Mastership in Chemical Analysis

Part A Examination

Burlington House

Wednesday 4th May 2016

13:00 – 16:00 hrs.
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.

1. (a) Define, and highlight the differences between, the following pairs of terms used in analytical chemistry:

i) qualitative analysis and quantitative analysis
ii) limit of detection and limit of quantitation
iii) random error and systematic error
iv) sensitivity and detection limit
v) direct calibration and standard addition techniques

(15 marks)

(b) A new method for the determination of the phosphate content of waste water samples using UV-Visible spectrophotometry has been worked up as a possible replacement for the existing ICP spectrometric method. The latter, which measures total phosphorus, converts values to assumed total phosphate. The phosphate results from eight measurements made using the two methods are shown below.

UV-Visible  3.55, 3.10, 2.95, 3.50, 3.65, 3.05, 3.45, 3.20 mg / L
ICP  4.20, 3.50, 4.80, 5.20, 4.35, 3.65, 4.10, 4.65 mg / L

Is there a significant difference between the two methods at the 95% confidence limit? What further comments can you make from the values obtained? All working steps must be shown.

(5 marks)
2. (a) Inductively coupled plasma optical emission spectrometry (ICP-OES) is an 'element-specific' technique that takes advantage of particular atomic-electronic processes.

Explain:

i) why this technique is considered “element-specific” and

ii) the electronic-excitation processes that are involved in the plasma, which allow an emission measurement to be made.

(6 marks)

(b) The following set of ICP emission data (Table 2.1) was acquired from the measurement for arsenic (As) at 189.0 nm in calibration and sample solutions. The analyst was unhappy with the instrument-calculated values and decided to manually calculate the arsenic (As) concentrations in the samples from the raw emission data. The approach to be taken would account for blank signals before any further data processing. Five readings for each solution were obtained as shown.
The sample solutions were acquired from a paint sample after acid digestion and dilution. The sample was analysed in triplicate. Each sub-sample weighed out was 0.2500g and the acid digest from each was made up to 100.0 mL in a volumetric flask. In order to bring the arsenic in this diluted extract within the calibration range, a further dilution was required. Aliquots of 5.00 mL were then added to a 100.0 mL volumetric flask and the content made up to the mark.

i) **Tabulate** the blank and sample-blank corrected ‘mean’ emission values from the spectrometer for the calibrants and the digest solutions respectively. From these corrected values calculate the equation for the linear relationship between the analyte concentration and its emission reading to three significant figures. **The corrected table must be submitted and all correction steps must be identified together with the calculated equation.**

(6 marks)
ii) Calculate the concentration in each diluted As-containing acid extract from the three sub-samples.  

(1 marks)

iii) Calculate the average concentration of the As in the original paint sample and an estimate of its associated uncertainty based on the data available.  

(5 marks)

iv) From the emission data provided in table 2.1, identify a reason why the analyst suspected the As concentration in the digest solutions given by the instrumental software was erroneous and how this could have easily been avoided.  

(2 marks)

All working steps must be shown and all parts submitted.
3. (a) Define the terms “quality assurance” and “quality control” and identify the difference between them, in the context of a regulatory analytical laboratory. 

(5 marks)

(b) Explain by use of examples what is meant by a ‘certified reference material’ (CRM).

How are CRMs prepared and how are they used in analytical laboratories? Comment on any advantages and limitations of CRMs.

(10 marks)

(c) Discuss the use of either:

i) Shewhart charts and their advantages in a working laboratory

OR

ii) In–house reference materials and their advantages in a working laboratory

(5 marks)

4. (a) A block diagram showing the main components of a typical instrument system for inductively coupled plasma mass spectrometry (ICP-MS) is shown in Figure 4.1. Describe the function and operation of each component.

(14 marks)

(b) Briefly discuss TWO other techniques that can be used for the measurement of trace/ultra-trace elements in aqueous prepared samples, highlighting the advantages and disadvantages of each.

(6 marks)
5. A sample of supermarket minced beef was submitted by trading standards officers to your laboratory because it was suspected of being:

1) Contaminated with horse meat

And

2) That the horse meat may contain the veterinary drug phenyl butazone

Describe with full details at least TWO different biochemical assays you would undertake, in order to identify and measure the two contaminants suspected in the meat sample. Your answer should include an explanation of the biochemical principle upon which the assays are based and the particular techniques employed in order to quantify the measurements.

(2 x 10 marks each)

6. Describe the physico-chemical principles behind, and the applications of, **FOUR** of the following analytical techniques:

(a) reversed phase high performance liquid chromatography with a UV detector
(b) X-ray fluorescence with a wavelength dispersive detector
(c) ligand-binding assay (including enzyme-linked immunoassay) with a selected visualisation detector
(d) gas chromatography with an electron capture detector
(e) UV-Visible spectrophotometry with a photodiode array detector
(f) gel electrophoresis with two examples of a visualisation detector

(5 marks for each part, total 20 marks)
7. (a) Sample preparation techniques for many solid samples have to be carefully chosen, in order to provide a representative sub-sample and maintain analyte integrity prior to its measurement. Describe with details of all the steps involved, how **TWO** of the following samples may be prepared for analysis, **up to** the point of measurement:

i) A fresh sample of a sprayed crop in order to measure the levels of a slightly volatile systemic molecular pesticide.

ii) A fresh fish sample in order to measure the levels of methyl-mercury present.

iii) An allotment soil sample in order to measure the levels of available-cadmium present.

iv) A fresh seaweed sample in order to measure the individual levels of different arsenic compounds present.

v) A fresh sediment sample in order to measure the levels of contaminant long term radionuclides present.

(10 marks)

(b) Describe and discuss **ONE** major technique used for the measurement of radionuclides in environmental or clinical samples. Your answer should include information on the underlying principles of the technique chosen and details of how it is used.

(10 marks)
8. The Environment Agency has asked for you, as an independent expert laboratory, to determine the levels of poly-aromatic hydrocarbons (PAHs) present in treated water being discharged from a waste water treatment plant.

Describe the practical analytical steps you would undertake to successfully complete this request, from representative sample collection through sample preservation, preparation including pre-concentration and analyte(s) measurement to finally presenting the values in a report. Your answer should include details of the principle techniques employed in each of these steps.

(20 marks)
Standard deviation

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

Pooled standard deviation

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

The F test:

\[ F_{calc} = \frac{s_1^2}{s_2^2}, \text{ where } s_1^2 > s_2^2 \]

One-sample t-test

In testing the null hypothesis that the population mean is equal to a specified value \( \mu_0 \), one uses the statistic

\[ t = \frac{\bar{x} - \mu_0}{s/\sqrt{n}} \]

The t-test assuming equal variance

\[ |t_{calc}| = \frac{|\bar{x}_1 - \bar{x}_2|}{S} \sqrt{\frac{1/n_1 + 1/n_2}{}} \]

The t-test assuming unequal variance

\[ |t_{calc}| = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{s_1^2/n_1 + s_2^2/n_2}} \]

Calculation of degrees of freedom

\[ \nu = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{s_1^4}{n_1^2(n_1-1)} + \frac{s_2^4}{n_2^2(n_2-1)}} \]
Critical values of t at the 95 % confidence level

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Table for $\alpha = 0.05$ (95%)