Analytical Chemistry: A Practical Approach

Extended Problems

Question 1 is structured in a similar way to Problem 5.1 in Chapter 5 but Parts (a) to (e) are a little more involved by bringing in correction of signal using an internal standard. Part (f) is covered in Chapter 9 but some further explanation is given here.

1. A large, relatively dry composite sample of soil from a disused south-west England fruit farm, on the banks of the Tamar River was taken for analysis. This was in order to evaluate the probable range of contaminants present, for when the land is to be used to grow crops for its new owner. This large soil sample was passed through a spinning riffler and sub-samples were fully dried at 80^{o} C overnight, then ground and sieved to less than 180 µm. A suitable quantity (1.0950 g) of this processed soil was selected as an exploratory test sample which was then digested under reflux for 2 hours in a round bottomed flask on an iso-mantle using 10 mL of aqua regia in order to extract one of the analytes of interest (As) contained within the soil. The resulting digest was passed through a pre-washed filter and the solution and washings collected in a 100.0 mL volumetric flask. The solution was made up to the mark and shaken. A 25.0 mL aliquot from this 100.0 mL volumetric solution was transferred to a 250.0 mL volumetric flask. This solution, together with a rhodium internal standard (IS; to correct for sample introduction matrix effects) was then made up to the mark with 2% HNO_3 solution in order for the arsenic to be measured using ICP atomic emission spectrometry (ICP-AES). A calibration was performed at 188.98 nm using a prepared series of standard arsenic solutions (containing the same rhodium IS as the sample) and the sample was then measured. The data shown in Table 1 were obtained:

Table 1.1 Data for the determination of arsenic in soil

As concentration / mg L^{-1}	**Emission signal from ICP-AES; counts/sec**					
	Arsenic replicate					**Internal standard (IS)**
0	1	2	1	2	1	1.0
0.5	102	101	102	101	101	1.0
1.0	202	201	202	201	201	1.0
1.5	301	302	301	301	302	1.0
2.0	402	402	401	401	401	1.0
Sample	244	242	244	242	242	0.95

(a) Create a table showing the following:
i) the standard As concentration
ii)the mean of the emission counts for each As standard and the sample
iii) the mean emission values for the calibrants corrected for both the IS and for the '0' As concentration solution emission reading, so that any future graphical line drawn, passes through the zero point on the 'x' and 'y' axes. **[See Chapter 5]**

(b) Construct a calibration graph on 'Excel graph paper'. Identify the axes and place units where appropriate. An equation for the line should be identified. **[See Chapter 5]**

(c) Use the '0' As concentration solution emission reading to correct the sample emission value **after** using the value of the internal standard to correct the emission value for the "matrix interference" effect, present in the sample solution. Include these values in the table. **[See Chapter 5 and this part's solution for extension of concept]**

(d) Use the graph (and / or the equation of the graph) to determine the zero-corrected and matrix-corrected concentration of As in the measured (diluted) solution. Identify this concentration. **[See Chapter 5]**

(e) Calculate the concentration of As (mg kg^{-1}) in the original soil. **[See Chapter 5]**

(f) Determine the approximate 'limit of detection' for As under these conditions, both in the solution measured and in the solid soil sample based upon the instrumental uncertainty. **[See chapter 9 and this part's solution for extension of concept]**

2. **Extended Problem / Activity: "Solve a scenario" [examples taken from the 40+ scenarios shown in the book] using the information tables from the chapters in the book and on-line sources.**

You can try this after you have covered chapters 1-4 and 6

Choose scenario 1 below to start the activity and complete steps A to E shown below. When you have completed this, choose one of the other scenarios, 2 to 10 and then undertake the same steps.

1. **A soil problem: A pesticide (see below examples of pesticides) residing in the soil at a farm (ADAS) and requiring analysis.**
2. A nutrition problem: Se in our diet (daily intake: FSA) – identify suitable food sources.
3. A food problem: mercury in tuna (FSA) – Fresh or canned.
4. A polycyclic aromatic hydrocarbon (PAH) problem: Levels of PAH in smoked and grilled meat and fish products for human consumption (FSA – PA and TS)
5. A health products problem: silicon in a toothpaste sample (Industrial)
6. Polychlorinated Biphenyls (PCBs; e.g. Decachlorobiphenyl). The presence of PCBs in contaminated ground from beneath a disused electrical sub-station (EA)
7. Arsenic in a paint sample. A 200 year old stately home with green coloured main hall walls believed to have been painted with copper arsenate (PA and NT).
8. Food additive E110 (Sunset Yellow) is suspected as being the colouring agent, present in high concentration in a child's confectionary but not disclosed (FSA and TS).
9. The measurement of levels of Antimony in fruit juices and the PET bottles that contain them, as sold to the public. (HSE, FSA and PA).
10. The determination of Pesticide and Growth-Modifier residues on Fruit and Vegetables e.g. Alar on apples; (FSA, PA, DEFRA) or from the list of pesticides below).

Having chosen your scenario, undertake the following:

A. Identify from an on-line search any regulatory or guidance levels associated with the analyte(s) of interest for your scenario, within the sample type or as total absolute amounts for human exposure / intake. This could be within the EU or from the EPA in the 'United States' etc.

B. Use these levels as a guide to identifying which instrumental technique(s) can be used to selectively measure this analyte(s) of interest after extraction from the sample matrix / type.

To achieve the requirements in “B”, you will need to make use of the tables from your book chapter on ‘Measurement’.

C. Using your book chapter on ‘sample preparation’, identify the preferred technique(s) for preparing the sample and isolating the analyte of interest from the sample matrix / type, while maintaining its integrity for measurement.

D. Select a suitable certified reference material (CRM) to be used for the analysis of your chosen analyte of interest in the particular sample matrix / type. Use the relevant chapter in the book and an on-line search to guide you.

E. Select an appropriate means of containing and preserving your freshly collected sample with the analyte of interest. See the relevant chapter in the book

Pesticides you could consider; look up on-line to acquire relevant information.

1. 2,4,5,6-Tetrachloro-*m*-xylene (SS)
2. α-BHC
3. γ-BHC
4. β-BHC
5. δ-BHC
6. Heptachlor
7. Aldrin
8. Heptachlor epoxide (isomer B)
9. *trans*-Chlordane*
10. *cis*-Chlordane*
11. Endosulfan I
12. 4,4'-DDE
13. Dieldrin
14. Endrin
15. 4,4'-DDD
16. Endosulfan II
17. 4,4'-DDT
18. Endrin aldehyde
19. Endosulfan sulfate
20. Methoxychlor
21. Endrin ketone
22. Hexachlorocyclopentadiene
23. Hexachlorobenzene
24. Simazine
25. Atrazine
26. Alachlor
27. *trans*-Nonachlor
28. *cis*-Nonachlor

3. You have just started a new job as quality control manager of a water treatment works. As one of your first jobs you have been asked to evaluate a new method for the determination of nitrate in drinking water by UV-Vis spectrophotometry. Use the data in Tables 3.1 – 3.4 to answer the following:

   (a) Evaluate the performance characteristics for the new method and hence demonstrate its validity. You will need to plot a graph to do this. **[See Chapter 9]**

   (b) Determine whether there is any statistically significant difference between the old method and the new method. **[See Chapter 9]**

   (c) Use box and whisker plots to compare the concentration of nitrate in drinking water from the two different treatment plants for a presentation you are to give to the Chief Executive. **[See Chapter 9 – box and whisker plots covered before in chapter 7 but used again in chapter 9]**

Table 3.1 Calibration data for the determination of nitrate by UV-Vis spectrometry using the new method

Concentration of nitrate / mg L^{-1}	Absorbance at 206 nm
0	0.00, 0.01, 0.03, 0.00, 0.04 0.02, 0.00, 0.01, 0.01, 0.02
0.1	0.06
0.2	0.15
0.4	0.32
1.0	0.65

Table 3.2 Replicate analysis of a quality control sample over 1 month using the new method

Certified nitrate concentration / mg L^{-1}	Mean measured nitrate concentration / mg L^{-1}	s	n
0.354	0.364	±0.012	30

Table 3.3 Comparison of two methods for nitrate in drinking water

	Concentration of nitrate / mg L^{-1}					Mean	s
Old method	0.420	0.350	0.480	0.520	0.435	0.441	0.0643
New method	0.355	0.310	0.295	0.350	0.365	0.335	0.0306

Table 3.4 Data for the concentration of nitrate in drinking water (in mg L^{-1}) determined over a period of 20 days at two different water treatment plants

Plant 1	0.31	0.25	0.13	0.41	0.34	0.23	0.92	0.94	0.91	0.31
	0.18	0.21	0.42	0.64	0.26	0.12	0.81	0.58	0.15	0.14
Plant 2	0.60	0.56	0.25	0.12	0.71	0.27	0.22	0.11	0.21	0.12
	0.11	0.31	0.11	0.37	0.23	0.32	0.25	0.15	0.41	0.84