Problem Set 3 –Figures of Merit, Calibration and Least Squares Analysis

Complete all problems on separate paper. Show all work for credit. Correct use of significant figures is required for full credit. You can use a spreadsheet or other software package for this problem set but make sure that you also understand how to find all of the values and their associated uncertainties by hand.

1. Here are the mass spectrometric signals for known concentrations of methane in H_2:

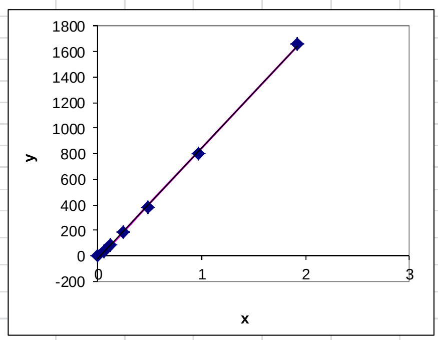
CH_4 (vol %)	0	0.062	0.122	0.245	0.486	0.971	1.921
Signal (mV)	9.1	47.5	95.6	193.8	387.5	812.5	1671.9

a) Subtract the blank value (9.1 mV) from all other values. Then use the method of least squares to find the slope and intercept and their uncertainties. Construct a calibration curve.

From the attached Excel Sheet:

m=	**870**	**+/-**	**30 mV/%**
b=	**-22**	**+/-**	**20 mV**

	x	y	xy	x^2	n	y_{calc}	d	d^2	$(y-y_{bar})^2$	$y_{Unknown}$
	0	0	0	0	7	-22.085	22.085208	487.76	203040	
	0.062	38.4	2.3808	0.0038		31.801	6.5988458	43.545	169909	
	0.122	86.5	10.553	0.0149		83.949	2.5507536	6.5063	132569	
	0.245	184.7	45.252	0.06		190.85	-6.152836	37.857	70703	
	0.486	378.4	183.9	0.2362		400.31	-21.91434	480.24	5212.8	
	0.971	803.4	780.1	0.9428		821.84	-18.44475	340.21	124468	
	1.921	1662.8	3194.2	3.6902		1647.5	15.27712	233.39	1E+06	
			0	0		0	0	0		
			0	0		0	0	0		
			0	0		0	0	0		
Sums	**3.807**	**3154.2**	**4216.4**	**4.948**		**3154.2**	**6.608E-13**	**1629.5**	**2E+06**	



D =	**20.143**			D = (E12*F2)-(B12*B12)
m=	**869.135**			m = ((D12*F2)-(C12*B12))/C14
b=	**-22.085**			b =((E12*C12)-(D12*B12))/C14
S_y=	**18.0527**			S_y = SQRT(I12/(F2-2))
S_m=	**10.6422**	**% S_m=**	**1.2245**	S_m = SQRT((C17^2*F2)/C14)
S_b=	**8.9474**	**% S_b=**	**-40.51**	S_b = SQRT((C17^2*E12)/C14)
S_x=	**0.02309**	**% S_x=**	**90.886**	S_x=(C17/ABS(C15))*SQRT((1/1)+(C21^2*F2/C14)+(E12/C14)-((2*C21*B12)/C14))
x_{unk}=	**0.02541**			x_{unk}=(J2-C16)/C15
x-int.=	**0.02541**			x-int.=-C16/C15
$S_{x\text{-}int.}$=	**0.0101**	**%$S_{x\text{-}int.}$=**	**39.732**	$S_{x\text{-}int.}$=(C17/C15)*SQRT((1/F2)+AVERAGE(C2:C11)^2/(C15^2*DEVSQ(B2:B11)))
R^2 =	**0.99925**			R^2 = 1-(I12/J12)
				t = TINV(0.05,F2-2)

	value	unc. (s)	% rel unc.
m	**869.1349**	**10.642**	**1.2245**
b	**-22.0852**	**8.947**	**-40.51**
x	**0.0254**	**0.02309**	**90.886**

95% Confidence Intervals			**t=**	**2.5706**
m=	**869.13**	**+/-**	**27.357**	
b=	**-22.09**	**+/-**	**23**	
x_{unk}=	**0.0254**	**+/-**	**0.0594**	
x-int.=	**0.0254**	**+/-**	**0.026**	

b) Replicate measurements of an unknown gave 144.1, 144.9, 143.9, and 145.1 mV. Determine the concentration of the unknown and its uncertainty. Determine the 95% confidence interval for the unknown.

To use our calibration curve, we must subtract the blank signal off first.

Raw Signal	Corrected Signal	Vol %	
144.1	135.0	0.180737	
144.9	135.8	0.181657	
143.9	134.8	0.180507	
145.1	136.0	0.181888	
	Mean	0.181197	%
	Stdev	0.000677	%
	t	3.182446	
	CI	0.001077	%

So the confidence interval is 0.181 ±0.001 %

c) A blank gave 8.4, 9.3, 10.8, 8.8, 9.6, 7.4 and 7.3 mV when measured multiple times. Determine the limit of detection at the 99% confidence level for the procedure.

From these values, the standard deviation of the blank signal is 8.77 mV with a standard deviation of 1.13 mV. Therefore our signal at the detection limit is:

$$8.77\text{mV} + 3(1.13) = 12.17 \text{ mV}$$

Again, to use the calibration relationship, we need to subtract the blank signal (9.1 mV) from this value: 12.17-9.1 = 3.07 mV.

Now we convert this to a concentration using the calibration relationship to find the LOD

LOD = (3.07-(-20))mV/(870 mV/%) = 0.027%

2. Pure water containing no mercury was spiked with 0.40 µg mercury /L. Seven replicate determinations gave 0.39, 0.40, 0.38, 0.41, 0.36, 0.35, and 0.39 µg/L mercury. Find the mean percent recovery of the spike and the detection limit for the method.

	µg mercury/L	%recovery
	0.39	97.5
	0.40	100
	0.38	95
	0.41	102.5
	0.36	90
	0.35	87.5
	0.39	97.5
Mean	0.382857	95.71429
Stdev	0.021381	5.345225
LOD	0.064143	

The percent recovery is 100%x($C_{\text{spiked sample}}$ – $C_{\text{unspiked sample}}$)/$C_{\text{added}}$. In our case $C_{\text{unspiked sample}}$ = 0 µg mercury/L and C_{added} = 0.40 µg mercury/L

To find the LOD, we need the standard deviation of the measurements. Since they are already in concentration units and since we assume that a 0 µg mercury/L sample would give 0 concentration, our LOD is simply 3 times the standard deviaton of the sample concentrations. LOD = 3(0.021381 µg mercury/L) = **0.06 µg mercury /L**

3. An unknown sample of Cu^{2+} gave an absorbance of 0.262 in an atomic absorption analysis. Then 1.00 mL of a solution containing 100.0 ppm (i.e. µg/mL) Cu^{2+} was mixed with 95.0 mL of the unknown and the mixture was diluted to 100.0 mL in a volumetric flask with DI water. The absorbance of the new solution was 0.500.
   a. Denoting the initial, unknown concentration as $[Cu^{2+}]_i$, write an expression for the final concentration, $[Cu^{2+}]_f$, after dilution. Units of concentration are ppm.

      $[Cu^{2+}]_f$ = (95 mL/100 mL)$[Cu^{2+}]_i$
   b. In a similar manner, write the final concentration of added standard Cu^{2+}, designated as $[S]_f$

      $[S]_f$ = (1 mL/100 mL)$[S]_i$ = (1/100)x100.0 ppm = 1.000 ppm

   c. Find $[Cu^{2+}]_i$ in the unknown.

$$\frac{I_S}{I_{S+Cu}} = \frac{0.262}{0.500} = \frac{[Cu]_i}{1.000 + 0.95[Cu]_i}$$

After some algebra, $[Cu^{2+}]_i$ = 1.04 ppm

4. A constant volume standard addition experiment is performed. Five flasks containing 25.00 mL of a serum with unknown concentration of Na^+ are labeled 1-5. Into each, varying volumes (see below) of 1.940 M NaCl standard is added. Each flask is then diluted to 50.00 mL.

Flask	1	2	3	4	5
Volume of standard added (mL)	0	1.000	2.000	3.000	4.000
Na^+ atomic emission signal (mV)	3.13	5.40	7.89	10.30	12.48

a. Use Excel or Minitab to prepare a standard addition graph and find the concentration of Na+ in the serum.

volume added (mL)	concentration added (M)	signal
0	0	3.13
1	0.0388	5.4
2	0.0776	7.89
3	0.1164	10.3
4	0.1552	12.48

From a least-squares analysis, we find the equation of our line to be:

Signal in mV = 60.825mV/M(concentration) + 3.12mV

Solving for the x-intercept (y=0)

0 mV = 60.825mV /M(concentration) + 3.12mV
Concentration = -(-3.12mV/(60.825mV /M)) = 0.05129 M

Since this was in the solution that was measured, we must account for dilution to determine the original concentration: 0.05129M(50.00mL/25.00mL) = **0.1025 M**

b. Determine the uncertainty in the result.

Here we need the $s_{x\text{-intercept}}$, which from our least squared analysis is 0.00173 or 3.367% relative standard deviation. So our uncertainty in the final concentration is 0.003367(0.1025 M) = 0.000345M

So our final result would be **0.1025±0.0003 M**, where we have estimated our uncertainty using the standard deviation. We could convert that to a confidence interval by multiplying by the appropriate t-value (t=3.1824 for 3 degrees of freedom)