CHEM 524 -- Course Outline (Part 11) Error— 2013

For html of 2005 notes with linked figures, click here

VII. **Error and Statistical Sampling:** Chap. 6 and Append. A (***Read** both, esp. Append. A*)

F. Statistical Sampling only applies to *random error*, Statistics yield evaluation of error

1. **Systematic error** more difficult-
   a. Calibration—pure analyte, concentrations must bracket unknown, be appropriate to analyte
   b. Matrix - Blank → all except unknown, concentration not interacting, no interfering species
   c. Sampling errors- e.g. uncalibrated pipette or aliquots with sequence effect

2. Data Sampling uses previous definitions, average and deviation:
   a. Averaging data from multiple measurements, μ is true average:

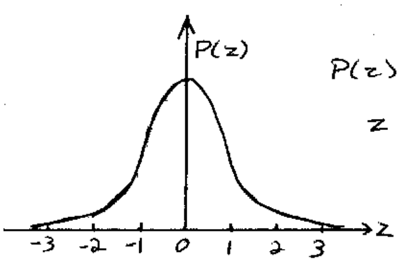
   $\tilde{E} = \Sigma E_i/n$ as $n \rightarrow$ very large, then $\tilde{E} \rightarrow \mu$

   b. Standard deviation (rms excursion from mean) σ = true S.D., but s is measured SD

   $s = [\Sigma (E_i-\tilde{E})^2/(n-1)]^{1/2}$ $n \rightarrow$ very large, then $s \rightarrow \sigma$

3. **Random distribution** of error is Gaussian -- *z test*, large set → P(z) is distribution of values

   $\mathbf{P(z) = (\sigma\sqrt{2\pi})^{-1} \exp(-z^2/2)}$ $\mathbf{z = (E-\mu)/\sigma}$ —–> where: μ = true mean; σ = true S.D.



$P(z) = (\sigma\sqrt{2\pi})^{-1} \exp(-z^2/2)$

$z = E - \mu/\sigma$

μ — true mean

σ — true std. dev.

$\alpha = P(z \geq z_\alpha) = (\sigma\sqrt{2\pi})\int_{z_\alpha}^{\infty} \exp(-z^2/2)\,dz$

ex:	
$z_\alpha = 0$	$\alpha = 0.500$
$= 1$	$= 0.159$
$= 2$	$= 0.023$
$= 3$	$= 0.0013$

$1-\alpha = P(z < z_\alpha)$, $1-2\alpha = P(|z| < z_\alpha)$

→ α – probability of being beyond a *z value*: $\alpha = P(z \geq z_\alpha) = \int_{z\alpha}^{\infty} P(z)$

alternate, within interval expressed as $\mathbf{P(z < z_\alpha) = 1 - \alpha}$, $\mathbf{P(|z| < z_\alpha) = 1 - 2\alpha}$ *(2 sided)*

--- values from table of z and α (Appendix: Table A1)

TABLE A-1

Probability table for the normal distribution

z	α	z	α	z	α	z	α	z	α	z	α	z	α	z	α	z	α
0.00	.5000	0.35	.3632	0.70	.2420	1.05	.1469	1.40	.0808	1.75	.0401	2.10	.0179	2.45	.0071	2.80	.0026
0.01	.4960	0.36	.3594	0.71	.2389	1.06	.1446	1.41	.0793	1.76	.0392	2.11	.0174	2.46	.0069	2.81	.0025
0.02	.4920	0.37	.3557	0.72	.2358	1.07	.1423	1.42	.0778	1.77	.0384	2.12	.0170	2.47	.0068	2.82	.0024
0.03	.4880	0.38	.3520	0.73	.2327	1.08	.1401	1.43	.0764	1.78	.0375	2.13	.0166	2.48	.0066	2.83	.0023
0.04	.4840	0.39	.3483	0.74	.2296	1.09	.1379	1.44	.0749	1.79	.0367	2.14	.0162	2.49	.0064	2.84	.0023
0.05	.4801	0.40	.3446	0.75	.2266	1.10	.1357	1.45	.0735	1.80	.0359	2.15	.0158	2.50	.0062	2.85	.0022
0.06	.4761	0.41	.3409	0.76	.2236	1.11	.1335	1.46	.0721	1.81	.0351	2.16	.0154	2.51	.0060	2.86	.0021
0.07	.4721	0.42	.3372	0.77	.2206	1.12	.1314	1.47	.0708	1.82	.0344	2.17	.0150	2.52	.0059	2.87	.0021
0.08	.4681	0.43	.3336	0.78	.2177	1.13	.1292	1.48	.0694	1.83	.0336	2.18	.0146	2.53	.0057	2.88	.0020
0.09	.4641	0.44	.3300	0.79	.2148	1.14	.1271	1.49	.0681	1.84	.0329	2.19	.0143	2.54	.0055	2.89	.0019
0.10	.4602	0.45	.3264	0.80	.2119	1.15	.1251	1.50	.0668	1.85	.0322	2.20	.0139	2.55	.0054	2.90	.0019
0.11	.4562	0.46	.3228	0.81	.2090	1.16	.1230	1.51	.0655	1.86	.0314	2.21	.0136	2.56	.0052	2.91	.0018
0.12	.4522	0.47	.3192	0.82	.2061	1.17	.1210	1.52	.0643	1.87	.0307	2.22	.0132	2.57	.0051	2.92	.0018
0.13	.4483	0.48	.3156	0.83	.2033	1.18	.1190	1.53	.0630	1.88	.0301	2.23	.0129	2.58	.0049	2.93	.0017
0.14	.4443	0.49	.3121	0.84	.2005	1.19	.1170	1.54	.0618	1.89	.0294	2.24	.0125	2.59	.0048	2.94	.0016
0.15	.4404	0.50	.3085	0.85	.1977	1.20	.1151	1.55	.0606	1.90	.0287	2.25	.0122	2.60	.0047	2.95	.0016
0.16	.4364	0.51	.3050	0.86	.1949	1.21	.1131	1.56	.0594	1.91	.0281	2.26	.0119	2.61	.0045	2.96	.0015
0.17	.4325	0.52	.3015	0.87	.1922	1.22	.1112	1.57	.0582	1.92	.0274	2.27	.0116	2.62	.0044	2.97	.0015
0.18	.4286	0.53	.2981	0.88	.1894	1.23	.1093	1.58	.0571	1.93	.0268	2.28	.0113	2.63	.0043	2.98	.0014
0.19	.4247	0.54	.2946	0.89	.1867	1.24	.1075	1.59	.0559	1.94	.0262	2.29	.0110	2.64	.0041	2.99	.0014
0.20	.4207	0.55	.2912	0.90	.1841	1.25	.1056	1.60	.0548	1.95	.0256	2.30	.0107	2.65	.0040	3.00	.0013
0.21	.4168	0.56	.2877	0.91	.1814	1.26	.1038	1.61	.0537	1.96	.0250	2.31	.0104	2.66	.0039	3.01	.0013
0.22	.4129	0.57	.2843	0.92	.1788	1.27	.1020	1.62	.0526	1.97	.0244	2.32	.0102	2.67	.0038	3.02	.0013
0.23	.4090	0.58	.2810	0.93	.1762	1.28	.1003	1.63	.0516	1.98	.0239	2.33	.0099	2.68	.0037	3.03	.0012
0.24	.4052	0.59	.2776	0.94	.1736	1.29	.0985	1.64	.0505	1.99	.0233	2.34	.0096	2.69	.0036	3.04	.0012
0.25	.4013	0.60	.2743	0.95	.1711	1.30	.0963	1.65	.0495	2.00	.0228	2.35	.0094	2.70	.0035	3.05	.0011
0.26	.3974	0.61	.2709	0.96	.1685	1.31	.0951	1.66	.0485	2.01	.0222	2.36	.0091	2.71	.0034	3.06	.0011
0.27	.3936	0.62	.2676	0.97	.1660	1.32	.0934	1.67	.0475	2.02	.0217	2.37	.0089	2.72	.0033	3.07	.0011
0.28	.3897	0.63	.2643	0.98	.1635	1.33	.0918	1.68	.0465	2.03	.0212	2.38	.0087	2.73	.0032	3.08	.0010
0.29	.3859	0.64	.2611	0.99	.1611	1.34	.0901	1.69	.0455	2.04	.0207	2.39	.0084	2.74	.0031	3.09	.0010
0.30	.3821	0.65	.2578	1.00	.1587	1.35	.0885	1.70	.0446	2.05	.0202	2.40	.0082	2.75	.0030	3.10	.0010
0.31	.3783	0.66	.2546	1.01	.1562	1.36	.0869	1.71	.0436	2.06	.0197	2.41	.0080	2.76	.0029	3.11	.0009
0.32	.3745	0.67	.2514	1.02	.1539	1.37	.0853	1.72	.0427	2.07	.0192	2.42	.0078	2.77	.0028	3.12	.0009
0.33	.3707	0.68	.2483	1.03	.1515	1.38	.0838	1.73	.0418	2.08	.0188	2.43	.0075	2.78	.0027	3.13	.0009
0.34	.3669	0.69	.2451	1.04	.1492	1.39	.0823	1.74	.0409	2.09	.0183	2.44	.0073	2.79	.0026	3.14	.0008

4. Smaller sample sets (less statistical): Student t-test (σ is unknown)

-- measure first ($n < 30$) – determine Ẽ and s, values for small sets (defined above)

-- for a small number of data, the error (uncertainty) increases

--- s and σ differ -- need table for α depend on n

--- **$t = (\tilde{E} - \mu)/(s/ n^{1/2})$**, where Ẽ - average of n samples table gives t (α, n),

one use, pick column for desired α and compute the t for that interval of confidence

recall, you are measuring Ẽ and s but do not know μ, i.e. if you found right value

same form – E within the interval around μ: **$P(t < t^n_\alpha) = 1 - \alpha$**, outside: **$P(t > t^n_\alpha) = \alpha$**,

also $P(|t| < t^n_\alpha) = 1 - 2\alpha$, and $P(0 < t < t^n_\alpha) = 0.5 - \alpha$,

Calculate t and find t_α closest but smaller, less than a probability α that a value differs from true mean *OR* that with confidence 1-α that some difference due to systematic error

Key is null hypothesis – assuming due to random and test that partially systematic

TABLE A-2

Critical values of *t*

n	$t_{.100}$	$t_{.050}$	$t_{.025}$	$t_{.010}$	$t_{.001}$	ν
2	3.078	6.314	12.706	31.821	63.657	1
3	1.886	2.920	4.303	6.965	9.925	2
4	1.638	2.353	3.182	4.541	5.841	3
5	1.533	2.132	2.776	3.747	4.604	4
6	1.476	2.015	2.571	3.365	4.032	5
7	1.440	1.943	2.447	3.143	3.707	6
8	1.415	1.895	2.365	2.998	3.499	7
9	1.397	1.860	2.306	2.896	3.355	8
10	1.383	1.833	2.262	2.821	3.250	9
11	1.372	1.812	2.228	2.764	3.169	10
12	1.363	1.796	2.201	2.718	3.106	11
13	1.356	1.782	2.179	2.681	3.055	12
14	1.350	1.771	2.160	2.650	3.012	13
15	1.345	1.761	2.145	2.624	2.977	14
16	1.341	1.753	2.131	2.602	2.947	15
17	1.337	1.746	2.120	2.583	2.921	16
18	1.333	1.740	2.110	2.567	2.898	17
19	1.330	1.734	2.101	2.552	2.878	18
20	1.328	1.729	2.093	2.539	2.861	19
21	1.325	1.725	2.086	2.528	2.845	20
22	1.323	1.721	2.080	2.518	2.831	21
23	1.321	1.717	2.074	2.508	2.819	22
24	1.319	1.714	2.069	2.500	2.807	23
25	1.318	1.711	2.064	2.492	2.797	24
26	1.316	1.708	2.060	2.485	2.787	25
27	1.315	1.706	2.056	2.479	2.779	26
28	1.314	1.703	2.052	2.473	2.771	27
29	1.313	1.701	2.048	2.467	2.763	28
30	1.311	1.699	2.045	2.462	2.756	29
inf.	1.282	1.645	1.960	2.326	2.576	inf.

5. **Hypothesis testing** -- *is difference between Ẽ and μ significant?*

--- test confidence interval $\mu = \tilde{E} \pm z\sigma/n^{1/2}$ (or $\mu = \tilde{E} \pm ts/n^{1/2}$)

two-tailed, **1-2α** level confidence

T-test – confidence interval

$\mu = \bar{E} \pm \frac{z\sigma}{\sqrt{n}}$ $\mu = \bar{E} \pm \frac{ts}{\sqrt{n}}$ (n<30)

"2-tailed" 1 – 2α level of confidence mean is within interval

	z	t (n=5)	t (n=10)	t (n=20)
95%	1.96	2.78	2.26	2.09
98%	2.33	3.75	2.82	2.54
99%	2.58			
99.5%	2.81			

note pattern: more confidence → bigger interval (less certain)
more data → smaller interval

-- confidence (or probability) that an **interval (error range) encloses the true mean**

-- as confidence increases, interval must increase, as n increases, interval decrease

-- example problem

Suppose you make 10 measurements of a signal

9 V
8 V
10 V
11 V
10 V
9 V
7 V
8 V
7 V
9 V

$n = 10$
$s = 1.32$
$\bar{E} = 8.8$

What is the confidence level that $\bar{E}$ differs from the expected true mean $\mu = 10$ by only random error?

$t = \frac{\bar{E} - \mu}{s/\sqrt{n}} = \frac{8.8 - 10}{(1.32/(10)^{1/2})} =$ ~~0.287~~ 2.87

$t_{0.01} = 2.82$ $t_{0.001} = 3.25$

~99% chance $E < \mu$ is systematic in part

~1% chance $\bar{E} < \mu$ is random totally

Suppose you know that $\mu = 10$ V and $\sigma = 1$ for the measurement you are making. If a given measurement gives a value of $E = 12$ V, what is the probability that a systematic error was made?

$z = \frac{12 - 10}{1} = \frac{E - \mu}{\sigma} = 2$

at 95% confidence part systematic

at 98%

$z = 2 \Rightarrow$ $\alpha = 0.0228$

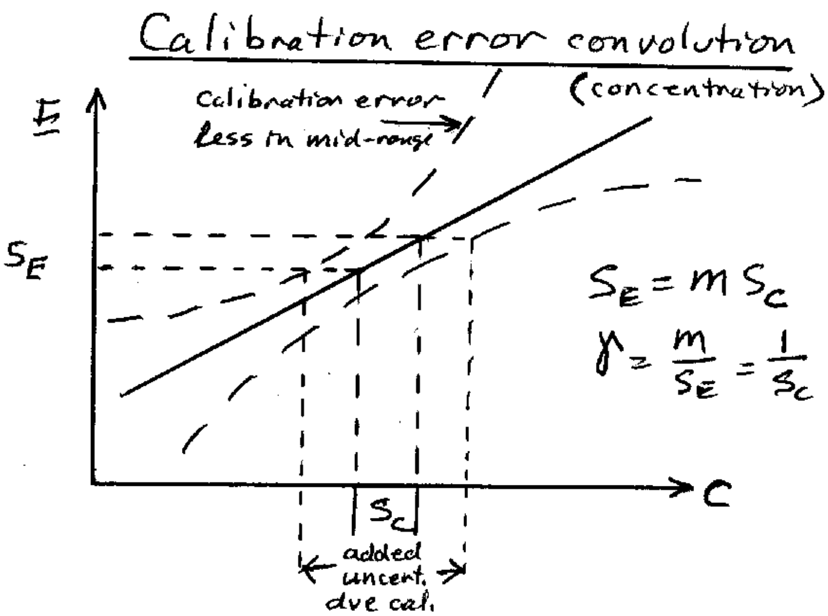
G. Concentration Sensitivity

1. Calibration curve gives **$E = f(c)$**, (book uses **S**) calibration sensitivity: **$m = \delta E/\delta c = \delta f(c)/dc$**

   -- Concentration Confidence interval: **$\mu_c = \underline{c} \pm ts_c/ n^{1/2}$** **$s_c = s/m$**

   -- Actual confidence (error) also affected by calibration error

   use **$t = (\underline{c}-\mu_c)/(s_c/n^{1/2})$**



   -- Analytical sensitivity: **$\gamma = m/s = 1/s_c$** corrects for gain, etc.

   note smaller error more sensitivity

2. Detection Limit—smallest signal/conc. at some level of confidence

   -- **$DL = k \cdot s_{bk} / m$** s_{bk} -- S.D. of blank, k -- confidence factor, m – calibration sensitivity

Detection limit

$DL = k\, s_{bk}/m$

k – confidence factor

$t = k/\sqrt{2}$

k	
1	84%
2	98%
3	99.9%

   -- limited sampling use t-test: **$t = k / 2^{1/2}$** 2 from sample + blank measurement

   (goal make measurements at >10*DL)

Homework – Statistical sampling (read Chap 6 and Append. A)

Discussion: Chap 6: #4, 5, 7, 8, 11, 12

To hand in: Problems Chap 6: #3, 6