Chapter 4

# Statistics

We have already seen in Chapter 3 that all laboratory measurements have errors.

## Errors in Chemical Analysis

Impossible to eliminate errors.

How reliable are our data?
Data of unknown quality are useless!

- Carry out replicate measurements
- Analyze accurately known standards
- Perform statistical tests on data

## Random Errors

- caused by uncontrollable variables which normally **cannot** be defined.
- The accumulated effect causes replicate measurements to fluctuate randomly around the mean.
- Random errors give rise to a normal or Gaussian curve.
- Results can be evaluated using statistics.

**Usually statistical analysis assumes a normal distribution.**

# The Statistical Treatment of Random Error

## A. The Population and the Sample Data

- POPULATION = total (infinite) number of observations
- SAMPLE = finite number of observations

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B. Properties of a Gaussian Curve - has a population mean, μ, and a population standard deviation (σ).

## 1. Population mean.

- In the absence of systematic error, μ is the true value for the measurement.
- Sample mean ($\bar{x}$) defined for small values of n.
- The sample mean, $\bar{x}$, approaches μ when the number of observations approach infinity.

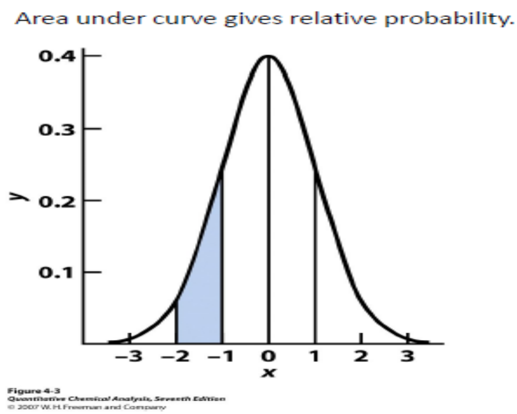
## 2. Population standard deviation (σ).

Random errors follow a Gaussian distribution of values about the central measurement.

The equation for a Gaussian curve is defined in terms of μ and σ, as follows:

Equation of Gaussian curve

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$




You don't need to memorize the above equation.

From equation above, 68.3% of the data lie within ±1σ of the mean (μ), i.e. 68.3% of the area under the curve lies between ±1σ of μ.

Similarly, 95.5% of the area lies between ±2σ, and 99.7% between ±3σ.

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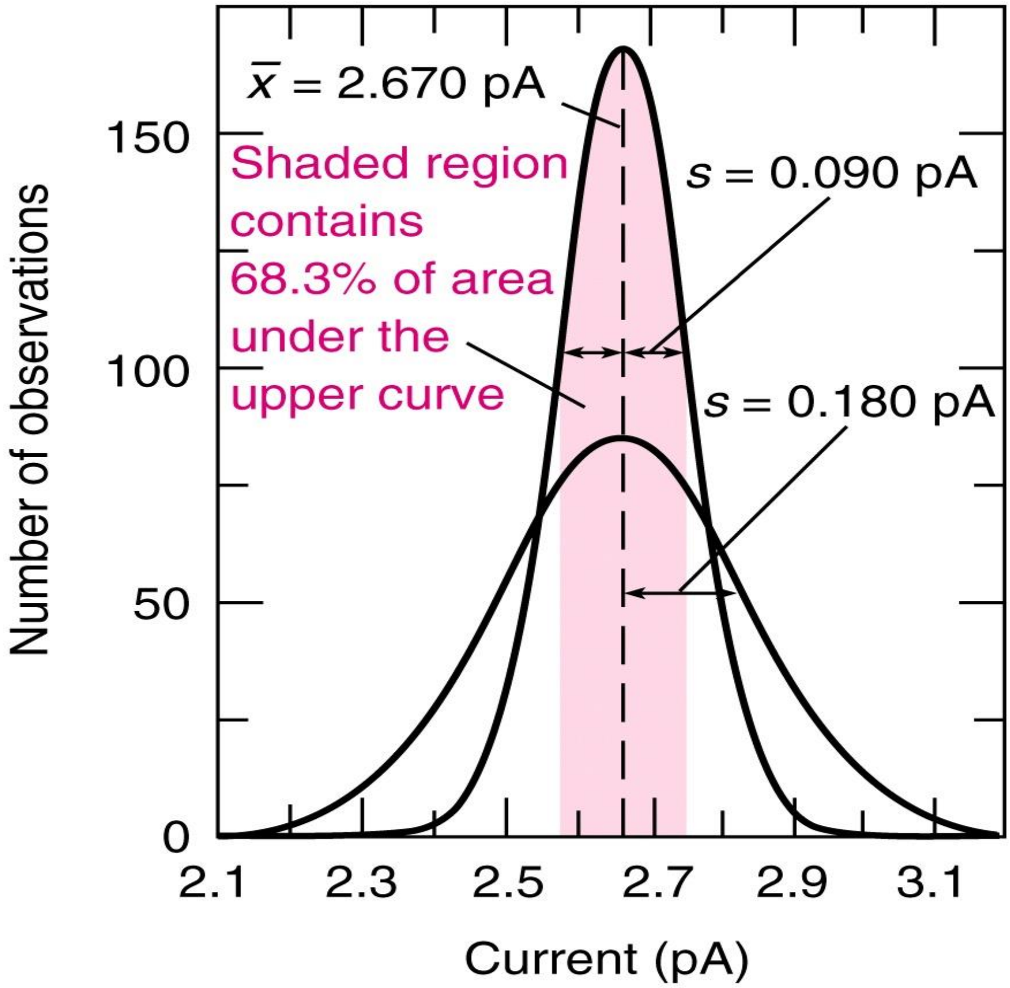
There are 68.3 chances in 100 that for a single datum the random error in the measurement will not exceed ±1σ.

The chances are 95.5 in 100 that the error will not exceeds ±2σ




Two Gaussian curves with two different standard deviations, $\sigma_{\text{lower curve}} = 2\sigma_{\text{upper curve}}$

The standard deviation measures the width of the Gaussian curve.
(The larger the value of *s*, the broader is the Gaussian curve.)

***Mean value or average*** – is a measurement of central tendency

$$x_{mean} = \frac{\Sigma_i (x_i)}{n}$$

where *i* represents each individual measurement, $\Sigma$ means the summation, and n is the number of measurements in that set of data.

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For a set of data, the closer your mean is to the true value, the more accurate your results are.

## *Standard Deviation (Reproducibility)*

• Standard deviation is based on the fact that you will assume that errors are the result of RANDOM events.
• It is based on the shape and distribution of the Gaussian Curve.
• A smaller standard deviation means that your results are more reproducible (they don't vary as much from measurement to measurement).

Standard deviation – is the measure of the width of the distribution about the central value.

$$S = \sqrt{\Sigma_i \frac{(x_i - x_{mean})^2}{n-1}}$$

The above defined standard deviation is for a limited or small set of data; for a large set of data the standard deviation is indicated by $\sigma$ and is defined as

$$\sigma = \sqrt{\Sigma_i \frac{(x_i - x_{mean})^2}{n}}$$

As the size of the data set increases there $(n-1) \to n$, so $\bar{x} \to \mu$ and $s \to \sigma$

Ordinarily analytical chemists will use the first value (*s*) for the standard deviation since we will typically deal with a small population or small data set.

The standard deviation expressed as a percentage of the mean value is called the relative standard deviation (RSD) or the coefficient of variation (CV).

$$Coefficient\ of\ variation\ (CV) = \frac{s}{\bar{x}} \times 100$$

The square of the standard deviation is called the variance ($s^2$)

$$S^2 = \frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1}$$

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*The Range* (*Spread*) is the difference between the highest and lowest values in the set of data.

**Example 1**: Find the *mean, standard deviation, relative standard deviation and the range* of the following set of student data acquired in the analysis of chloride in a sample:

$x_i$ = 18.56%; 18.65%; 18.49%; 18.54%; 18.70%, 18.53%

**Use your calculator to calculate the mean (average) and the standard deviation:**

$\bar{x} = 18.57_8$ and $s = 0.08_0$

Retain one or more insignificant digits to avoid introducing round-off errors into subsequent work.

The *average* and the *standard deviation* should both end at the same decimal place.

The coefficient of variation is the percent relative uncertainty:

$$CV = \frac{0.08_0}{18.57_8} \times 100 = 0.4_3 = 0.4$$

Range = 18.70% - 18.49% = 0.21%

We commonly express experimental results in the form

$\bar{x} \pm s = 18.58 \pm 0.08 \ (n = 6)$

**Question**) measurements of Fe (III) concentrations:

19.5; 19.6; 19.4; 19.8; 20.1; and 20.3 ppm

What are the mean, standard deviation, variance, coefficient of variation (CV) and range (w) of the data set?

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$\bar{x} =$ , $s =$ , $CV =$ , $s^2 =$ , $range =$

## Standard Deviation of the Mean

Standard deviation of the mean of sets of n values: $\sigma_n = \frac{\sigma}{\sqrt{n}}$

$\sigma_4 = \frac{\sigma}{\sqrt{4}}$

The more times you measure a quantity, the more confident you can be that the average is close to the population mean.

Uncertainty decreases in proportion to $\frac{1}{\sqrt{n}}$, where *n* is the number of measurements.

You can decrease uncertainty by a factor of $2(=\sqrt{4})$ by making 4 times as many measurements and by a factor of $10(=\sqrt{100})$by making 100 times as many measurements.

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# Use of Statistics in Data Evaluation

● How can we relate the observed mean value ($\bar{x}$) to the true mean (μ)? The latter can never be known exactly.

● The range of uncertainty depends how closely s corresponds to σ

● We can calculate the limits (above and below) around $\bar{x}$ that μ must lie, with a given degree of probability.

**Confidence Limit (CL):** define an interval around mean ($\bar{x}$) that probably contains population mean (μ).

➢ Set limits around an experimental mean within which the population mean (μ) lies with a given degree of probability.

➢ Limits are called confidence limits, and the interval is called as **Confidence Interval**

## Confidence Intervals

• Student's t is a statistical tool used most frequently to express **confidence intervals** and to **compare results** from different experiments. Abdul-Wahab Rjoob

$$Confidence\ interval = \bar{x} \pm \frac{t \times s}{\sqrt{n}}$$

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 | 63.656 | 127.321 | 636.578 |
| 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.*

Table 4-2
*Quantitative Chemical Analysis, Seventh Edition*


- Values of Student's t increases with increasing confidence level.
- Values of Student's t decreases with increasing number of measurements within the same confidence level.

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Example 2: Lets go back to the % chloride data and calculate the 50%, 90%, 95% and 99% confidence intervals for the results.

$x_i$ $\bar{x}$ = **18.57$_8$** **s = 0.08$_0$**

18.56%
18.65%
18.49%
18.54%
18.70%
18.53%

At the 50% confidence level:

$$\mu = 18.57_8 \pm \frac{(0.727)(0.08_0)}{\sqrt{6}} = 18.57_8 \pm 0.02_4$$

$(18.55_4 - 18.60_2)$

Now repeating the calculation with the appropriate values of t

At the 90% confidence level:

$$\mu = 18.57_8 \pm \frac{(2.015)(0.08_0)}{\sqrt{6}} = 18.57_8 \pm 0.06_6$$

At the 95% confidence level:

$$\mu = 18.57_8 \pm \frac{(2.571)(0.08_0)}{\sqrt{6}} = 18.57_8 \pm 0.08_4$$

At the 95% confidence level:

$$\mu = 18.57_8 \pm \frac{(4.032)(0.08_0)}{\sqrt{6}} = 18.57_8 \pm 0.13_2$$

Question: For n = 3, the $\bar{x}$ and s were found to be 15.78 and 0.30 respectively. Calculate the 95% confidence interval.

For n = 3, n-1 = 2: $t_{95,2} = 4.303$

$$\mu = 15.78 \pm \frac{(4.303)(0.30)}{\sqrt{3}} = 15.78 \pm 0.75$$

Repeat the previous calculation for n = 7 with the same $\bar{x}$ and s values. Calculate the 95% confidence interval.

$$\mu = 15.78 \pm \frac{(2.447)(0.30)}{\sqrt{7}} = 15.78 \pm 0.28$$

# Comparison of Mean with Student's t

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Case 1. Comparing a Measured Result with a "Known" Value

Calculate confidence interval $\bar{x} \pm \frac{ts}{\sqrt{n}}$

If the known value is not within the 95% confidence interval, then the results do not agree.

Example 3: A reliable assay shows that the ATP (adenosine triphosphate) content of a certain cell type is 111 µmol/100 mL. You developed a new assay, which gave the following values for replicate analyses:
117, 119, 111, 115, 120 µmol/100 mL (average =116.4).

Does your result agree with the known value at the 95% confidence level?

Use your calculator to determine $\bar{x}$ and s

$\bar{x} = 116._4$ and $s = 3._6$

$$116._4 \pm \frac{(2.776)(3._6)}{\sqrt{5}} = 116._4 \pm 4._5$$

$$= 111._9 \text{ to } 120._9 \ \mu\text{mol/100 mL}$$

The 95% confidence interval does not include the accepted value of 111 µmol/100 mL, so the **difference is significant**.

## Case 2. Comparing Replicate Measurements

Do the results of two different sets of measurements agree "within experimental error"? Abdul-Wahab Rjoob

Case 2 - compare two measured average values for two analyses

Calculate $t_{calc}$

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

where $$s_{pooled} = \sqrt{\frac{s_1^2(n_1-1)+s_2^2(n_2-1)}{n_1+n_2-2}}$$

If $t_{calc} > t_{table}$ then the two values are different

**Example 4 – As the director of a research laboratory you are paid to decide if there is a significant difference between the mean values of two sets of data obtained by two different scientists, a senior scientist and one recently hired.**

**Data of Senior Scientist: $x_{mean}$ = 24.66% with s = 0.06% for n = 5**

**Data of the New Kid: $x_{mean}$ = 24.55% with s = 0.10% for n = 7**

What we need to do here is the compare the two mean values, $x_{1\ mean}$ to $x_{2\ mean}$ as their difference ($x_{1mean}$-$x_{2\ mean}$) to ($\pm ts / \sqrt{n}$). Because there are two different standard deviations, we need to calculate the pooled standard deviation, $s_{pool}$ which is defined as

$$s_{pool} = \sqrt{\{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2\} / (n_1 + n_2 - 2)}$$

$$s_{pool} = \{(5 - 1)(0.06)^2 + (7 - 1)(0.10)^2 / (5 + 7 - 2)\}^{1/2}$$

$s_{pool} = \{(4)(0.0036) + (6)(0.010) / (10)\}^{1/2} =$
$\{(0.018 + 0.060) / (10)\}^{1/2} = \{0.0078\}^{1/2}$

$$s_{pooled} = 0.086 = 0.09$$

***Note that the value of $s_{pool}$ will always fall between the two individual values of s; it is like a weighed average value.***

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

$$t_{calculated} = \frac{|24.66 - 24.55|}{0.086} \sqrt{\frac{5 \times 7}{5 + 7}}$$

$= 2.184$

We will use the value of $t_{95}$ for 7 + 5 – 2 or 10 degrees freedom; according to Table 4-2, $t_{95,10} = 2.228$.

$t_{table} = 2.228$

No, there is no significant difference between the mean values of the two scientists.

**Case 3. Paired *t* Test for Comparing Individual Differences**

In this case, we use two methods to make single measurements on several different samples.

No measurement has been duplicated. Do the two methods give the same answer “within experimental error”?

Case 3- compare two methods using single measurements on multiple samples

- use the Paired t-test

- compute difference for each sample

$$d_i = x_{i(method 1)} - x_{i(method 2)}$$

$$-calculate\ \bar{d}\ and\ s_d$$

$$s_d = \sqrt{\frac{\sum (d_i - \bar{d})^2}{n-1}}$$

$$\text{compute } t_{calc} = \frac{|\bar{d}|}{s_d}\sqrt{n}$$

Case 3 Example: eleven different samples were analysed for aluminum using two different methods. Do the two methods give the same result at the 95% confidence level?

| | A | B | C | D |
|---|---|---|---|---|
| 1 | Comparison of two methods for measuring Al | | | |
| 2 | | | | |
| 3 | Sample | Method 1 | Method 2 | Difference |
| 4 | number | (μg/L) | (μg/L) | ($d_i$) |
| 5 | 1 | 17.2 | 14.2 | −3.0 |
| 6 | 2 | 23.1 | 27.9 | 4.8 |
| 7 | 3 | 28.5 | 21.2 | −7.3 |
| 8 | 4 | 15.3 | 15.9 | 0.6 |
| 9 | 5 | 23.1 | 32.1 | 9.0 |
| 10 | 6 | 32.5 | 22.0 | −10.5 |
| 11 | 7 | 39.5 | 37.0 | −2.5 |
| 12 | 8 | 38.7 | 41.5 | 2.8 |
| 13 | 9 | 52.5 | 42.6 | −9.9 |
| 14 | 10 | 42.6 | 42.8 | 0.2 |
| 15 | 11 | 52.7 | 41.1 | −11.6 |
| 16 | | | mean = | −2.491 |
| 17 | | | std dev = | 6.748 |
| 18 | | | $t_{calculated}$ = | 1.224 |

$t_{table}$ = 2.228 for 95% and d.o.f. = 10

So the two methods are not significantly different

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## Comparison of Standard Deviations with the *F* Test

To decide whether Rayleigh's two sets of nitrogen masses in Figure 4-7 are "significantly" different from each other, we used the *t* test. If the standard deviations of two data sets are not significantly different from each other, then we use Equation 4-8 for the *t* test. If the standard deviations are significantly different, then we use Equation 4-8a instead.

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The ***F* test** tells us whether two standard deviations are "significantly" different from each other. *F* is the quotient of the squares of the standard deviations:

$$F_{calculated} = \frac{s_1^2}{s_2^2}$$

We always put the larger standard deviation in the numerator so that F $\geq 1$ . We test the hypothesis that $s_1 > s_2$ by using the one-tailed *F* test in Table 4-4. If $F_{\text{calculated}} > F_{\text{table}}$, then the difference is significant.

If $F_{\text{calculated}} > F_{\text{table}}$, use equation 4-8

If $F_{\text{calculated}} < F_{\text{table}}$, use equation 4-8a

**TABLE 4-4** 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 |

*Critical values of F for a one-tailed test of the hypothesis that $s_1 > s_2$. There is a 5% probability of observing F above the tabulated value.*

*You can compute F for a chosen level of confidence with the Excel function FINV(probability, deg_freedom1, deg_freedom2). The statement "=FINV(0.05,7,6)" reproduces the value F = 4.21 in this table. The statement "=FINV(0.1,7,6)" gives F = 3.01 for 90% confidence.*

## Example page 81:

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**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 |

*SOURCE: R. D. Larsen, J. Chem. Ed. 1990, 67, 925; see also C. J. Giunta, J. Chem. Ed. 1998, 75, 1322.*

**Table 4-3**
***Quantitative Chemical Analysis, Seventh Edition***

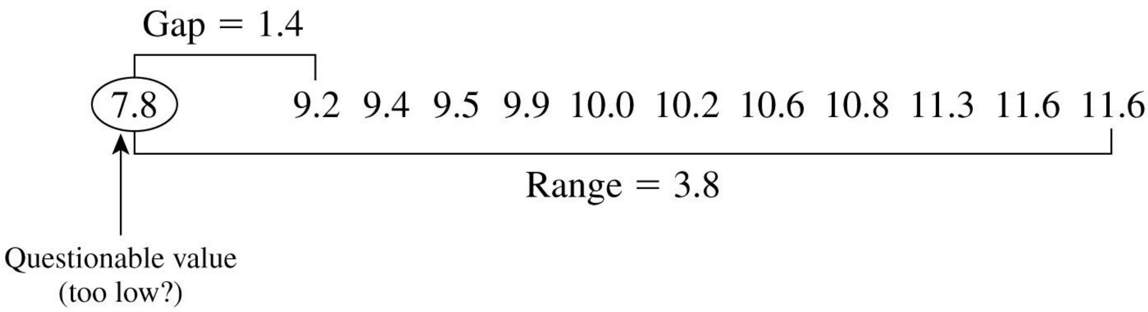

From table 4-3: $s_1 = 0.00138$ (for $n_1 = 8$ measurements)
and $s_2 = 0.00014_3$ (for $n_2 = 7$ measurements)

$$F_{calculated} = \frac{s_1^2}{s_2^2} = \frac{(0.00138)^2}{(0.00014_3)^2} = 93._1$$

In Table 4-4, look for $F_{table}$ in the column with 7 degrees of freedom for $s_1$ (because degrees of freedom = $n - 1$) and the row with 6 degrees of freedom for $s_2$. $F_{table}$ in the column under 7 and across from 6 is 4.21.

*Because $F_{calculated}$ (= 93.1) > $F_{table}$ (=4.21), the standard deviations are different from each other above the 95% confidence level.*

## 4-6 Grubbs Test for an Outlier (Gross Error)




$$G_{calculated} = \frac{|questionable\ value - \bar{x}|}{s}$$

*If $G_{calculated}$ is greater than G in Table 4-5, the questionable point should be discarded (rejected).*

$\bar{x}$ = 10.16 and s = 1.11

$$G_{calculated} = \frac{|7.8-10.16|}{1.11} = 2.13$$

In table 4.5, $G_{table}$ = 2.285 for 12 measurements. Because $G_{calculated} < G_{table}$, the questionable point should be retained.

***There is more than a 5% chance that the value 7.8 is a member of the same population as the other measurements.***

Testing for bad data – *G* test

12.47

12.48

12.53

12.56

12.67

*x(bar) = 12.542*

$s_x$ *= 0.0804*

$$G_{calc} = \frac{|12.67 - 12.542|}{0.0804} = 1.59$$

Note: Harris 7th edition uses Q-test.
Don't confuse the two.

**TABLE 4-5 Critical values of *G* for rejection of outlier**

| Number of observations | *G* (95% confidence) |
|---|---|
| 4 | 1.463 |
| 5 | 1.672 |
| 6 | 1.822 |
| 7 | 1.938 |
| 8 | 2.032 |
| 9 | 2.110 |
| 10 | 2.176 |
| 11 | 2.234 |
| 12 | 2.285 |
| 15 | 2.409 |
| 20 | 2.557 |

$G_{calculated}$ = |*questionable value − mean*|/*s. If* $G_{calculated} > G_{table}$, *the value in question can be rejected with 95% confidence. Values in this table are for a one-tailed test, as recommended by ASTM.*

SOURCE: *ASTM E 178-02 Standard Practice for Dealing with Outlying Observations, http://webstore.ansi.org; F. E. Grubbs and G. Beck, Technometrics* **1972**, *14, 847.*

Harris, *Quantitative Chemical Analysis*, 8e





Should the value 216 be rejected from the set of results 192, 216, 202, 195, and 204?