Mastership in Chemical Analysis

Part A Examination

Online

17th April 2024

1000 – 1300

Plus 10 minutes reading time

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 equations and 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 required.

Question 1. Answer **ALL** parts

In evaluating a method for the determination of glyphosate in an agricultural winter bean crop the following results (µg/g) were obtained: 26.05, 21.89, 24.25, 27.65, 22.66, 26.21, 22.58, 23.81 and 21.89 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 (µg/g): 19.56 and 0.96, 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 results of sampling for benzo(a)pyrene determined the following data:

sample	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
P (x_i) µg mL^{-1}	91	95	104	82	95	103	97	89	85	89
x (mean)										
(x_i - x)										
$(x_i - x)^2$										

After completing the table determine the number of samples required such that the maximum error does not exceed ± 3 µg/mL, at the 95% confidence interval.

[Note: Sampling equations are presented at the end of the examination paper.]

(5 marks)

(b) Outline a method for the preparation for analysis of dried smoked fish from a port health authority. The method should include steps from when the sample arrives in the laboratory until it is available for injection into a gas chromatograph. Include all necessary details and considerations.

(10 marks)

(Question 2 continues on the next page)

(c) Based on the following data, obtained by gas chromatography (i) calculate the limit of quantitation (LOQ) of the method and (ii) how might the sensitivity of the analytical method be improved?

Data set	Calibration equation (y = mx + c)	Slope (m)	Intercept (c)
1	y = 11.854x - 28.082		
2	y = 11.942x - 33.706		
3	y = 11.640x - 26.002		
4	y = 11.902x - 34.188		
5	y = 11.765x - 36.253		
6	y = 11.987x - 44.464		

[Note: The LOD and LOQ can be determined using replicate preparation of the calibration curve. **For example**, the slope of the curve and the standard deviation of the intercept can be used to calculate the LOD based on the following equation: LOD = 3.3σ / s, where σ is the standard deviation of intercept and s is the slope.]

(2 + 3 marks)

Question 3. Answer **ALL** parts

(a) Summarise a method for the introduction of a sample for analysis by gas chromatography.

[Note: no details of the analysis are required.]

(1 mark)

(b) In the gas chromatographic analysis of a mixture of compounds the detector used can have a significant impact on the quality of the data obtained. In each case outline details of a suitable detector and why selected. Note you cannot select the same detector for each answer:

(i) Analysis of an organophosphorus pesticide?

(ii) Analysis of sulfur?

(iii) Analysis of organochlorine pesticides?

(iv) Analysis of polycyclic aromatic hydrocarbons?

(2 + 2 + 2 + 2 marks)

(c) Quinaldine and nicotine have retention times of 5.9 and 6.2 minutes, respectively on a 30 cm x 0.25 mm id x 0.25 µm film thickness DB5 column. If the peak width of quinaldine is 0.16 mins and for nicotine is 0.18 mins, calculate the following:

(i) Capacity factor for quinaldine and nicotine

(ii) Column Resolution

(iii) Average number of theoretical plates in the column (column efficiency, N) per compound

(iv) Plate height (HETP) in mm (for quinaldine and nicotine)

[Note: the retention time of the unretained component is 1.0 min.]

(4 + 1 + 4 + 2 marks)

Question 4. Answer **ALL** parts

(a) By technique, list the different methods of ionization used in gas chromatography - mass spectrometry and those used in high performance - liquid chromatography mass spectrometry.

(5 marks)

(b) A single quadrupole mass spectrometer can collect data in terms of full scan mode (total ion current mode) and selected ion monitoring mode. Explain, using appropriate illustrations, each mode of data collection and indicate a situation where each monitoring method would be preferable.

(5 marks)

(c) Explain the principles of normal phase and reversed phase high performance liquid chromatography. In your answer highlight the differences in polarity of the stationary and mobile phases.

(5 marks)

(d) UV-visible absorbance is commonly used for detection in HPLC. Explain, with the aid of labelled diagrams, how detection is achieved, and why it is so popular.

(5 marks)

Question 5. Answer **ALL** parts

(a) Describe how an inductively coupled plasma (ICP) is formed.

(6 marks)

(b) Using a clear diagram, discuss the merits and drawbacks of a pneumatic concentric nebulizer for ICP-Atomic Emission Spectroscopy.

(4 marks)

(c) Sequential multi-element analysis can be achieved using a monochromator. A requirement of the monochromator is for moderate to high resolution. Using the expression:

$$R = m.N$$

Describe how the resolution (R) can be improved, and using suitable values, show a numerical example.
m = spectral order
N = number of grooves on the grating

(3 marks)

(d) Describe the principle, using text and diagrams, of the operation of a photomultiplier tube.

(7 marks)

Question 6. Answer **ALL** parts

(a) Describe, with the aid of text and diagrams, the construction, operation and processes that occur within the special light source required for analytical atomic absorption spectroscopy.

(7 marks)

(b) Explain the purpose and role of such a light source in this technique.

(3 marks)

(c) Flame atomic absorption spectroscopy (FAAS) is prone to interferences.

(i) Briefly outline possible sources of interference in FAAS.

(ii) Describe in terms of the effect on the signal (absorbance) in FAAS of a 20 μg ml^{-1} Ca solution with progressively larger concentrations of phosphate solution added. Suggest a method to alleviate this problem.

(5 + 5 marks)

Question 7. Answer **ALL** parts

(a) With the aid of diagrams, where necessary, describe how primary X-rays are generated in a Coolidge X-ray tube.

(6 marks)

(b) List the major components on an energy dispersive X-ray Fluorescence (ED-XRF) instrument and briefly describe the function of these components.

(5 marks)

(c) Explain the problems which can arise in obtaining a representative sample from bulk solid.

(5 marks)

(d) Describe two methods for preparing such samples as described in part (c), for XRF analysis.

(4 marks)

Question 8. Answer **ALL** parts

(a) Solid phase extraction (SPE) is used to preconcentrate aqueous samples for chromatographic analysis. Outline the typical steps required to perform SPE.

(5 marks)

(b) An aqueous sample (50 ml) suspected of containing dieldrin is preconcentrated using SPE. The determinand is eluted in 5 ml of methanol, evaporated to dryness, and re-dissolved in 1 ml of solvent. The sample was then analysed using gas chromatography - mass spectrometry and a peak area of 520 obtained. A calibration plot was prepared which produced the following data:

Volume of a 1 µg/ml stock solution diluted to 10 ml (ml)	**Internal standard corrected peak area for dieldrin**
0	0
0.5	15000
1.0	29900
1.5	47500
2.0	70500

Calculate the concentration in ng/ml of dieldrin in the original sample.

(5 marks)

(c) Solid phase microextraction (SPME) is a commonly used technique to pre-concentrate analytes prior to introducing them into a gas chromatograph. Describe, with the aid of a diagram, the physical components of a SPME probe, and explain the principle of the technique.

(4 marks)

(d) Briefly describe the analytical protocol for the extraction and subsequent chromatographic analysis of **THREE** of the following. Note you cannot select the same extraction method for each answer:

(i) DDT and its metabolites from a contaminated milk.

(ii) Hexaconazole (a fungicide) from fruit and vegetables.

(iii) Phenols in a process water sample.

(iv) Dichloromethane in decaffeinated coffee.

(6 marks)

Useful Sampling Equations

$$E = \pm t\,(V)^{0.5}$$

$$V = S^2 / n$$

$$S = \Sigma\,(x_i - x)^2 / (n - 1)$$

$$n = t^2\,S^2 / E^2$$

Useful Statistical 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

$$\mathrm{F} = \frac{\mathrm{S}_1^2}{\mathrm{S}_2^2}$$

Useful Chromatography Equations

$$k' = \frac{t_R - t_M}{t_M}$$

$$R_S = \frac{2[t_{RB} - t_{RA}]}{WA + WB}$$

$$\mathrm{N} = 16 \left(\frac{t_R}{w_b} \right)^2 \text{ or } \mathrm{N} = 5.54 \left(\frac{t_R}{w_{1/2}} \right)^2$$

$$\mathrm{H} = \frac{\mathrm{L}}{\mathrm{N}}$$

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

Degrees of freedom is (n-1), where n = sample size.

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