_{1/2} \frac{-0.0592}{n} \log\left(\frac{I}{I_L - I}\right)$$

(7 marks)

(c) Describe the principle of *anodic stripping* and the major advantage of this in voltammetry.

(5 marks)

Question 8. Answer **ALL** parts

(a) In food microbiological analysis what is the purpose of Gram staining? What is the primary stain that is used? What is the mordant that is used?

(2+1+1 marks)

(b) What simple test is used to distinguish *Staphylococcus* and *Micrococcus spp***.** from *Streptococcus* and *Enterococcus spp.?* What is the key reagent used in this test?

(2+2 marks)

(c) What are the key components of culture media used to identify bacteria?

(4 marks)

(d) A newer approach to analyse bacteria is to use MALDI-MS. What does the acronym MALDI stand for? Propose an appropriate laser absorbing matrix for the analysis of bacteria? What type of laser is used for MALDI? What is the selected laser's operating wavelength?

(2+2+2+2 marks)

Useful Equations

Variance

$$S^2 = \frac{\sum(x_i - \bar{x})^2}{n-1}$$

Student t-test

$$\mu = \overline{x} \pm t_{(v=n-1)}\left(\frac{s}{\sqrt{n}}\right)$$

F-test

$$F = \frac{S_1^2}{S_2^2}$$

Critical values, two-sided, of Students' t- statistics at various confidence intervals

Number of degrees of freedom	Confidence interval (%)						
	90	95	98	99	99.5	99.8	99.9
1	6.314	12.71	31.82	63.66	127.3	318.3	636.6
2	2.920	4.303	6.965	9.925	14.09	22.33	31.60
3	2.353	3.182	4.541	5.841	7.453	10.21	12.92
4	2.132	2.776	3.747	4.604	5.598	7.173	8.610
5	2.015	2.571	3.365	4.032	4.773	5.893	6.869
6	1.943	2.447	3.143	3.707	4.317	5.208	5.959
7	1.895	2.365	2.998	3.499	4.029	4.785	5.408
8	1.860	2.306	2.896	3.355	3.833	4.501	5.041
9	1.833	2.262	2.821	3.250	3.690	4.297	4.781
10	1.812	2.228	2.764	3.169	3.581	4.144	4.587
11	1.796	2.201	2.718	3.106	3.497	4.025	4.437
12	1.782	2.179	2.681	3.055	3.428	3.930	4.318
∞	1.645	1.960	2.326	2.576	2.807	3.090	3.291

Critical values of F for a two-sided test at P = 0.05

Degrees of freedom of denominator	Degrees of freedom of numerator									
	1	2	3	4	5	6	7	8	9	10
1	647.8	799.5	864.2	899.6	921.8	937.1	948.2	956.7	963.3	968.6
2	38.51	39.00	39.17	39.25	39.30	39.33	39.36	39.37	39.39	39.40
3	17.44	16.04	15.44	15.10	14.88	14.73	14.62	14.54	14.47	14.42
4	12.22	10.65	9.979	9.605	9.364	9.197	9.074	8.980	8.905	8.844
5	10.01	8.434	7.764	7.388	7.146	6.978	6.853	6.757	6.681	6.619
6	8.813	7.260	6.599	6.227	5.988	5.820	5.695	5.600	5.523	5.461
7	8.073	6.542	5.890	5.523	5.285	5.119	4.995	4.899	4.823	4.761
8	7.571	6.059	5.416	5.053	4.817	4.652	4.529	4.433	4.357	4.295
9	7.209	5.715	5.078	4.718	4.484	4.320	4.197	4.102	4.026	3.964
10	6.937	5.456	4.826	4.468	4.236	4.072	3.950	3.855	3.779	3.717

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