

Exam 1 * Chem 454 * February 12, 2020

$$\bar{x} = \frac{\sum_i x_i}{n} \quad s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}} \quad \mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}} \quad G = \frac{|value - \bar{x}|}{s}$$

Values of Grubbs Statistic (G)

Number of Observations n	Confidence Level (%)					
	99.9	99.5	99	97.5	95	90
3	1.155	1.155	1.155	1.155	1.153	1.148
4	1.499	1.496	1.492	1.481	1.463	1.425
5	1.780	1.764	1.749	1.715	1.672	1.602
6	2.011	1.973	1.944	1.887	1.822	1.729
7	2.201	2.139	2.097	2.020	1.938	1.828
8	2.358	2.274	2.221	2.126	2.032	1.909
9	2.492	2.387	2.323	2.215	2.110	1.977
10	2.606	2.482	2.410	2.290	2.176	2.036
11	2.705	2.564	2.485	2.355	2.234	2.088
12	2.791	2.636	2.550	2.412	2.285	2.134
13	2.867	2.699	2.607	2.462	2.331	2.175
14	2.935	2.755	2.659	2.507	2.371	2.213
15	2.997	2.806	2.705	2.549	2.409	2.247

$$F = \frac{s_1^2}{s_2^2}$$

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{pooled} = \sqrt{\frac{s_1^2(n_1-1) + s_2^2(n_2-1)}{n_1 + n_2 - 2}} \quad \text{d.f.} = n_1 + n_2 - 2$$

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}}$$

$$\text{d. f.} = \frac{\left[\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right]^2}{\frac{\left(\frac{s_1^2}{n_1}\right)^2}{n_1-1} + \frac{\left(\frac{s_2^2}{n_2}\right)^2}{n_2-1}}$$

Table 4-1 Ordinate and area for the normal (Gaussian) error curve,

$$y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$$

$ z ^a$	y	Area ^b	$ z $	y	Area	$ z $	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 4-2 Values of Student's t

Degrees of freedom	Confidence level (%)						
	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

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Name: _____

80 points total, 8 questions at 10 points each.

1. Estimate the limit of detection for the measurement of an analyte below. Assume the concentration units are in mM and the best fit line is ¹

$$y = 0.525x + 0.22$$

	Low Conc. Signal	Blank
1	0.55	0.27
2	0.51	0.35
3	0.60	0.26
4	0.49	0.31
5	0.55	0.24
6	0.57	0.29
7	0.52	0.32
s.d.	0.04	0.04
avg	0.54	0.29

2. Can any of the following values be discarded with 95% confidence? ²

192 216 202 195 204

Mean = 201.8 S.D. = 9.34

3. Two sets of data are compared for their scatter. Based on the following are the two standard deviations statistically different from each other? ³

$$\sigma_1 = 0.0122 \quad n = 6$$

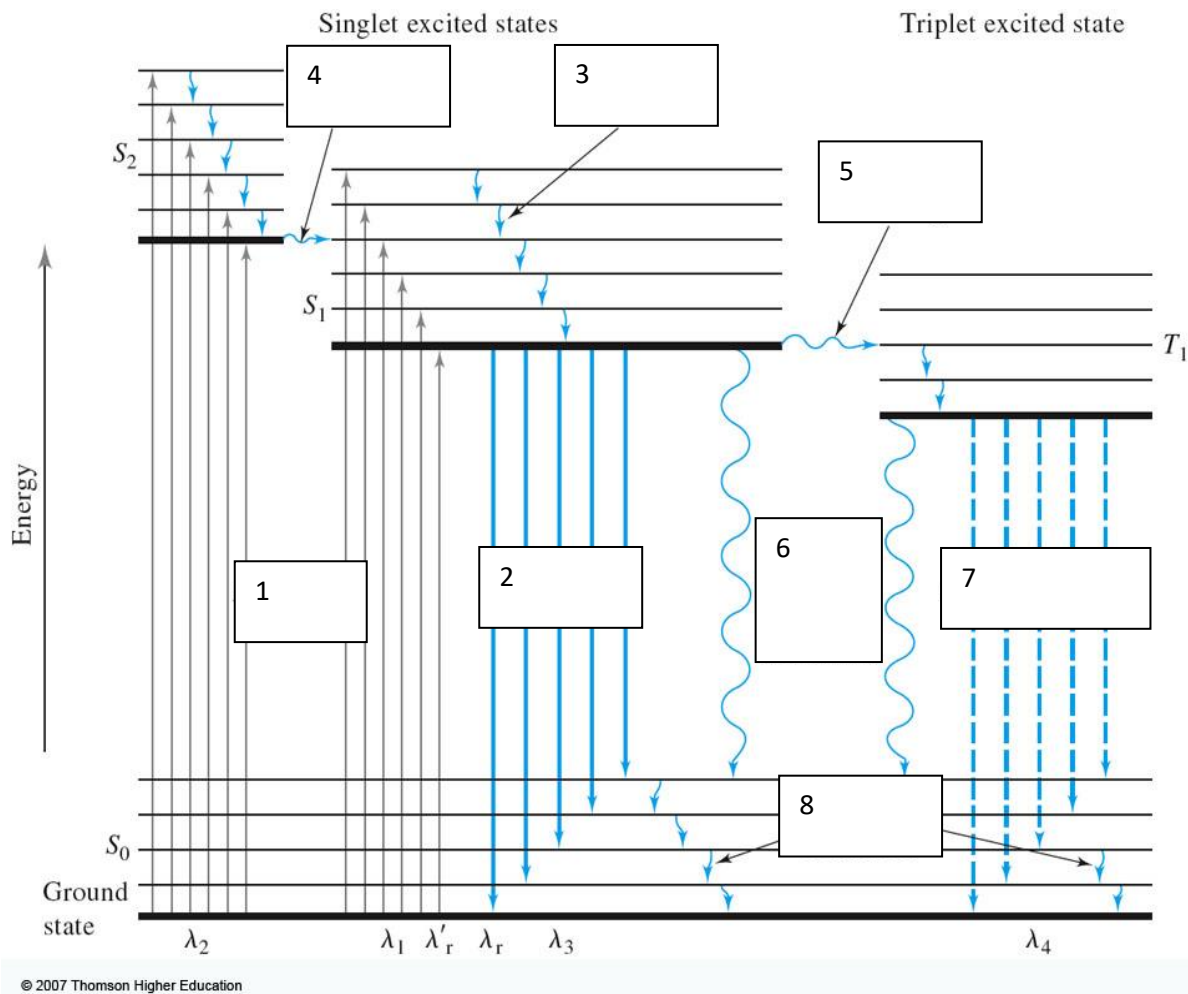
$$\sigma_2 = 0.0057 \quad n = 7$$

4. Calculate the 95% confidence level for the following data set. ⁴

117.1 122.7 121.1 119.4 120.9

5. Illustrate a block diagram of a single beam spectrophotometer include P and P₀ in that diagram ⁵

6. Fill in the blanks below. ⁶



7. What are flicker, 60 Hz, and shot noises, how does appear in a power density vs. frequency spectrum. ⁷

8. A Beer's law measurement was made at 425 nm on a 5.00 mL sample with analyte X. After dilution to 10.00-mL its absorbance A was found to be 0.200. A spike of 1.0 mL of 1.00 mM compound X was made on that sample and after dilution its A was found to be 0.250. What is the concentration of X in the sample? ⁸

Answers

1 $LOD = 3s/m = 3(0.04)/0.525 = 0.23 \text{ mM}$

2 Use the Grubbs test. $G = \frac{|value - \bar{x}|}{s}$

G-calc = $216 - 201.8/9.34 = 1.52$ G-table is 1.672, The value should be retained.

3 $F\text{-calc} = 0.0122^2/0.0057^2 = 1.49e-4/3.25e-5 = 4.58$

Locate F-table with DF = 5 and 6 F-table = 4.39

F-calc > F-table the two s.d. are different from each other.

4 First calculate mean: 120.2 the calculate s.d. = 2.1 use $\mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}}$

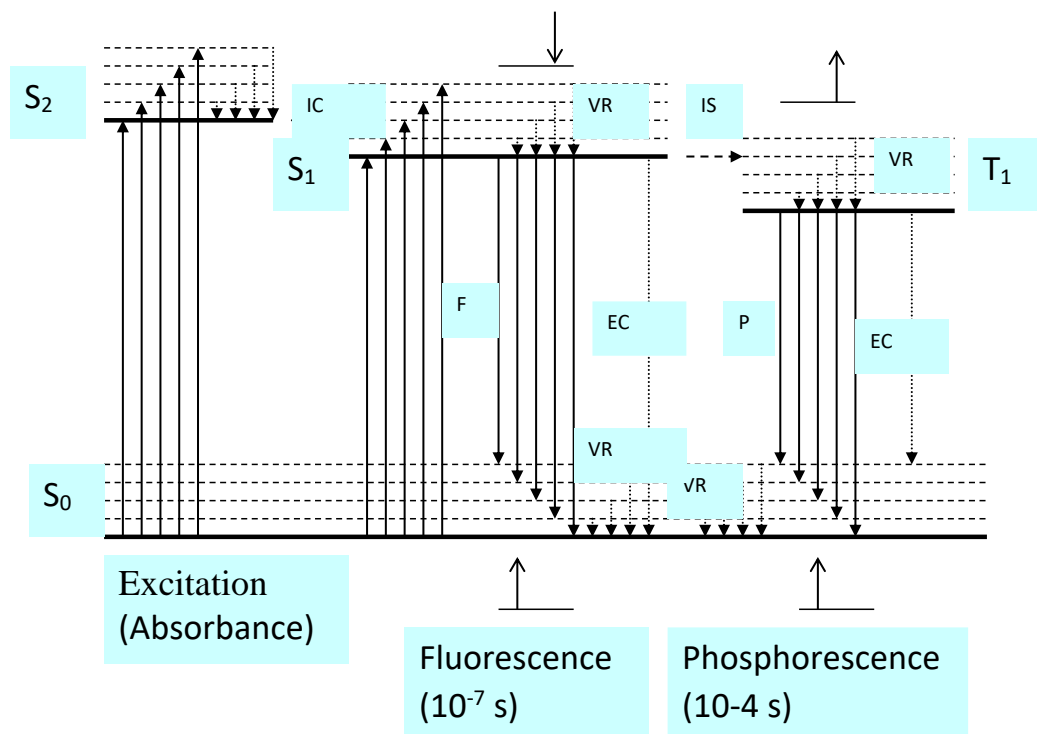
$$\mu = 120.2 \pm 2.776 * 2.1 / \sqrt{5} = 120.2 \pm 2.6$$

There's a 85% chance that the true mean lies between 122.8 and 117.6

5

Light \rightarrow Wavelength $\rightarrow P_0 \rightarrow$ Sample $\rightarrow P \rightarrow$ Detector
Source Selector (Cuvette) (Transducer)
(Monochromator)

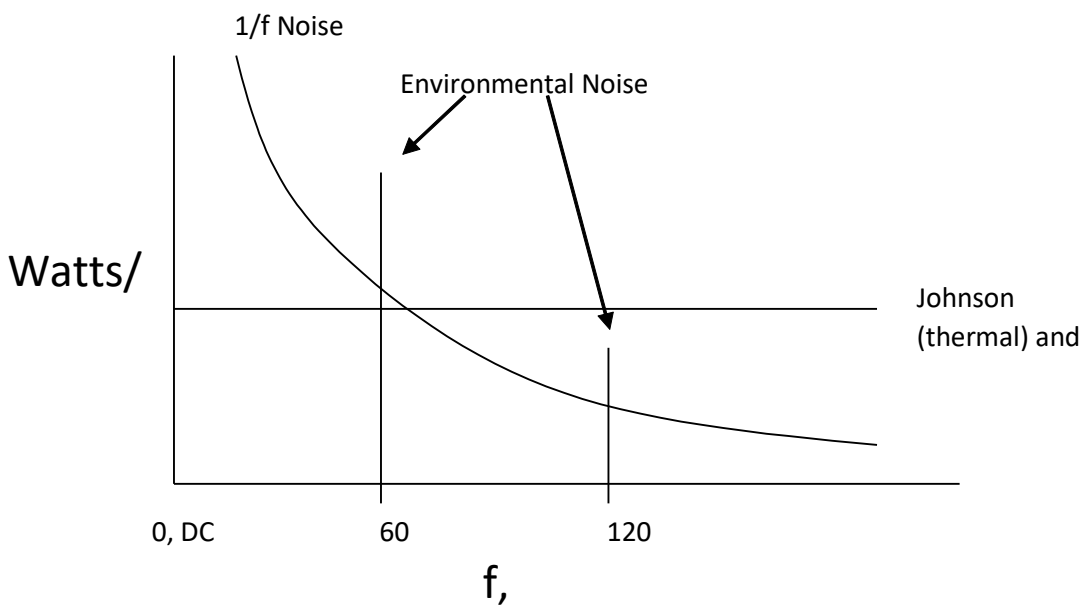
6



⁷ Flicker – Is low frequency noise whose origins are not clearly understood.

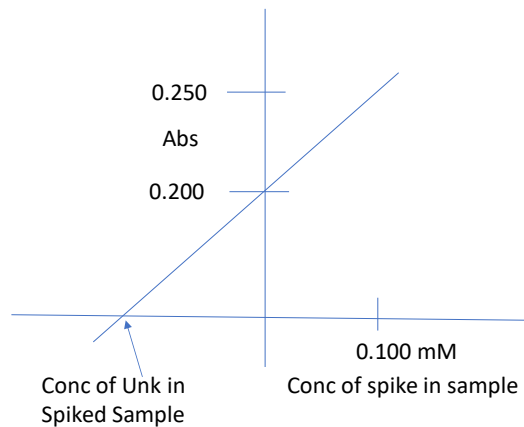
Shot Noise - Arises from the statistical fluctuations across electrical junctions, e.g N-P junction of a transistor. It occurs at all frequencies.

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



8 First calculate conc of spike in diluted sample.

$C_s = 1.00 \text{ mM} (1.00/10.00) = 0.100 \text{ mM}$ next plot response against absorbance



Next find slope of line, $m = (0.250 - 0.200) / 0.100 \text{ mM} = 0.50$

Now find x-int, we know that y-int or $b = 0.200$

$$Y = mx + b \quad \text{or} \quad 0 = 0.50 * x + 0.200$$

$x = 0.400 \text{ mM}$ but this is the conc of the unkn after dilution.

Conc of unkn before dilution = $0.400 (10.00/5.00) = 0.800 \text{ mM}$

Also you could set up proportions.

$$A_1 = ebc = 0.200 \text{ where } c = \text{unkn conc}$$

$$A_2 = ebc + eb * 0.1 \text{ mM} = 0.250$$

$$0.200/0.250 = c / c + 0.1$$

$c = 0.4 \text{ mM}$ and Conc of unkn before dilution = $0.400 (10.00/5.00) = 0.800 \text{ mM}$