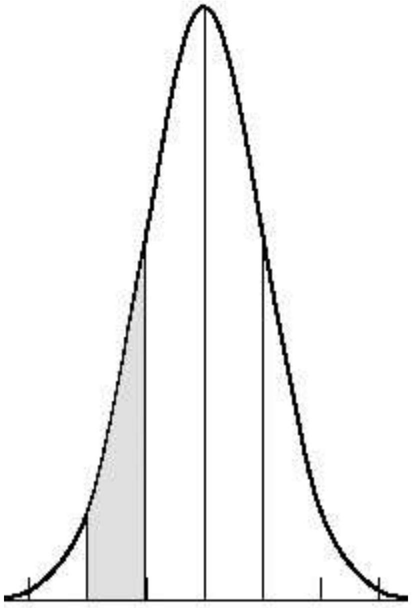
Lecture 5

Random Errors in Chemical Analysis -II



A measurement x_1, with

μ and σ

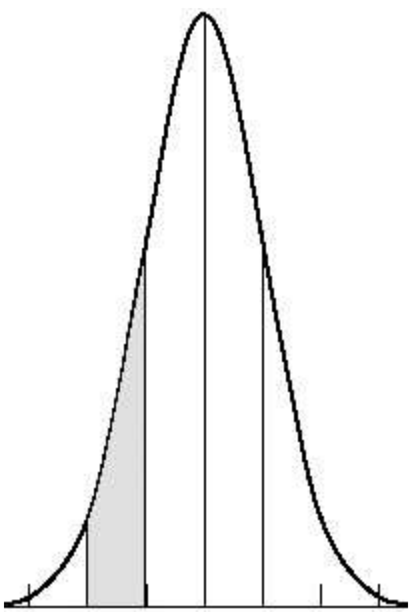
Random!

I am making a second measurement x_2
of the same analyte.

It has the same μ

We do not know it!

It has the same σ

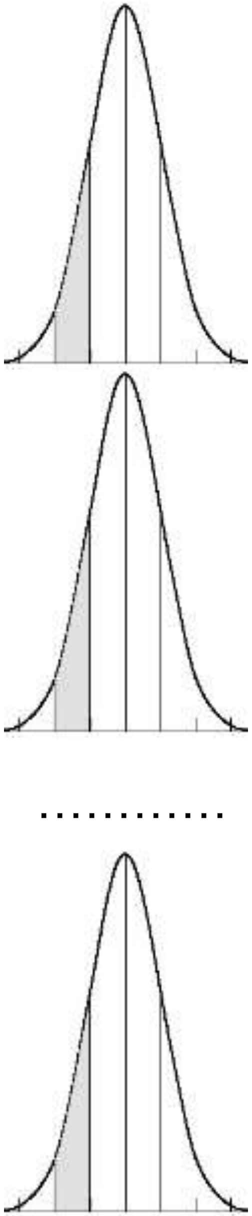


As an estimate of my unknown μ
I will use average

$$\bar{x} = \frac{x_1 + x_2}{2}$$

$$\sigma_{1+2} = \sqrt{\sigma_1^2 + \sigma_2^2} = \sqrt{2\sigma^2} = \sqrt{2} \times \sigma$$

$$\sigma_{av} = \frac{\sigma_{1+2}}{2} = \frac{\sqrt{2} \times \sigma}{2} = \frac{\sigma}{\sqrt{2}}$$



If I am making ***N*** measurements of the same value

$$\bar{x} = \frac{x_1 + x_2 + ... + x_N}{N}$$

$$\sigma_{av} = \frac{\sigma}{\sqrt{N}}$$

Range	Percentage of measurements
$\mu \pm 1\sigma$	68.3
$\mu \pm 2\sigma$	95.5
$\mu \pm 3\sigma$	99.7

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			

a. $z = (x - \mu)/\sigma$.

Case 3: **We know:**

Standard deviation **σ**

Real value ?

Take **N** measurements; calculate average as

$$\bar{x} = \frac{x_1 + x_2 + \ldots + x_N}{N}$$

$$\mu = \bar{x} \pm \frac{2\sigma}{\sqrt{N}}$$

with 95% probability

Coinfidence interval (CI)

Case 4 We know nothing:

Mean - ? **Standard deviation -?**

Take **N** measurements; calculate **average** as

$$\bar{x} = \frac{x_1 + x_2 + ... + x_N}{N}$$

Calculate **standard deviation** as

$$s = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + ... + (x_N - \bar{x})^2}{N - 1}}$$

Confidence interval?

I do not know σ !

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

NOTE: In calculating confidence intervals, σ may be substituted for s in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-6 comes from the bottom row of Table 4-2.

Case 4 We know nothing:

Mean - ? **Standard deviation -?**

Take **N** measurements; calculate **average** as

$$\bar{x} = \frac{x_1 + x_2 + ... + x_N}{N}$$

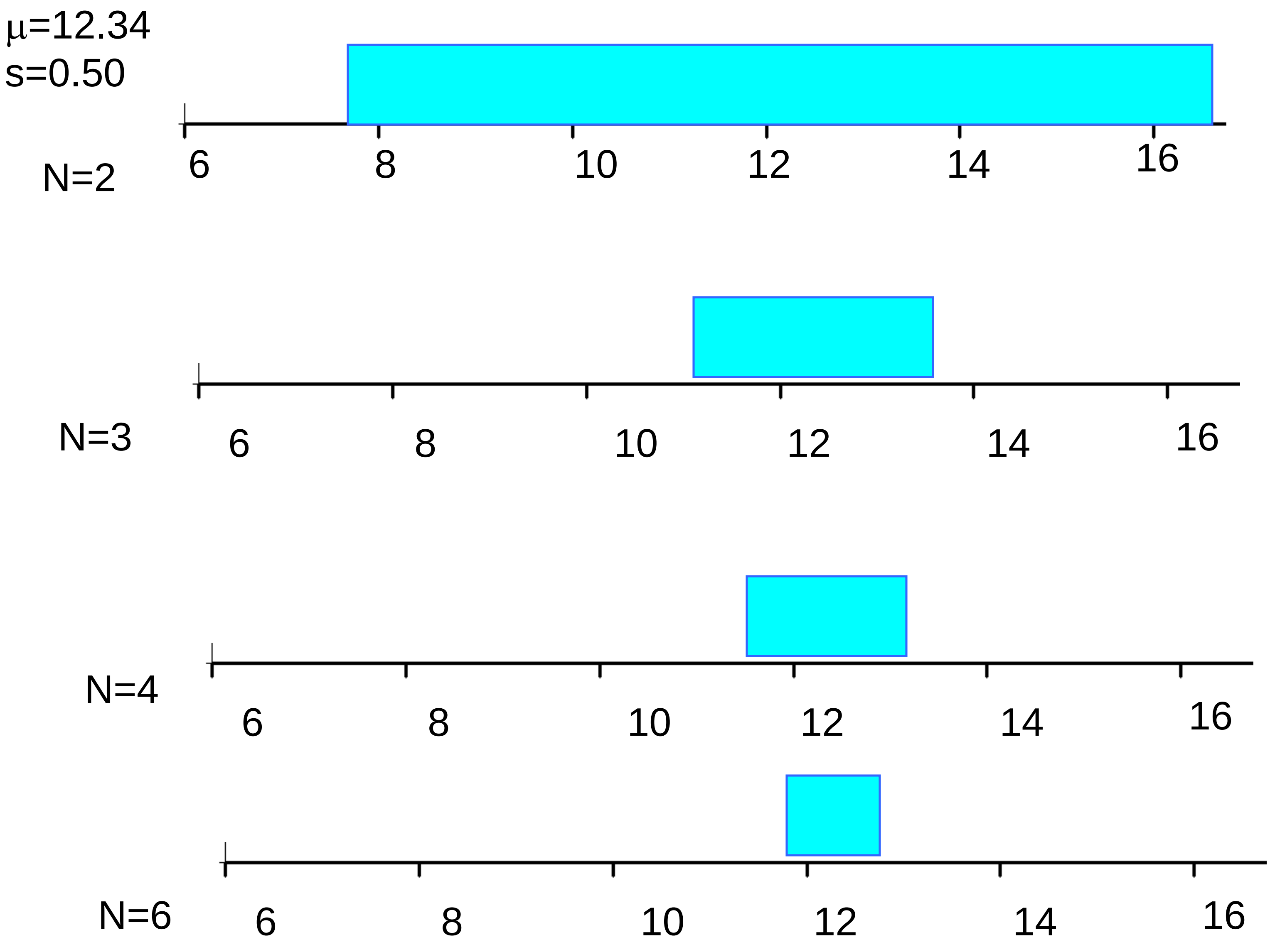
Calculate **standard deviation** as

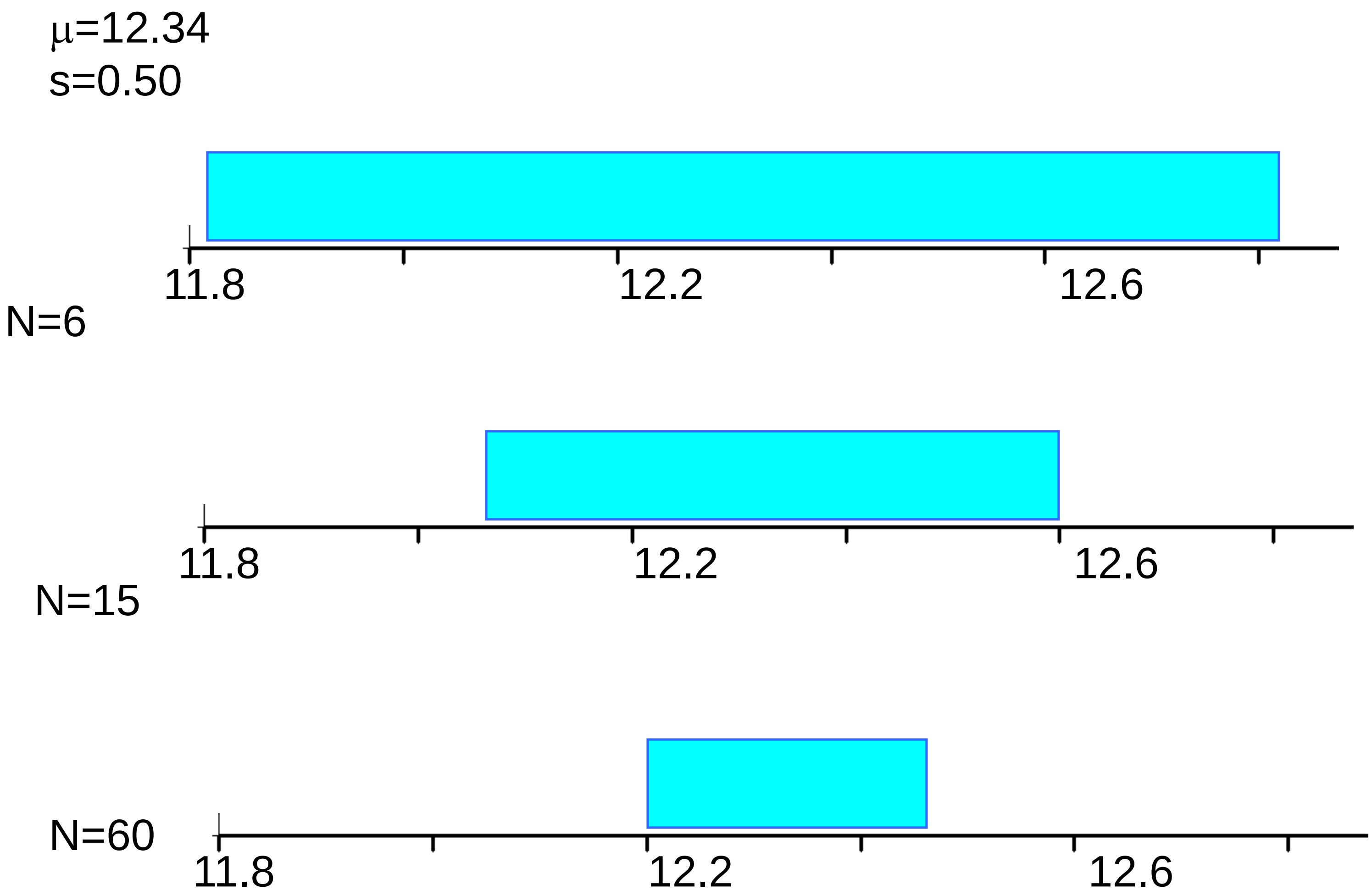
$$s = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + ... + (x_N - \bar{x})^2}{N - 1}}$$

$$\mu = \bar{x} \pm \frac{t_{95} s}{\sqrt{N}}$$

with 95% probability

Coinfidence interval (CI)


μ=12.34
s=0.50
N=2
6 8 10 12 14 16
N=3
6 8 10 12 14 16
N=4
6 8 10 12 14 16
N=6
6 8 10 12 14 16


μ=12.34
s=0.50
11.8
12.2
12.6
N=6
11.8
12.2
12.6
N=15
N=60
11.8
12.2
12.6

I titrate an unknown solution using a class A 50 mL burette. My results show standard deviation of 0.05 mL. How many mesurements I need in order to get confidence interval of ±0.01 mL?

U_{bur} = 0.05 mL

$$u_{total} = \sqrt{u_{bur}^2 + u_{random}^2}$$

N=2 $$\pm\frac{12.7\times 0.05}{\sqrt{2}} = \pm 0.44$$ $$u_{total} = \sqrt{0.44^2 + 0.05^2} = 0.44$$

N=4 $$\pm\frac{3.18\times 0.05}{\sqrt{4}} = \pm 0.08$$ $$u_{total} = \sqrt{0.08^2 + 0.05^2} = 0.095$$

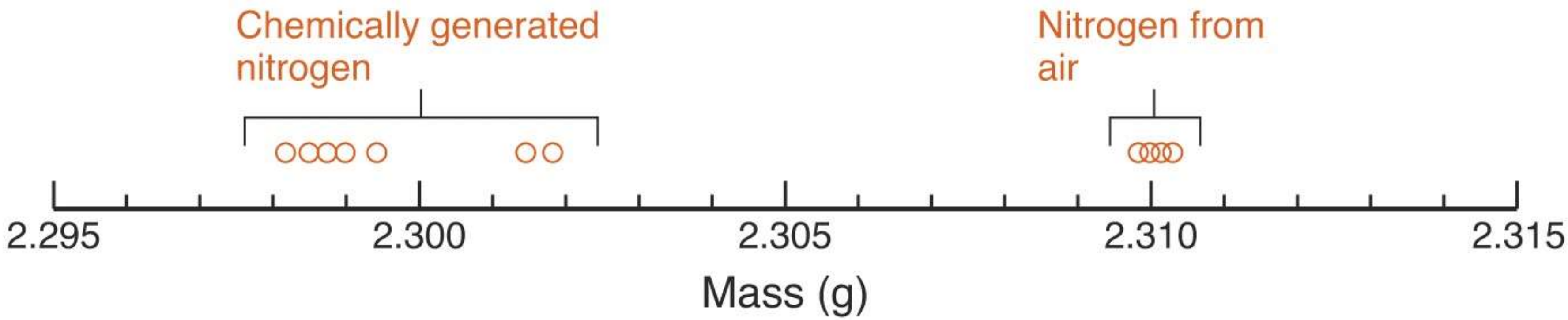
N=9 $$\pm\frac{2.3\times 0.05}{\sqrt{9}} = \pm 0.038$$ $$u_{total} = \sqrt{0.038^2 + 0.05^2} = 0.06$$

N=20 $$\pm\frac{2.1\times 0.05}{\sqrt{20}} = \pm 0.02$$ $$u_{total} = \sqrt{0.02^2 + 0.05^2} = 0.054$$

N=120 $$\pm\frac{1.98\times 0.05}{\sqrt{120}} = \pm 0.009$$ $$u_{total} = \sqrt{0.009^2 + 0.05^2} = 0.05$$

Table 4-3 Masses of gas isolated by Lord Rayleigh

From air (g)	From chemical decomposition (g)
2.310 17	2.301 43
2.309 86	2.298 90
2.310 10	2.298 16
2.310 01	2.301 82
2.310 24	2.298 69
2.310 10	2.299 40
2.310 28	2.298 49
—	2.298 89
Average	
2.310 11	2.299 47
Standard deviation	
$0.000\ 14_3$	0.001 38



A very simple rule:

CIs overlap – the same

CIs do not overlap - different