Table 4-1 Ordinate and area for the normal (Gaussian) error curve, $y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$

$\lvert z\rvert$[a]	y	Area[b]	$\lvert z\rvert$	y	Area	$\lvert z\rvert$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5			

Table 4-6 Values of Q for rejection of data

Q (90% confidence)[a]	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

Table 4-2 Values of Student's t

	Confidence level (%)						
Degrees of freedom	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

Table 4-5 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

Chem 454 – Exam 1 – February 8, 2006

Name:

Show all work for full credit. 100 total points

Note – I normally distribute graded exams the lecture after the exam. Due to circumstances concerning university committee obligations I will not be able complete exam grading until Tuesday, February 14th. I will post the answers of this exam at the course web site this afternoon.

1] What is the 95% confidence interval for 6 measurements whose average is 4.22 and with a standard deviation of 0.07? (5 points)

2] An analysis of chromium in a steel sample was repeated 5 times. The results are listed below. Using the Q-test which of the five results may be removed in the determination of the mean? (5 points)

Run #	Cr mass %
1	5.22
2	8.55
3	6.02
4	5.98
5	5.43

3] Part a) Based on the $E^{0'}$ potentials in the following table (E^0 at pH 7), which is the strongest reducing agent? Which is the strongest oxidizing agent?

Strongest reducing agent _____ _____ (3 points)

Strongest oxidizing agent _____ _____ (3 points)

3] Part b) What would be the spontaneous balanced redox reaction between the strongest reducing agent and the strongest reducing agent? (5 points) What would be E_{cell} for this reaction? (5 points)

Table 14-2 Reduction potentials of biological interest

Reaction	E° (V)	$E^{\circ\prime}$ (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.816
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	+0.771
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.535	+0.535
Cytochrome a (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome a (Fe^{2+})	+0.290	+0.290
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695	+0.281
Cytochrome c (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome c (Fe^{2+})	—	+0.254
2,6-Dichlorophenolindophenol + $2H^+ + 2e^- \rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2H^+ + 2e^- \rightleftharpoons$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2H^+ + 2e^- \rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2H^+ + 2e^- \rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2H^+ + 2e^- \rightleftharpoons$ glycolate	—	−0.090
Oxaloacetate + $2H^+ + 2e^- \rightleftharpoons$ malate	+0.330	−0.102
Pyruvate + $2H^+ + 2e^- \rightleftharpoons$ lactate	+0.224	−0.190
Riboflavin + $2H^+ + 2e^- \rightleftharpoons$ reduced riboflavin	—	−0.208
FAD + $2H^+ + 2e^- \rightleftharpoons FADH_2$	—	−0.219
$(Glutathione\text{-}S)_2 + 2H^+ + 2e^- \rightleftharpoons$ 2 glutathione-SH	—	−0.23
Safranine T + $2e^- \rightleftharpoons$ leucosafranine T	−0.235	−0.289
$(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons 2C_6H_5SH$	—	−0.30
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	−0.105	−0.320
$NADP^+ + H^+ + 2e^- \rightleftharpoons NADPH$	—	−0.324
Cystine + $2H^+ + 2e^- \rightleftharpoons$ 2 cysteine	—	−0.340
Acetoacetate + $2H^+ + 2e^- \rightleftharpoons$ L-β-hydroxybutyrate	—	−0.346
Xanthine + $2H^+ + 2e^- \rightleftharpoons$ hypoxanthine + H_2O	—	−0.371
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	−0.414
Gluconate + $2H^+ + 2e^- \rightleftharpoons$ glucose + H_2O	—	−0.44
$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$	—	−0.454
$2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$	—	−0.527

4] What is the relative population in pph (%) that lies below the value of 88.7 for a Gaussian distribution whose mean is 64.4 and with a standard deviation of 17.3? (5 points)

5] An anodic stripping voltammetric (ASV) analysis was conducted on a soil sample for leachable Cd^{2+} (AW 112.411 g/mol). A 100-gm sample of soil was extracted with 100-mL of 10% CH_3COOH(aq). ASV analysis of that 100-mL extract yielded a Cd(0) oxidation current of 4.31 μA. A 10-μL spike of 1.51e-3 M solution of Cd^{2+} was added to the sample solution and the ASV current was measured as 6.77 μA. What is the concentration of Cd^{2+} in ppb the original sample? (20 points)

6] A Ag/AgCl electrode is in contact with a solution that is 0.150 M in KCl(aq). What is the potential of that electrode if measured against the SHE? (10 points)

$$AgCl(s) + e^- \leftrightharpoons Ag(s) + Cl^- \qquad E^0 = 0.2223\ V$$

7] Sketch the ideal versus real response of the pH electrode. Plot E vs. pH. What is the numerical value of the slope of this line? What is the typical linear range for the pH response? (10 points)

8] Sketch and label a diagram that illustrates the concepts of (10 points)

a) linear range
b) sensitivity
c) detection limit
d) background

9] A Cl^- ISE responds to a 1.57e-4 M NaCl solution with a potential of 842.7 mV. An solution of unknown [Cl^-] yields a potential of 689.5 mV. What is the concentration of Cl^- in that unknown solution? (15 points)

10] Why is it necessary to use the method of standard addition rather than the calibration curve? What advantages would the calibration curve have over the method of standard addition? (10 points)

Chem 454 – Exam 1 – February 8, 2006 – Answers

Name: Key

1] What is the 95% confidence interval for 6 measurements whose average is 4.22 and with a standard deviation of 0.07? (5 points)

μ = x-bar $\pm$ ts/$n^{1/2}$ = 4.22 $\pm$ 2.776 (0.07)/$(6)^{1/2}$ = 0.08 μ = 4.22 $\pm$ 0.08

2] An analysis of chromium in a steel sample was repeated 5 times. The results are listed below. Using the Q-test which of the five results may be removed in the determination of the mean? (5 points)

Run #	Cr mass %
6	5.22
7	8.55
8	6.02
9	5.98
10	5.43

Q = 8.55 – 6.02 / 8.55 – 5.22 = 0.80 Q_{table} = 0.64

Q > Q_{table} therefore we can discard 8.55

3] Based on the $E^{0'}$ potentials in the following table (E^0 at pH 7), which is the strongest reducing agent? Which is the strongest oxidizing agent?

Strongest reducing agent _____$S_2O_4^{2-}$_____ (3 points)

Strongest oxidizing agent _____O_2_____ (3 points)

What would be the spontaneous balanced redox reaction between the strongest reducing agent and the strongest reducing agent? (5 points) What would be E_{cell} for this reaction? (5 points)

$O_2 + 4H^+ + 4e^- = 2H_2O$ $\quad E_{red}^0 = 1.229$ V

$2S_2O_4^{2-} + 4H_2O = 4SO_3^{2-} + 8H^+ + 4e^-$ $\quad E_{red}^0 = -0.527$

$O_2 + 2S_2O_4^{2-} + 2H_2O = 4SO_3^{2-} + 4H^+$ $\quad E_{cell} = 1.229 - (-0.527) = 1.756$ V

Table 14-2 Reduction potentials of biological interest

Reaction	E° (V)	$E^{\circ\prime}$ (V)
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.229	+0.816
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.771	+0.771
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.535	+0.535
Cytochrome a (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome a (Fe^{2+})	+0.290	+0.290
$O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.695	+0.281
Cytochrome c (Fe^{3+}) + $e^- \rightleftharpoons$ cytochrome c (Fe^{2+})	—	+0.254
2,6-Dichlorophenolindophenol + $2H^+ + 2e^- \rightleftharpoons$ reduced 2,6-dichlorophenolindophenol	—	+0.22
Dehydroascorbate + $2H^+ + 2e^- \rightleftharpoons$ ascorbate + H_2O	+0.390	+0.058
Fumarate + $2H^+ + 2e^- \rightleftharpoons$ succinate	+0.433	+0.031
Methylene blue + $2H^+ + 2e^- \rightleftharpoons$ reduced product	+0.532	+0.011
Glyoxylate + $2H^+ + 2e^- \rightleftharpoons$ glycolate	—	−0.090
Oxaloacetate + $2H^+ + 2e^- \rightleftharpoons$ malate	+0.330	−0.102
Pyruvate + $2H^+ + 2e^- \rightleftharpoons$ lactate	+0.224	−0.190
Riboflavin + $2H^+ + 2e^- \rightleftharpoons$ reduced riboflavin	—	−0.208
FAD + $2H^+ + 2e^- \rightleftharpoons FADH_2$	—	−0.219
$(Glutathione\text{-}S)_2 + 2H^+ + 2e^- \rightleftharpoons$ 2 glutathione-SH	—	−0.23
Safranine T + $2e^- \rightleftharpoons$ leucosafranine T	−0.235	−0.289
$(C_6H_5S)_2 + 2H^+ + 2e^- \rightleftharpoons 2C_6H_5SH$	—	−0.30
$NAD^+ + H^+ + 2e^- \rightleftharpoons NADH$	−0.105	−0.320
$NADP^+ + H^+ + 2e^- \rightleftharpoons NADPH$	—	−0.324
Cystine + $2H^+ + 2e^- \rightleftharpoons$ 2 cysteine	—	−0.340
Acetoacetate + $2H^+ + 2e^- \rightleftharpoons$ L-β-hydroxybutyrate	—	−0.346
Xanthine + $2H^+ + 2e^- \rightleftharpoons$ hypoxanthine + H_2O	—	−0.371
$2H^+ + 2e^- \rightleftharpoons H_2$	0.000	−0.414
Gluconate + $2H^+ + 2e^- \rightleftharpoons$ glucose + H_2O	—	−0.44
$SO_4^{2-} + 2e^- + 2H^+ \rightleftharpoons SO_3^{2-} + H_2O$	—	−0.454
$2SO_3^{2-} + 2e^- + 4H^+ \rightleftharpoons S_2O_4^{2-} + 2H_2O$	—	−0.527

4] What is the relative population in pph (%) that lies below the value of 88.7 for a Gaussian distribution whose mean is 64.4 and with a standard deviation of 17.3? (5 points)

$Z = (64.4 - 88.7)/17.3 = 1.40$ use table 4-1 area = 0.4192

Above = 0.5000 – 0.4192 = 0.0808 or 8.08%

Therefore the population below is 91.92%

5] An anodic stripping voltammetric (ASV) analysis was conducted on a soil sample for leachable Cd^{2+} (AW 112.411 g/mol). A 100-gm sample of soil was extracted with 100-mL of 10% CH_3COOH(aq). ASV analysis of that 100-mL extract yielded a Cd(0) oxidation current of 4.31 μA. A 10-μL spike of 1.51e-3 M solution of Cd^{2+} was added to the sample solution and the

ASV current was measured as 6.77 μA. What is the concentration of Cd^{2+} in ppb the original sample? (20 points)

Plot current vs. $[Cd^{2+}]_{spike}$. Conc of spike = (10e-6 L * 1.51e-3M)/0.100-L = 1.51e-7 M

Slope = (6.77 – 4.31 μA) / (1.51e-7 M - 0) = 1.63e7 uA / M

y-int = 4.31 uA

line: y = (1.63e7 uA / M) x + 4.31 uA
x-int: 0 = (1.63e7 uA / M) x + 4.31 uA
x = - 2.65e-7 M (15 points)

conc in 100-gm sample

2.65e-7 M * 0.100-L * 112.411 g/mol * 10e9/100-gm = 29.8 ppb (5 points)

6] A Ag/AgCl electrode is in contact with a solution that is 0.150 M in KCl(aq). What is the potential of that electrode if measured against the SHE? (10 points)

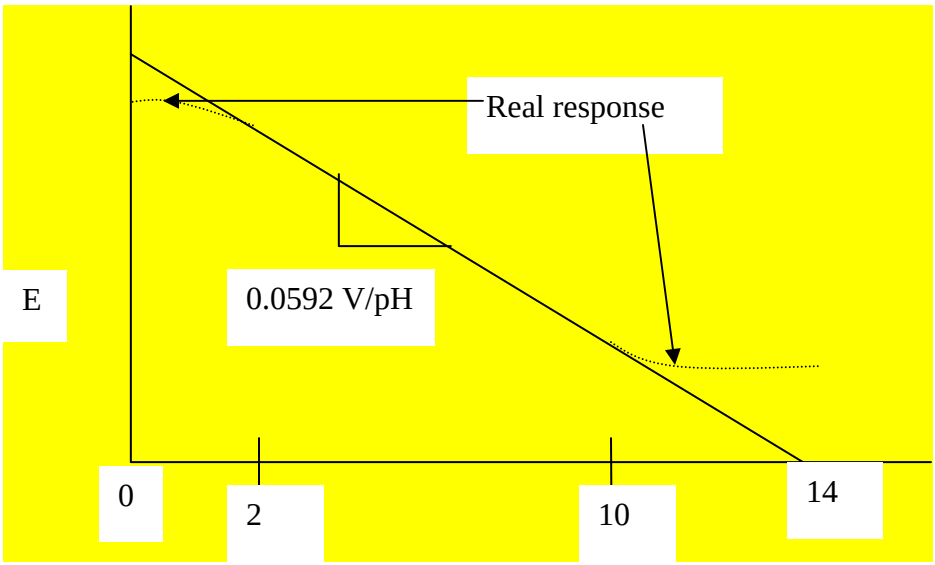
$AgCl(s) + e^- \leftrightharpoons Ag(s) + Cl^-$ $E^0 = 0.2223$ V

E = 0.2223 – 0.0592 log 0.150 = 0.271 V

7] Sketch the ideal versus real response of the pH electrode. Plot E vs. pH. What is the numerical value of the slope of this line? What is the typical linear range for the pH response? (10 points)

E = y-int + 0.0592 log $[H^+]$

E = y-int – 0.0592 pH



8] Sketch and label a diagram th strates the concepts of (10 points)

e) linear range
f) sensitivity
g) detection limit
h) background

9] A Cl^- ISE responds to a 1.57e-4 M NaCl solution with a potential of 842.7 mV. An solution of unknown [Cl^-] yields a potential of 689.5 mV. What is the concentration of Cl^- in that unknown solution? (15 points)

$E = y\text{-int} - 0.0592 \log [Cl^-]$

$0.8427\ V = y\text{-int} - 0.0592 \log 1.57e\text{-}4$
$-(0.6895\ V = y\text{-int} - 0.0592 \log X)$
$0.1532 = 0.0592 \log X/1.57e\text{-}4$
$X = 6.08e\text{-}2\ M$

10] Why is it necessary to use the method of standard addition rather than the calibration curve? What advantages would the calibration curve have over the method of standard addition? (10 points)

Exam 2 – Chem 454 – March 8, 2006

Show all work for full credit. 100 total points

1] Draw a Jablonski diagram and clearly label the following (10 points):

a) Vibrational Relaxation
b) Absorption
c) Fluorescence
d) Phosphorescence
e) Excitation

2] Why is the phosphorescence lifetime longer than the one for fluorescence? (5 points)

3] What are flicker, 60 Hz, and shot noises, how does appear in a power density vs. frequency spectrum. (12 points)

4] Why do methods based on fluorescence have generally a lower limit of detection than those based on absorbance? (5 points)

5] What is a disadvantage of using fluorescence as opposed to absorption? (5 points)

6] What is the difference between atomic emission and atomic fluorescence? (5 points)

7] What is Doppler broadening in AA spectroscopy? (10 points)

8] What are the refractory oxides? Name two examples. Why are they are a problem in AA spectroscopy? (8 points)

9] How does the graphite furnace AA spectrometer achieve a lower limit of detection than the flame AA one? (10 points)

10] Describe two reasons as to how ICP-AE achieve a much lower detection limit than flame AE. (10 points)

Take home assignment.

11] The following problem is to be completed by 1:30 pm March 9th. Submit your answer to me by email (ifcheng@uidaho.edu). This is NOT a team project and the work presented should be of your own. Please type up your answers in a logical short report format. Do not send me a raw spreadsheet and expect me to fill in what you've done, think instead of a memo that you will present to your future boss and/or grant administrator. (20 points)

Analysis by flame AA spectroscopy was conducted on an archeological sample consisting of pottery shard for cadmium. The 2.3451 g shard sample was digested by addition of 2-mL of 40% HF and 2-mL of 65% HNO_3. This sample was then diluted to 25.00 mL with doubly distilled

water. A standard addition analysis was conducted with the treated sample. Aliquots of 1-mL of the treated sample were added to 5 10-mL volumetric flask. The following volumes of 200 ppm $Cd(NO_3)_2$ standard solution were added followed by dilution to the 10-mL mark. The flame AA signal for measured for each and summarized below:

vol spike (mL)	signal
0	0.156
1	0.272
2	0.397
3	0.511
4	0.626

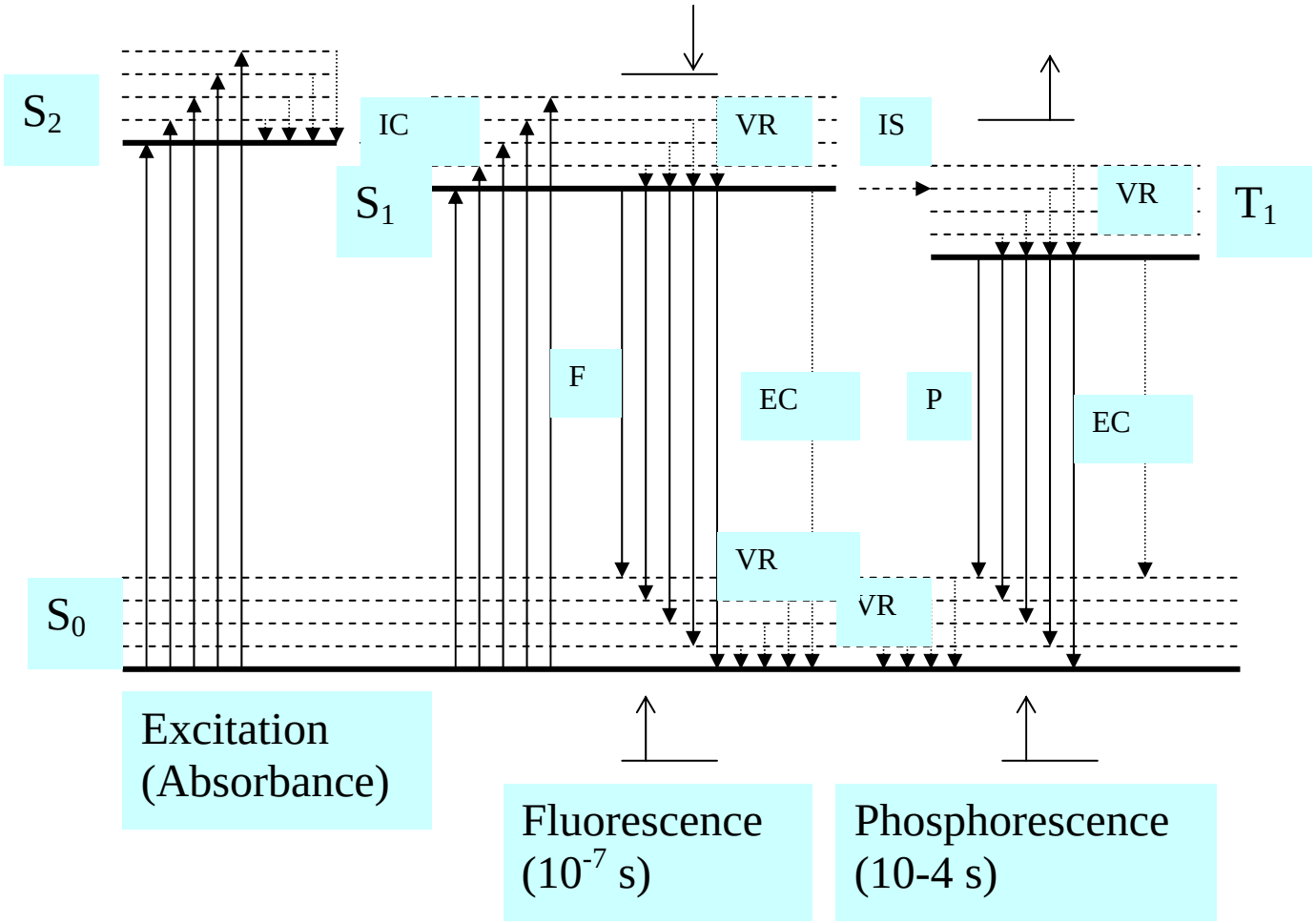
Part a) What is the concentration of Cd in the pottery shard (in ppm)?

Part b) What is the uncertainty for that answer in Part a?

Answers

1] Draw a Jablonski diagram and clearly label the following (10 points):

f) Vibrational Relaxation
g) Absorption
h) Fluorescence
i) Phosphorescence
j) Excitation



2] Why is the phosphorescence lifetime longer than the one for fluorescence? (5 points)

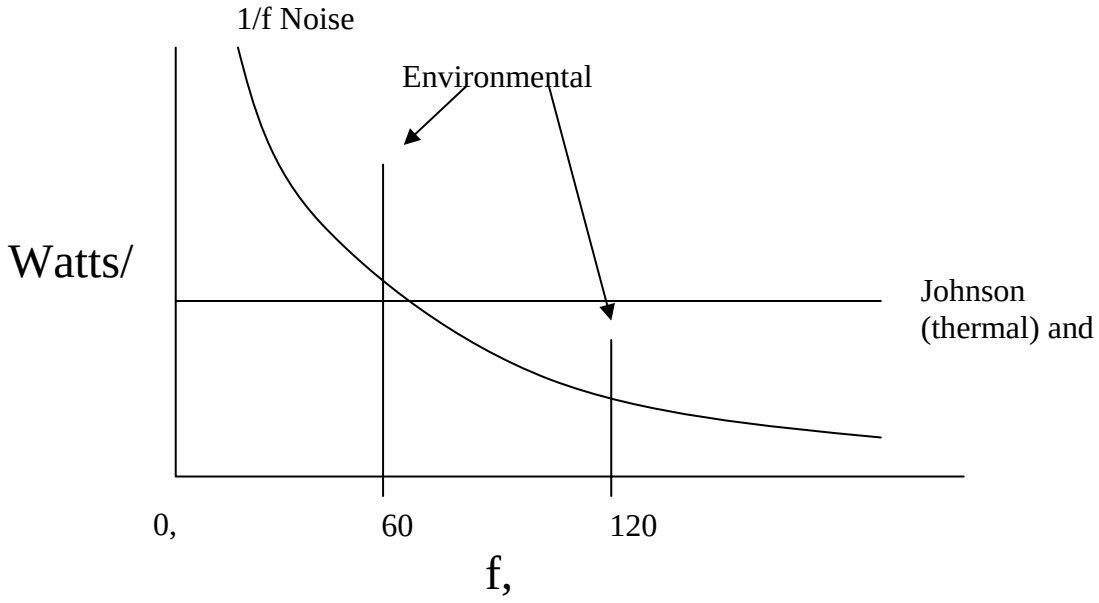
The relaxation route for phosphorescence goes through a spin forbidden triplet to singlet transition, whereas the one for fluorescence goes through a singlet to singlet transition.

3] What are flicker, 60 Hz, and shot noises, how does appear in a power density vs. frequency spectrum. (12 points)

Flicker – Is low frequency noise whose origins are not clearly understood.

Shot Noise - Arises from the statistical flucuations across electrical junctions, e.g N-P juction of a transistor. It occurs at all frequencies.

60 Hz – Is a form of environmental noise that comes from AC wiring.



4] Why do methods based on fluorescence have generally a lower limit of detection than those based on absorbance? (5 points)

a) *The intensity of the fluorescence signal is directly proportional to the power of the incident radiation source (P_0).*

$$I = kP_0c$$

The signal in optical absorbance is due to a ratio of the emergent beam power relative to the incident one.

A = - log (P/P_0)

Increasing beam power will increase signal in fluorescence unlike absorption.

b) *Fluorescence is a scattering technique. The signal is measured outside of the axis of incident beam and therefore without the background of that beam. This background is inherent to absorption techniques.*

5] What is a disadvantage of using fluorescence as opposed to absorption? (5 points)

There could be many, I must read and consider your answer. One obvious problem is that fewer molecules fluoresce when compared to the absorption phenomenon.

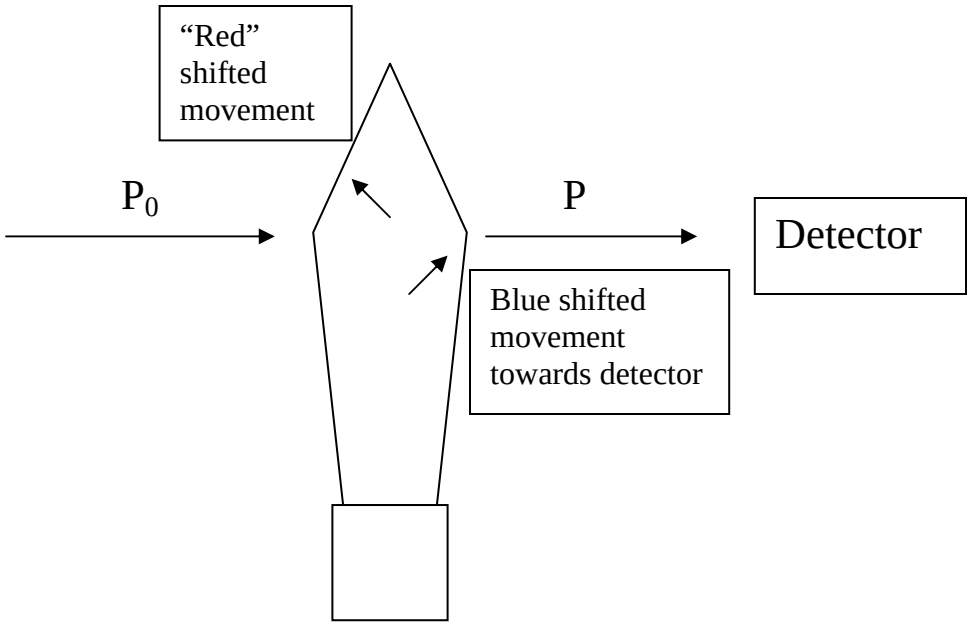
6] What is the difference between atomic emission and atomic fluorescence? (5 points)

AE – is based on the relaxation of atomic electrons that are promoted by flame temperature.

AF – based on the relaxation of atomic electrons promoted by an external radiation source.

7] What is Doppler broadening in AA spectroscopy? (10 points)

Doppler Broadening – chaotic motion in the flame itself will cause some atomic species to move away or closer to the detector. This causes line broadening as the AA and AE lines now assume a band of frequencies as opposed to a single frequency.



8] What are the refractory oxides? Name two examples. Why are they are a problem in AA spectroscopy? (8 points)

The refractory oxides are the translucent heat-stable forms of the metal/metalloid oxides that cause light scattering within the flame. This is an non-absorption route for the decrease in the power of the emergent beam, and thus adds to the background. Examples: Al_2O_3, SiO_2, B_2O_3, SnO_2…

9] How does the graphite furnace AA spectrometer achieve a lower limit of detection than the flame AA one? (10 points)

A detailed discussion of the GFAA or of flame AA is not needed. It is simply based on the GFAA creating a nearly instantaneous plume of concentrated analyte as opposed to the flame AA which requires a constant feed of sample solution into the flame.

10] Describe two reasons as to how ICP-AE achieve a much lower detection limit than flame AE. (10 points)

Higher temperatures with the plasma increase the population of excited state atoms. (see the discussion on the Boltzmann distributiuon)

Higher temperatures within the plasma are better able to break up the refractory oxides.

11] Take home assignment. The following problem is to be completed by 1:30 pm March 9th. Submit your answer to me by email (ifcheng@uidaho.edu). This is NOT a team project and the work presented should be of your own. Please type up your answers in a logical short report format. Do not send me a raw spreadsheet and expect me to fill in what you've done, think instead of a memo that you will present to your future boss and/or grant administrator. (20 points)

Analysis by flame AA spectroscopy was conducted on an archeological sample consisting of pottery shard for cadmium. The 2.3451 g shard sample was digested by addition of 2-mL of 40% HF and 2-mL of 65% HNO_3. This sample was then diluted to 25.00 mL with doubly distilled water. A standard addition analysis was conducted with the treated sample. Aliquots of 1-mL of the treated sample were added to 5 10-mL volumetric flask. The following volumes of 200 ppm $Cd(NO_3)_2$ standard solution were added followed by dilution to the 10-mL mark. The flame AA signal for measured for each and summarized below:

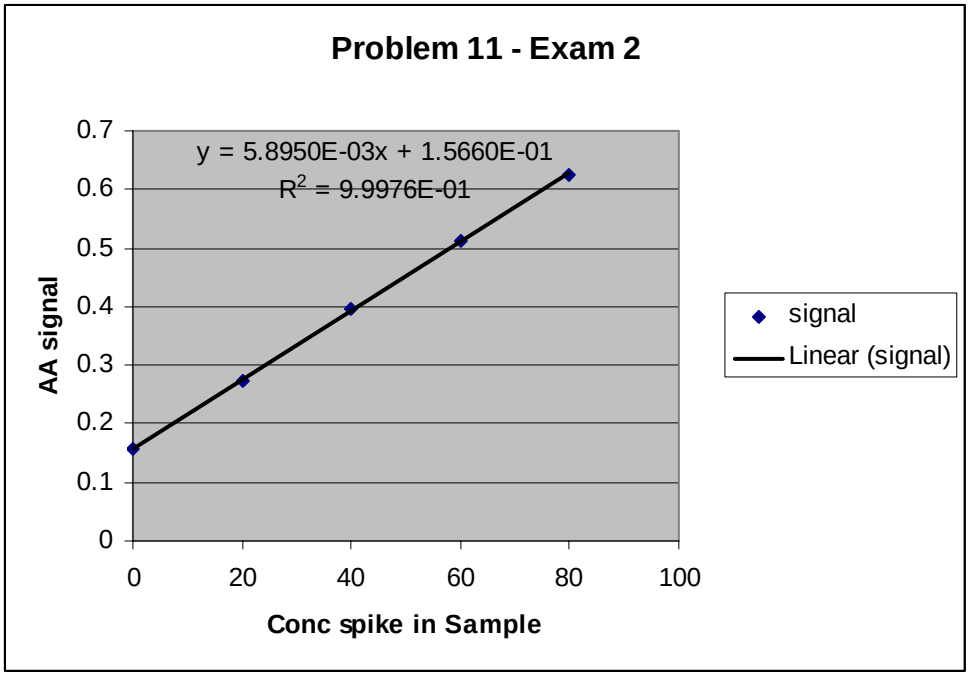
vol spike (mL)	signal
0	0.156
1	0.272
2	0.397
3	0.511
4	0.626

Part a) What is the concentration of Cd in the pottery shard (in ppm)?

Part b) What is the uncertainty for that answer in Part a?

Answer:

Part a)



Find the x-int:

0 = 5.895e-3 (x) + 0.1566

x = 26.56 ppm

26.56 ppm (10 ml/1 ml) = 256.6 ppm in the 25-mL treated sample solution.

*(256.6 g Cd / 1e6 g solution) * 25 g solution = 0.006415 g Cd*

*(0.006415 g Cd / 2.3451 g shard sample) * 1e6 = 2735 ppm Cd in pottery shard*

Part b) You can use the spreadsheet I distributed to you earlier:

vol spike (mL)	conc spike in sample (ppm)	signal	x^2	difference y-y(line)	d^2
0	0	0.156	0	-0.0006	3.6E-07
1	20	0.272	400	-0.0025	6.25E-06
2	40	0.397	1600	0.0046	2.12E-05
3	60	0.511	3600	0.0007	4.9E-07
4	80	0.626	6400	-0.0022	4.84E-06
sum	200		12000		3.31E-05

Equation 5-17:

$$s_{x-\text{int}} = \frac{s_y}{m\sqrt{D}}\sqrt{n(x-\text{int})^2 - 2(x-\text{int})\sum x_i + \sum(x_i^2)}$$

n is the number of data points, m is the slope, D is as follows (5-5):

$$D = \left(\sum x_i^2 \times n - \sum x_i \times \sum x_i\right)$$

s_y is the standard deviation in the y-axis. It calculated as (5-7) where d is the difference between the least squares fitted line and the data point.

$$s_y = \sqrt{\frac{\sum d_i^2}{n-2}} = \sqrt{\frac{3.31\times10^{-5}}{5-2}} = 3.32\times10^{-3}$$

Now for $D = \left(\sum x_i^2 \times n - \sum x_i \times \sum x_i\right) = 12000\times5 - 200\times200 = 2.00\times10^4$

Plug into 5-17

$$s_{x-\text{int}} = \frac{3.32e-3}{5.895e-3\sqrt{2.00e4}}\sqrt{5\times(-26.56)^2 - 2(-26.56)200 + 12000} = 0.644$$

So the x-int with uncertainty is

x = 26.56 ppm ± 0.64

in relative uncertainty its

x = 26.56 ppm ± 2.4%

The final answer is 2735 ± 2.4% ppm Cd in pottery shard

Chem 454 – Exam 3 – April 19, 2006

Show all work for full credit. 100 total points

1] What would be the relative advantages and disadvantages of using FT-IR as a HPLC detector? Discuss at least 2 advantages and 2 disadvantages. Comment on the universality (or lack of) of the detector (20 points)

2] What is meant by the term "population inversion" in its description of lasers? How is this phenomenon achieved? Contrast this to the Boltzmann distribution. Is it possible to reach population inversion based on the effects of heating? (20 points)

$$\frac{N_2}{N_1} = \exp \frac{-(E_2 - E_1)}{kT}$$

3] How does the capillary column configuration achieve its advantages over the packed column setup in gas chromatography? (10 points)

4] What is pulsed flow in HPLC, why does it occur, and why is this not a desirable feature? (10 points)

5] What is an FID and how does it work? What types of analytes does the FID respond to? (10 points)

6] Explain electroosmotic effect necessary for flow and separation in CE. What are the migration time trends for cations, anions, and neutral species? (10 points)

7] An HPLC analysis was conducted for caffeine on "Super-Extra-Energy Formula 2.2 with Hyper-Drive Now!" sports drink. A 10.1 ppm methanol IS standard was introduced both into the sample and a standardized solution of 304 ppm of caffeine. The measured by a diode-array detector at each λ_{max} for the absorptions for methanol and for caffeine are summarized in the table below. What is the concentration of caffeine in that sports drink? (20 points)

	IS	Caffeine
Sample	23141	52777
304 ppm Caffeine standard	28441	77313

Answers

1] What would be the relative advantages and disadvantages of using FT-IR as a HPLC detector? Discuss at least 2 advantages and 2 disadvantages. Comment on the universality (or lack of) of the detector (20 points)

Advantages:

Collection of the entire IR spectrum of analytes is possible. FT-IR data acquisition is rapid so it works well with a flowing system such as HPLC.

It is nearly universal in its response to analytes. A few have no IR active modes, but most especially larger molecules have some sort of IR active vibration.

Disadvantages:

FT-IR detection is difficult in mobile phases that are highly polar such as water and alcohols that have intense absorptions.

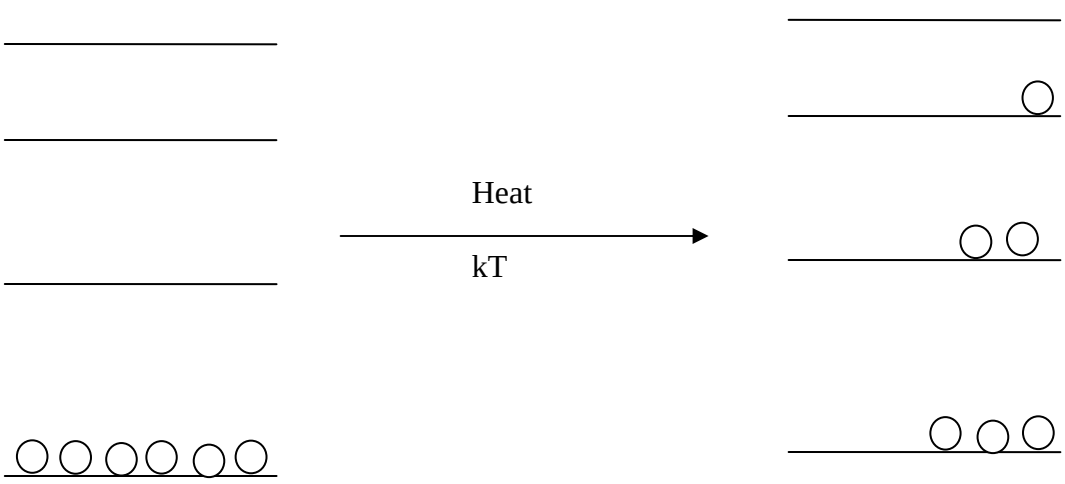
The limit of detection is high relative to other HPLC detectors. Molar absorpitivity for IR transitions is low compared with electronic ones.

There are other possibilities for both advantages and disadvantages. I'll have to read consider your answers.

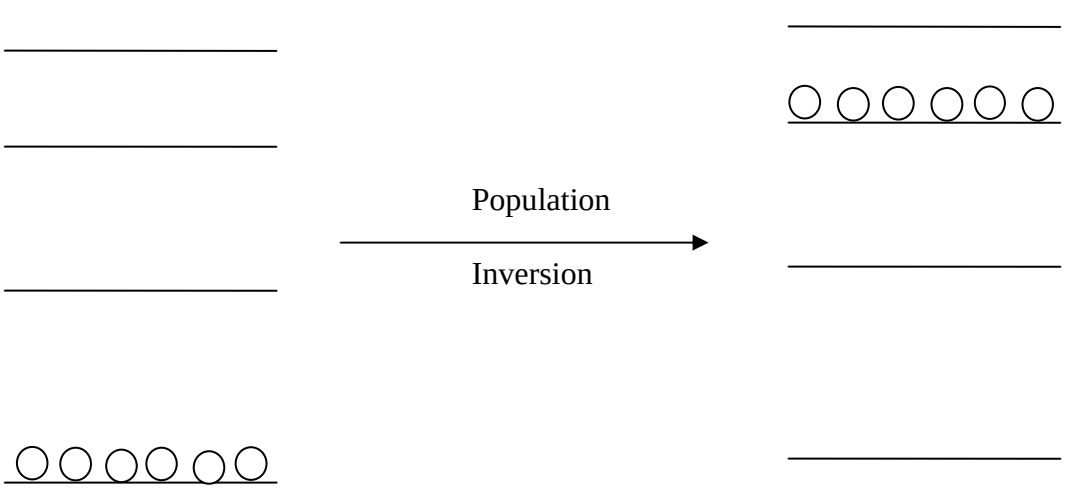
2] What is meant by the term "population inversion" in its description of lasers? How is this phenomenon achieved? Contrast this to the Boltzmann distribution. Is it possible to reach population inversion based on the effects of heating? (20 points)

$$\frac{N_2}{N_1} = \exp \frac{-(E_2 - E_1)}{kT}$$

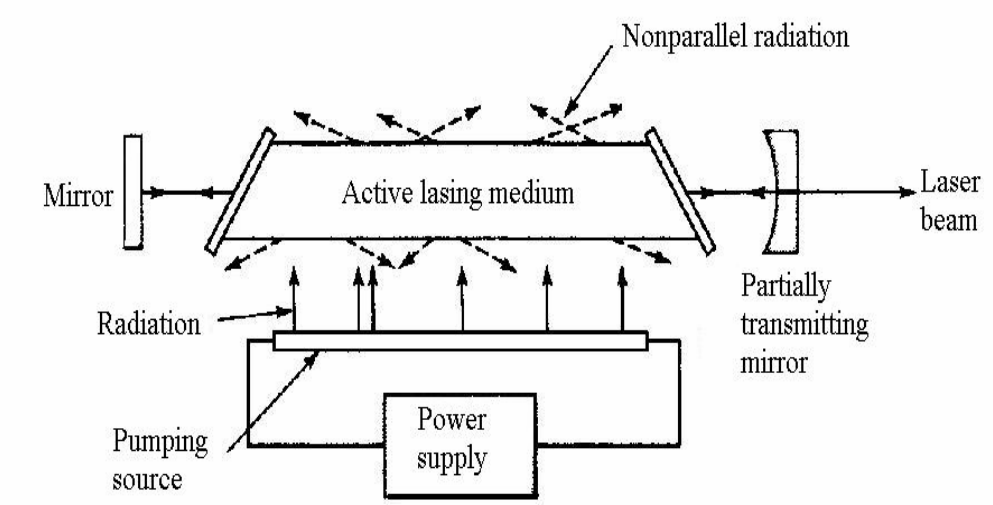
Population inversion is required for the emission processes of a laser. This is when the population of an excited state is greater than a lower state. The Boltzmann distribution statistics predicts that excited states will never be more than the lower states. The effect of increasing the temperature will increase the populations in the excited states but never more than the lower states. The energy diagram below illustrates a Boltzmann distribution and the effects of heating:



Population inversion is demonstrated below:



For lasers this is achieved by the pumping of a lasing material:



3] How does the capillary column configuration achieve its advantages over the packed column setup in gas chromatography? (10 points)

Starting with the van Deemter equation: H = A + B/u + Cu we should consider all three terms.

A – the dispersion of peak area due to multiple paths in the column is not a consideration in the capillary column as only one path predominates.

B/u – this is the longitudinal diffusion term which tells us that the longer the time the analyte band spends in the column the more dispersion. This is the most significant of the three terms in the band broadening characteristics of the van Deemter equation. Flow of the mobile phase through a capillary column is relatively unimpeded when in comparison with a packed column. This allows for a faster mobile phase flow rate through the column.

Cu – The mass transfer between the m.p. the s.p. term is of less importance in the considerations of the GC capillary column however, the s.p. is made as thin as possible to accommodate facile kinetics between the s.p. and the m.p.

4] What is pulsed flow in HPLC, why does it occur, and why is this not a desirable feature? (10 points)

Pulsed flow is the rhythmic flow pattern that occurs due to the cycles within a reciprocating pump. This is not a desirable feature as it causes remixing of the solutes in HPLC. Note – it is partially addressed by pulse dampers.

5] What is an FID and how does it work? What types of analytes does the FID respond to? (10 points)

The flame ionization detector (FID) for GC is based on the formation of organic radicals, CH and CHO^+ within a flame. These radicals are reduced at a cathode and the current flow is proportional roughly to the number of organic carbons in the analyte. The flow or

effluent from the separation column is fed to a flow air and fuel (H_2) where the analytes are combusted. A cathode is further upstream from the flame. The FID is responsive only to organic carbons.

6] Explain electroosmotic effect necessary for flow and separation in CE. What are the migration time trends for cations, anions, and neutral species? (10 points)

The electroosmotic flow is based on the flow of adsorbed of cations to the $-O^-$ sites on the surface of the silica capillary. These cations will migrate towards the cathode dragging along with it a solvation sphere of water molecules (and thus neutrals) along with solvated anions. All three major types are pulled to the cathode with migration time trends of

$$t\ (cations) < t\ (neutrals) < t\ (anions)$$

7] An HPLC analysis was conducted for caffeine on "Super-Extra-Energy Formula 2.2 with Hyper-Drive Now!" sports drink. A 10.1 ppm methanol IS standard was introduced both into the sample and a standardized solution of 304 ppm of caffeine. The measured by a diode-array detector at each λ_{max} for the absorptions for methanol and for caffeine are summarized in the table below. What is the concentration of caffeine in that sports drink?

	IS	Caffeine
Sample	23141	52777
304 ppm Caffeine standard	28441	77313

First normalize caffeine peaks with the response by the IS.

	IS	*Caffeine*	*Caffeine/IS*
Sample	*23141*	*52777*	*2.2807*
304 ppm Caffeine standard	*28441*	*77313*	*2.7184*

Assume that

$y = mx + b$ *with y the normalized detector response and x the concentration. This one point analysis assumes that b = 0.*

$2.7184 = m(304)$

$m = 8.92\underline{7}e\text{-}3$ *Now calculate the analyte concentration.*

$2.2807 = 8.92\underline{7}e\text{-}3\ (x)$

$x = 255$ ppm *see http://wilstar.com/caffeine.htm for typical caffeine concentrations.*

Also using Formula 5-19 from Harris:

$A_x/C_x = F\ (A_s/C_s)$

77313/304ppm = F (28441/10.1ppm)

F = 9.031e-2

For the sample:

$52777/C_x = 9.031e\text{-}2\ (23141/10.1)$

$C_x = 255\ ppm$