Analytical Chemistry: A Practical Approach

Extended Problems: Solutions

1.

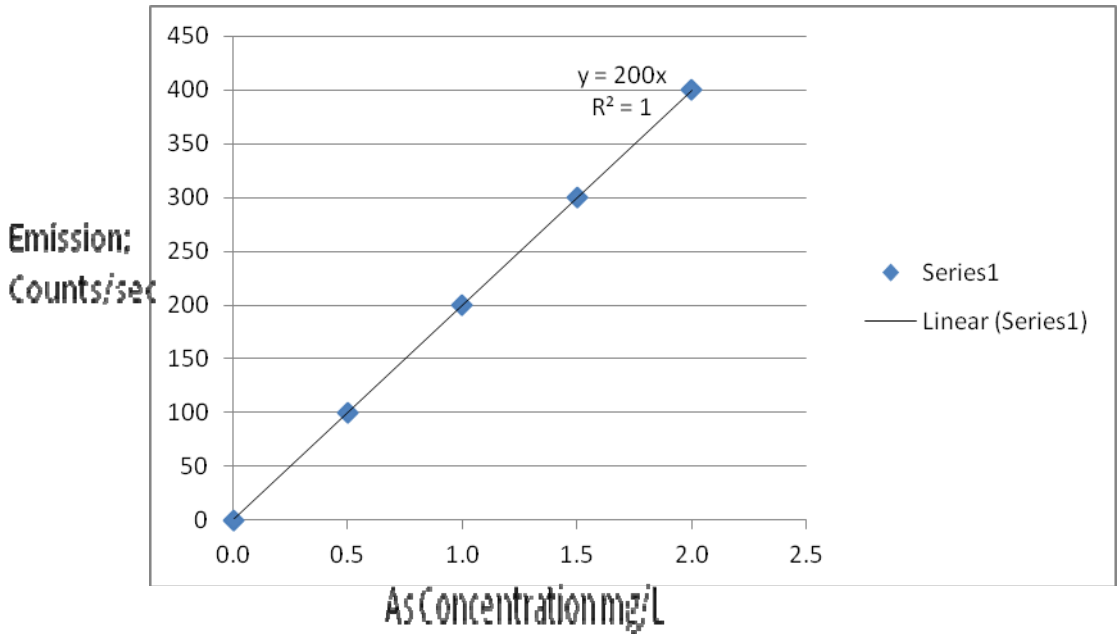
a) Create a table showing the following:

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 line drawn passes through the zero point on the 'x' and 'y' axes. **[See Chapter 5]**

a) Create a table as directed and shown below: Note that the Internal Standard (IS) which is being monitored from the calibrants, has a value of 1.0. Therefore, the 'Mean As counts' do not require an 'IS correction', just a correction for the '0' As counts, as shown in the final column. Remember that only the calibrants are being processed and corrected at this stage.

As Conc. mg/L	**As Emission Counts**					**Mean As Counts**	**'0' Corrected As counts**
0.0	2	1	2	1	1	1.4	**0**
0.5	102	101	102	101	101	101.4	**100**
1.0	202	201	202	201	201	201.4	**200**
1.5	301	302	301	301	302	301.4	**300**
2.0	402	402	401	401	401	401.4	**400**
Sample	244	242	244	242	242	242.8	

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]**

Correct for internal standard (IS) first, then correct for the '0' As concentration solution mean value, within the standards run:

For IS from sample = 0.95, then correcting:

242.8 / 0.95 = 255.6 Counts

Then:

255.6 - 1.4 = 254.2 'mean' As counts: corrected for '0' (zero) As concentration solution

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]**

From equation and from graph: 254.2 counts = **1.27(1) mg As / L of solution**

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

Now, there are 1.27(1) mg of As in every litre of final sample digest solution

Therefore, if there are 1.27(1)mg As / L, then there are 0.317(8) mg in this final 250 mL volumetric solution;
Now, what is in that 250 mL volumetric solution actually came from a 25.0 mL aliquot
So,
≡ 0.317(8) mg / 25.0 mL (taken from the 250 mL volumetric digest solution)

Therefore, there are 4 x 0.317(8) mg in the whole 100.0 mL of digest solution:

1.27(1) mg As are therefore in the original 100.0 mL volumetric digest solution.

Now,
1.0950 g of the prepared soil was digested and made up to the above 100 mL,

So, the 1.27(1) mg of As came from this digested 1.0950 g of digested soil.
Hence, in concentration terms we have:
1.27(1) mg As per 1.0950 g soil

Correcting to mg / kg we have,
1.2741x 1000 / 1.0950 mg / kg; which = 1161 mg kg^{-1}

Therefore there are 1160 mg As per kg of soil (3 sig. fig.)

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]**

As you can see in chapter 9, we can calculate the LOD based upon the 'Y' axis counts (y_{LOD}) and upon the concentration axis units. Here, we have sufficient '0' As concentration solution data to use the former:

We calculate the mean 'y_o' value of the '0' As conc. solution **+** 3 x s_o [where s_o = standard deviation of the '0' As conc. solution 'y' value], all in counts to start with and then use the slope of the graph (from regression analysis) to convert this emission value into a concentration in solution. The sample standard deviation (SD) in counts/sec, is calculated as shown in chapter 7

Mean 'y_o' value of the '0' As conc. solution + 3 x s_o = 1.4 + [3 x 0.5477] counts/sec

This total instrumental uncertainty equals 3.04(3) emission counts/sec.

Now the equation of the graph is **y** = 200 **x**; so let '**y**' = 3.04(3) and find '**x**', the LOD conc.

x = 3.04(3) / 200 = 0.0152(2) mg / L which is the LOD in the '0' As concentration solution measured.

The LOD from the zero As solution measured is 0.02 mg / L (1sf) [see chapter 9 on this point]

To convert this to the LOD equivalent in the solid soil sample, you retrace the steps taken from weighing the solid sample to the point where the digested sample's final volumetric solution was measured; i.e.

1.0950 g was digested and the solution extract from this digestion was made up to 100 mL; then a 25.0 mL aliquot was taken from this and made up to 250 mL.

As the 0.0152(2) mg / L 'LOD' was measured in this final 250 mL, then this is equivalent to changing the concentration in the solid to the final solution by a factor of: 1000 / 1.0950.

Use this factor to multiply the solution LOD just calculated;

this gives → 0.0152(2) mg / L x 1000 / 1.0950 mg / kg = 13.9(0) mg As / kg of sample

The LOD in the solid is estimated as 14 mg As / kg of sample (2sf; if keeping to 1sf then convert up to 20 mg As per kg sample - you should not 'round down' for a LOD measurement)

(to note that this LOD is based upon the instrumental uncertainty measurement of a prepared '0' As concentration solution and then scaled up, based upon just the single, exploratory sample).

2. No answers are provided for this problem.

3.

(a) You should provide calculated values for each of the following performance characteristics using the data provided in the tables:

Performance characteristic	**Procedure that could be used**	**Quantitative data**
Limit of detection	Determine standard deviation of replicates of zero standard and use calibration data to determine: $x_{LOD} = \frac{3s_0}{b}$	Yes in Table 3.1
Limit of quantitation	Determine standard deviation of replicates of zero standard and use calibration data to determine: $x_{LOQ} = \frac{10s_0}{b}$	Yes in Table 3.1
Bias estimate	Analyse CRM or spiked sample and perform a two-tailed t-test	Yes in Table 3.2
Linear range	The method can be used between the LOD or the LOQ and the upper linear range of the calibration	Yes in Table 3.1
Selectivity	Analyse CRM or spiked sample and perform a two-tailed t-test to help	Possibly using Table 3.2

	confirm this.	
Precision		
Repeatability	Repeat analysis of a CRM or homogeneous sample and calculate RSD	Yes in Table 3.2
Reproducibility	Several laboratories perform repeat analyses of a CRM or homogeneous sample	No
Ruggedness	Identify components of the method that require special control, e.g. development of colour in UV-Vis spectrometry	No

(b)

Perform an F-test

$$F = \frac{s_1^2}{s_2^2} = \frac{0.0643^2}{0.0306^2} = \frac{0.00413}{0.000936} = 4.415$$

F_{calc} = 4.415

F_{crit} = 9.60 (use 95% for a two-tailed table and n-1=4 and n-1=4 degrees of freedom)

$F_{calc} < F_{crit}$ so the standard deviations are not significantly different and can be combined

Calculate the combined standard deviation

$$s_c = \sqrt{\frac{s_1^2(n-1)+s_2^2(n_2-1)}{(n_1+n_2-2)}} = \sqrt{\frac{0.00413(4)+0.000936(4)}{5+5-2}} = 0.0503$$

Perform a t-test

$$t = \frac{\bar{x}_1 - \bar{x}_2}{s_c\sqrt{\frac{1}{n_1}+\frac{1}{n_2}}} = \frac{0.441-0.335}{0.0503\times\sqrt{0.4}} = 3.332$$

t_{calc} = 3.332

t_{crit} = 2.306 (two sided for 95% confidence and n_1+n_2-2 degrees of freedom)

$t_{calc} > t_{crit}$ so you can reject the null hypothesis and conclude that there is a significant difference between the two methods at the 95% confidence level.

(c)

Plant 1

Position of median = (n + 1)/2 th value = (20 + 1)/2 = 10.5th value = 0.31

Lower quartile, Q1 = 0.25(20+1)th result = value of the 5.25th result = 0.1875

Upper quartile, Q3 = 0.75(20+1)th result = value of the 15.75th result = 0.625

IQR = 0.625 – 0.1875 = 0.4375

LW = Q_1 - 1.5(IQR) = 0.1875-0.65625 = -0.469 so = 0.12

UW = Q_3 + 1.5(IQR) = 0.625+0.65625 = 1.281 so = 0.94

Plant 2

Position of median = (n + 1)/2 th value = (20 + 1)/2 = 10.5th value = 0.25

Lower quartile, Q1 = 0.25(20+1)th result = value of the 5.25^{th} result = 0.1275

Upper quartile, Q3 = 0.75(20+1)th result = value of the 15.75^{th} result = 0.400

IQR = 0.4 – 0.1275 = 0.2725

LW = Q_1 - 1.5(IQR) = 0.1275-0.40875 = -0.28125 so = 0.11

UW = Q_3 + 1.5(IQR) = 0.4+0.40875 = 0.80875 so = 0.71

0.84 is an outlier