



## QMS Quick Learning Activity

# Analytical Measurement Uncertainty

ISO/IEC 17025:2005



# Abbreviations and Acronyms

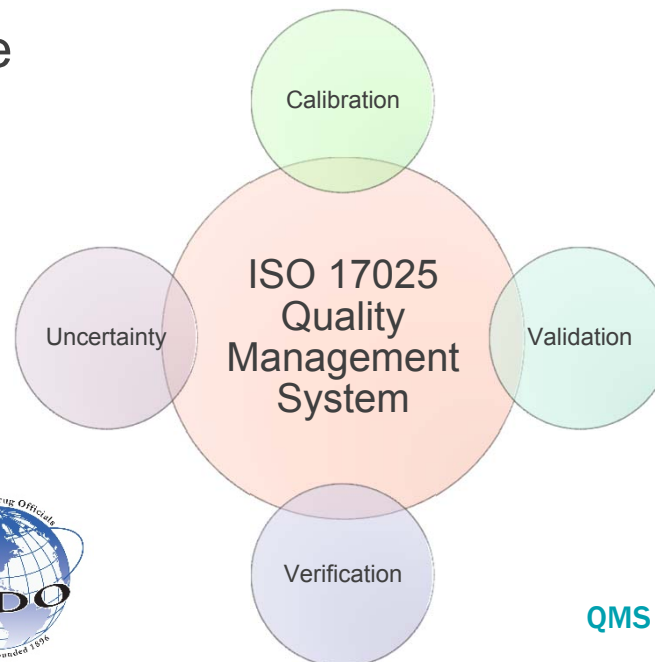
- Please see the accompanying Analytical Measurement Uncertainty Learning Aid, including Dictionary of Terms
- **FDA**-Food and Drug Administration
- **SOP**-Standard Operating Procedure
- **EPA**-Environmental Protection Agency
- **NIOSH**-National Institute for Occupational Safety and Health
- **OSHA**-Occupational Safety and Health Administration
- **ASTM**-American Society for Testing and Materials International
- **AIHA**-American Industrial Hygiene Association



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# Why ISO/IEC 17025 Accreditation?

- Accreditation provides formal recognition that laboratories can achieve a level of reliable testing and measurement.
- Customers are then able to identify and select laboratories that produce services to meet their needs.
- The Food and Drug Administration (FDA) will be requiring ISO/IEC 17025 accredited laboratories for human and animal food testing.
- Becoming ISO compliant
  - “General requirements for the competence of testing and calibration laboratories”, ISO/IEC 17025:2005.
    - Section 5.4.6  
**Estimation of Analytical Uncertainty**



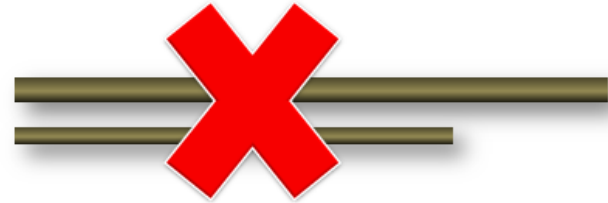
# Overview-What do I need to know?

- What is Measurement?
- What is Measurement Uncertainty?
- Measurement Techniques
  - Review some basic statistics
- Terms and Calculations



# What is not a measurement?

- There are some processes that might seem to be measurements, but are not.
  - Counting is not normally viewed as a measurement, it is a number.
  - Comparing two pieces of string to see which is longer is not really a measurement.
- A measurement usually has two components, a number and a unit of measure.



## Number

- >350
- 12.3
- 6
- 1124.7
- <1

## Unit of Measure

- Feet
- Meters
- Mg%
- g/kg
- mL



# What is a Measurement?

Measurement is:

- A set of operations that determine the value of a quantity.
- It tells us about a property of something (how heavy, hot, or long an object is).
- They are made using an instrument (e.g., rulers, weighing scales, stopwatches, thermometers, etc.)
- A measurement is taken by comparing an unknown quantity, such as the length of the stick we looked at previously... with a standard unit like a ruler.
- The instruments used to make these comparisons can be simple ones, like rulers, scales, stopwatches and thermometers or they can be complex scientific instruments.



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# What is the Purpose of Measurement?

- To obtain a *value* (result).
- To provide information about a **quantity** of interest—a **measurand**.
- Definition of Measurand:
  - A particular **quantity** (of something) being measured.
- Use “analyte” to refer to the substance being measured, not the quantity.



# A Measurement System Contains:

- The **sampling** techniques used in collecting the sample,
- The **subsampling** technique used in the laboratory,
- The **procedure/method** (SOP) used,
- The skill of the **operator**,
- The **environment** (temperature, barometric pressure, etc.).



Temperature

Barometric Pressure

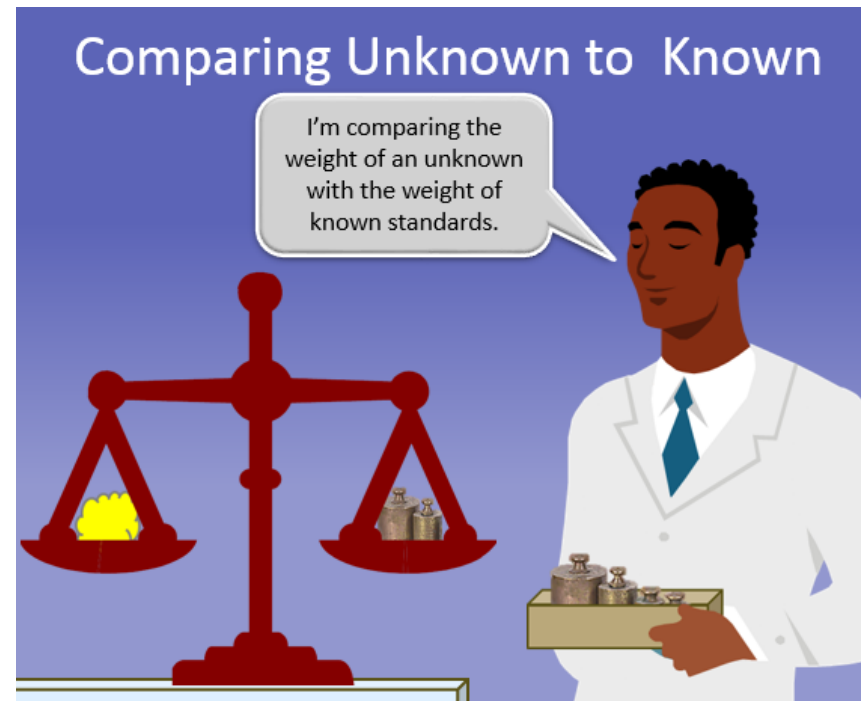
Humidity



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# Comparing Unknown to Known

- No matter what instrument or unit of measure we use or how carefully we perform the measurement, we are still making a comparison.
- A comparison cannot ever be perfect, even with very precise instruments. So all measurements inherently include some degree of error.



# Logic 101

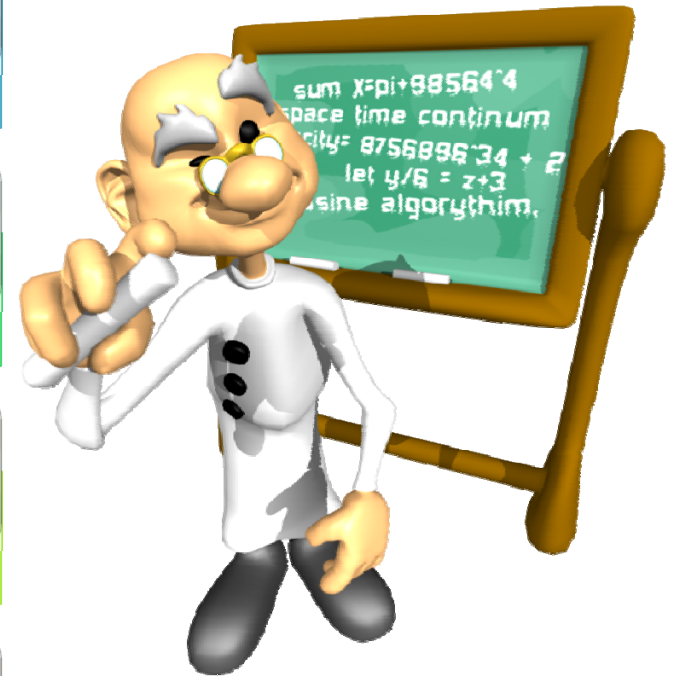
Follow along as the professor presents his logic:

A **True value** is obtained only by a perfect measurement.

No measurement system is perfect!

Therefore, we can never obtain a **true value**.

So, some **statistical predicatability** must be provided in a measurement.



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# What is Measurement Uncertainty (MU)?

- MU is the doubt that exists about the result of any measurement.
- You might think that well-made rulers, thermometers, and scales always give the right answer. But for every measurement - even the most careful one - there is always a margin of doubt.
- This is expressed in our everyday lives as 'give or take'.



My cat weighs twelve pounds, give or take an ounce or two.

# Think about it

You may be interested in measurement uncertainty just because you want to make good, quality measurements and to be able to understand the results, or because your clients or certifying agency requires it. Here are a few specific instances when you'll have to be aware of measurement uncertainty.

Calibration-the uncertainty of the measurement has to be reported on the certificate.

Test-where the uncertainty of measurement is needed to determine pass or fail.

Meet a Tolerance-you have to know the uncertainty before you can decide if the tolerance is met.

You must read & understand a calibration certificate or a written specification for a test or measurement.

Quality matters to me!



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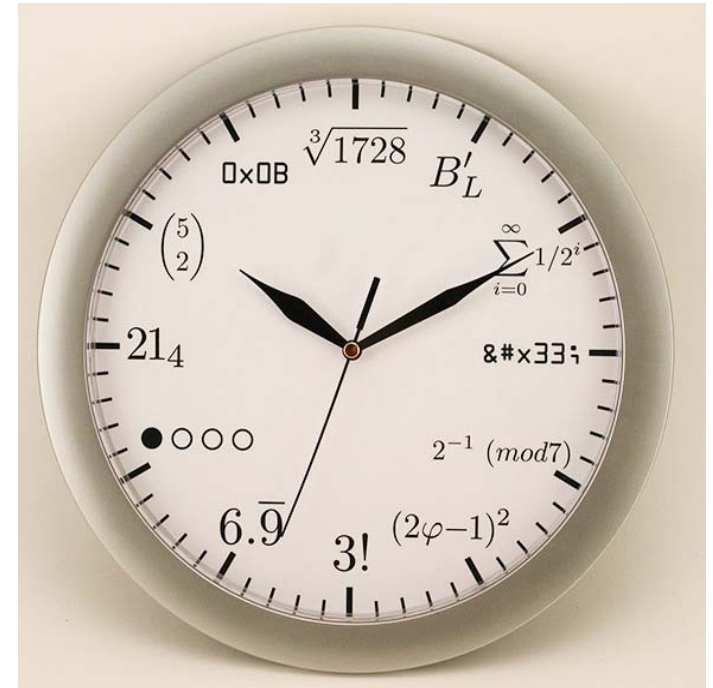
# Analyte vs. Measurand

- Analyte:
    - Use “analyte” to refer to the substance being measured, not the quantity.
    - Examples: mercury, arsenic, *Escherichia coli*, *Salmonella*, pesticides,
  - Measurand:
    - A particular Quantity (of something) being measured.
    - Which uses a Unit of measurement.
    - Is based on a Matrix-examples: fish, feed, vegetables, juice, etc.
    - And contains the Analyte (the substance being measured).
- Measurand is expressed as:
- The fish (matrix) contains 462 (quantity)  $\mu\text{g/kg}$  (units) of arsenic (analyte).

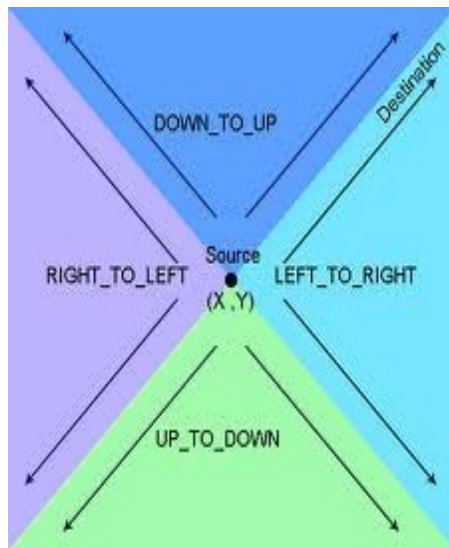


# Begin With a Reference Point:

- What are the units (degree or quantity) of the measuring instrument or device?
  - Example: a clock can indicate seconds, minutes, hours. If I say it is 'one', do I mean 'one second', 'one hour', or 'one o'clock'?
  - What units does your instrument use for measuring? Is it measuring weight (e.g.,  $\mu\text{g}/\text{kg}$ ,  $\text{kg}$ ), degrees, wavelength, volume (e.g.,  $\text{mL}$ ), etc.?



# Other Reference Points:

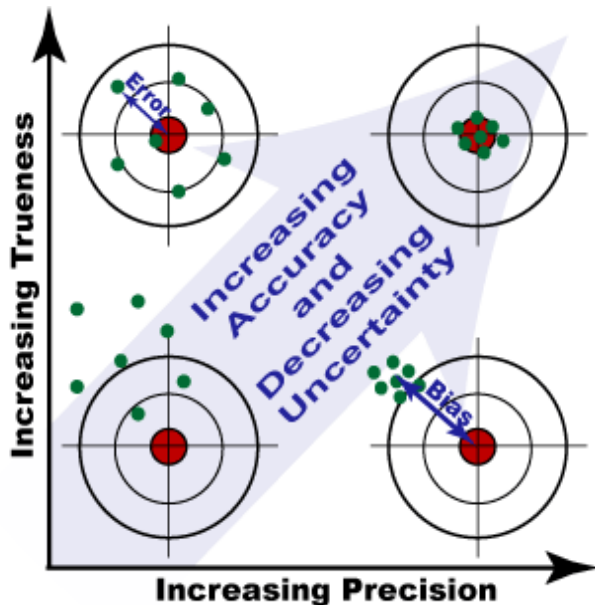


- The uncorrected result (raw number),
- The corrected result (calculations used in the method),
- Whether averages were used to obtain result.



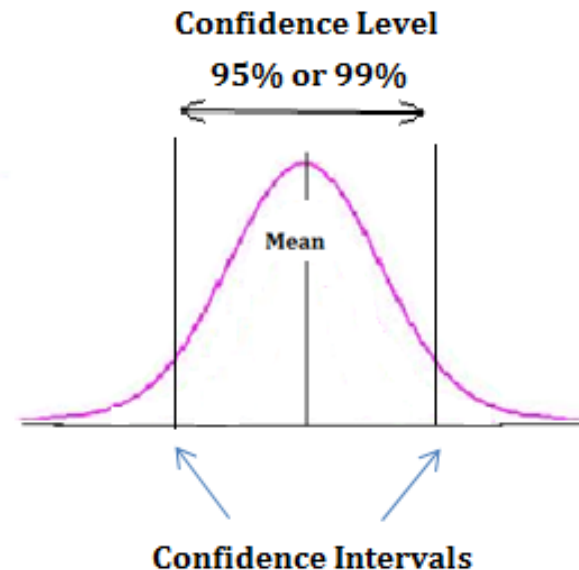
# To Express Uncertainty

- You need to know:
  - “How big is the margin (possible range)?”
    - Example: working in the linear portion of the calibration curve vs. working close to the detection limits.
  - “How bad is the doubt?” (Do I trust this value?)
  - Once you know the possible range, you can decide if you trust the value.



# You need 2 numbers to express (quantify) an uncertainty

- Confidence Intervals:
  - A range of values about something (a parameter, e.g., the length of my shoe). We estimate that the true value lies within this range.
- Confidence level:
  - The doubt that exists that my true value falls within the range.



# Expressing, or Quantifying, Uncertainty

- Confidence intervals: the width of the margin (range)
  - Can be based on standard deviation.
  - The fewer the numbers, the wider the margin. Narrow margins are preferred, so use more data points.
  - Applies only to a parameter, not the individual numbers of each measurement.
    - Example: my shoe length (parameter) measures between 9 and 11 inches every time I measure it (9, 9.5, 9.7, 10.6, 10.9, 11).
- Confidence level: how sure are we that the true value is within the margin (interval)?
  - Example: “I can be 95% sure that my value is correct.”



# Example



- The length of a shoe is 10 inches plus or minus 1 inch, at the 95 percent confidence level

Written as, “10 in.  $\pm$  1 in., at a level of confidence of 95%

- “I’m 95% sure that the shoe is 9-11 in. long”

# Uncertainty is Not Error!

- Uncertainty should not be confused with:
  - Errors or mistakes,
  - Tolerances (which are usually based on instrumentation),
  - Specifications (which can be method or instrument based),
  - Accuracy, or rather, Inaccuracy,
  - Statistical Analysis (uncertainty analysis is one of the **uses** of statistics).
- **Uncertainty is the quantification of the doubt about the measurement result.**



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# Error vs. Uncertainty

- Error is the difference between the measured value and the true value of the measurand, which can never be exactly known.
- Uncertainty is quantifiable.
- Uncertainty is not an estimate of error or its limits unless you are sure that no systematic effects have been overlooked.
- There are two types of errors:
  - Systematic; also called measurement bias.
    - Remains constant.
  - Random; when the repeated value is different from the previous value.
    - Cannot be predicted.



# Systematic Error is also known as Measurement Bias

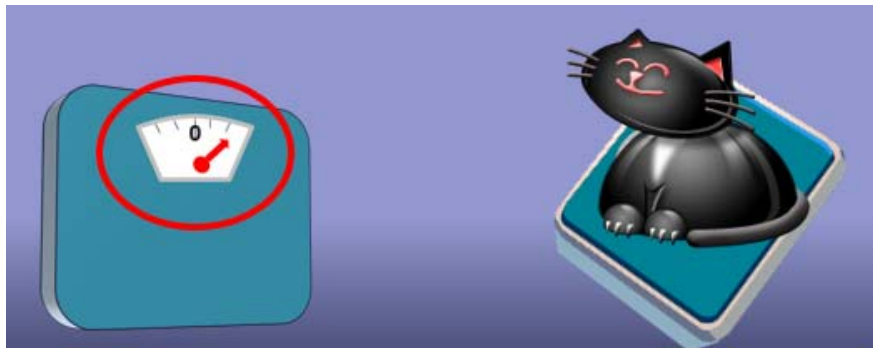
- Measurement Bias is a component of error that remains constant.
  - Example: the analyst consistently uses the incorrect pipette setting each time of use - 20 end results will be incorrect 20 times.
  - The error cannot be fixed by repeating the measurement, no matter how many times you do it.
- Sometimes, systematic error can be reduced by applying a calibration factor to correct an instrument reading.
  - Adding, subtracting, multiplying or dividing by a correction factor that's recognized when calibrating a standard.



# Correcting Systematic Error

## Offset Value

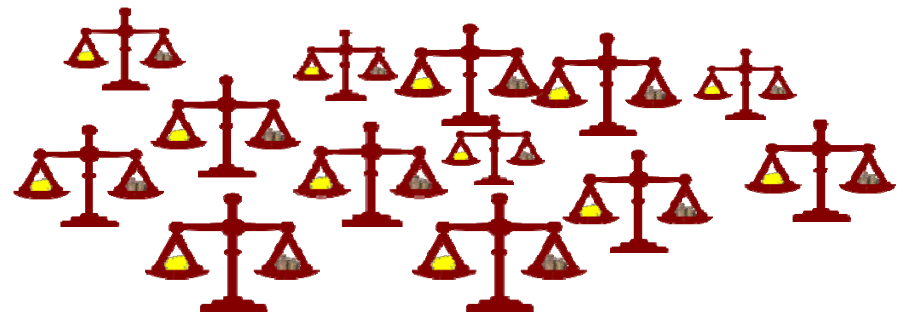
- An offset value is the amount by which a measurement is affected due to some other factor or effect.
- If my bathroom scale, with nothing on it, reads 3 pounds, I can weigh my cat as many times as I can catch her and every measurement will be affected by the same offset value of three pounds. Since I know the scale should read zero with nothing on it, I can compensate for the offset by subtracting three pounds from each measurement I make.



# Error

## Random Error

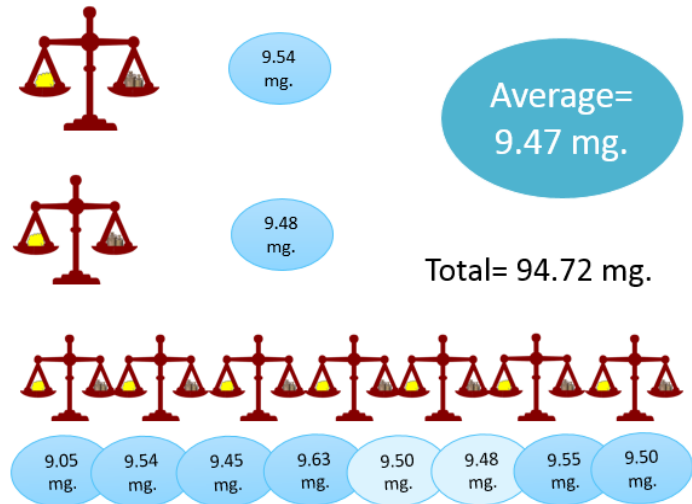
- Random error is always present in a measurement and is caused by variations in the readings of the instrument due to precision limitations or in the operator's interpretations.
- Random errors can not be predicted because every repeated value is different from the previous value.
- Unlike systematic errors, random errors can be reduced by averaging a large number of observations.



# Reducing random error

- Reduce the effects of random error by increasing the number of measurements.
  - The first time the scientist weighed the substance, the result was 9.54 milligrams.
  - The second measurement was 9.48 mg.
  - We have no way of knowing if either of these two numbers is close to the true weight.
- Random error is closely related to precision.
  - The greater the precision of a measurement instrument, the smaller the variations in its readings.

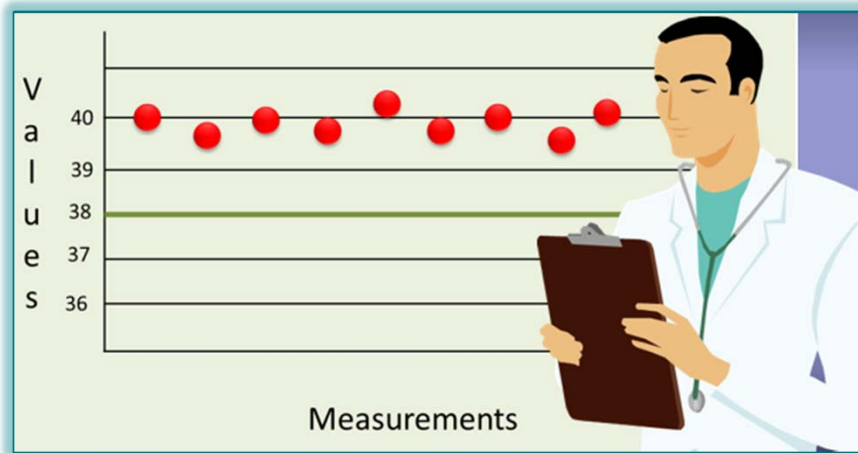
- By taking ten separate measurements, we can total them and find the average, or mean value.
- Taking multiple measurements reduces the effects of random error and the average provides a better estimate of the true value than does a single measurement.



# Precision

The measurement repeats and is reproduced under certain circumstances.

- Precision exists when the same, or nearly the same, measurement repeats again and again.

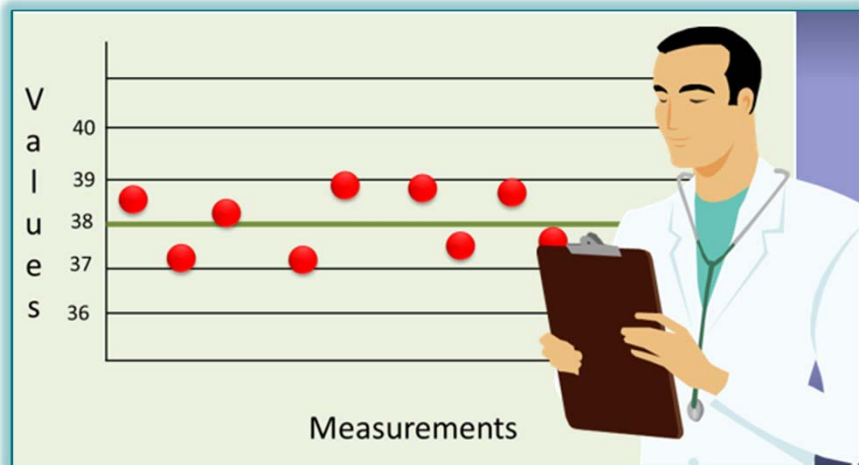


In the diagram, the center line represents the true value of 38 and the red dots indicate the measurement results.

Here, the results are all close to the same value, 40, indicating precision, but they are not near the true value and are therefore not accurate.

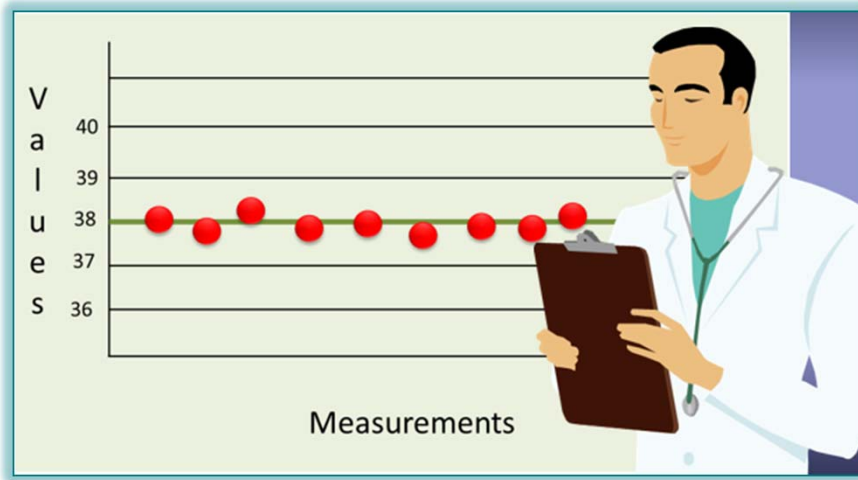
# Accuracy

How much your measurement differs from the true value.

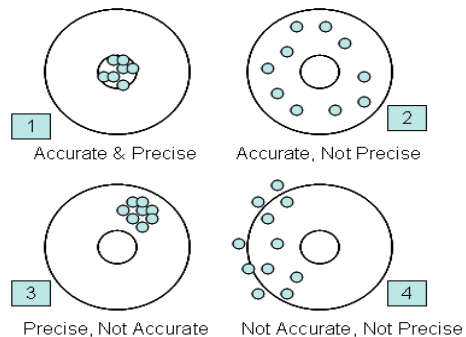


- Accuracy indicates how much your measurement differs from the true value.
- Here, we can see that every measurement value is close to the true value, but the same measurement is not repeated again and again.
- This indicates accuracy, but not precision.

# Accuracy and Precision

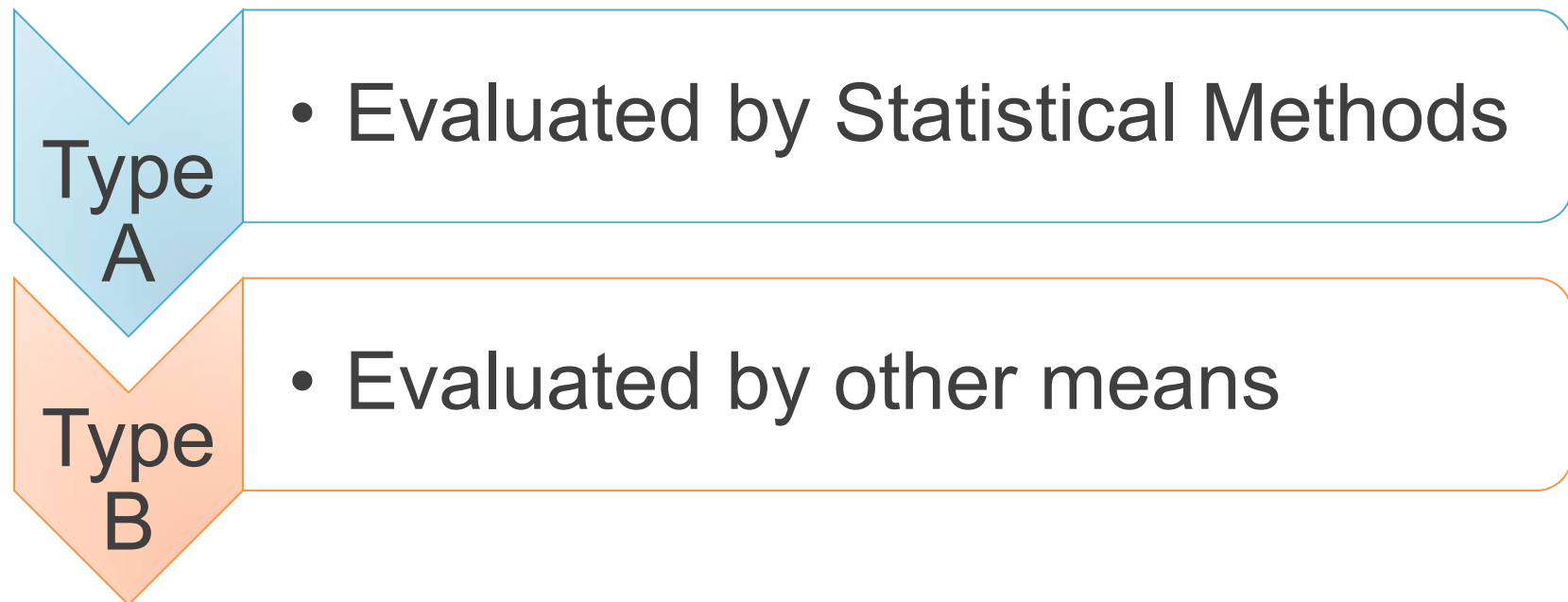


- The diagram now shows results that are accurate, because they are near or at the true value and precise, because the results are repeated again and again.
- Highly precise instruments may give the same result over and over. That doesn't mean the result is accurate.
- Accuracy can never be better than the precision and the constraints in the system.



# You have numbers, now what?

So, how do we arrive at a statement of uncertainty to accompany the value? The uncertainty, which must be quantitative, can be divided into two categories.



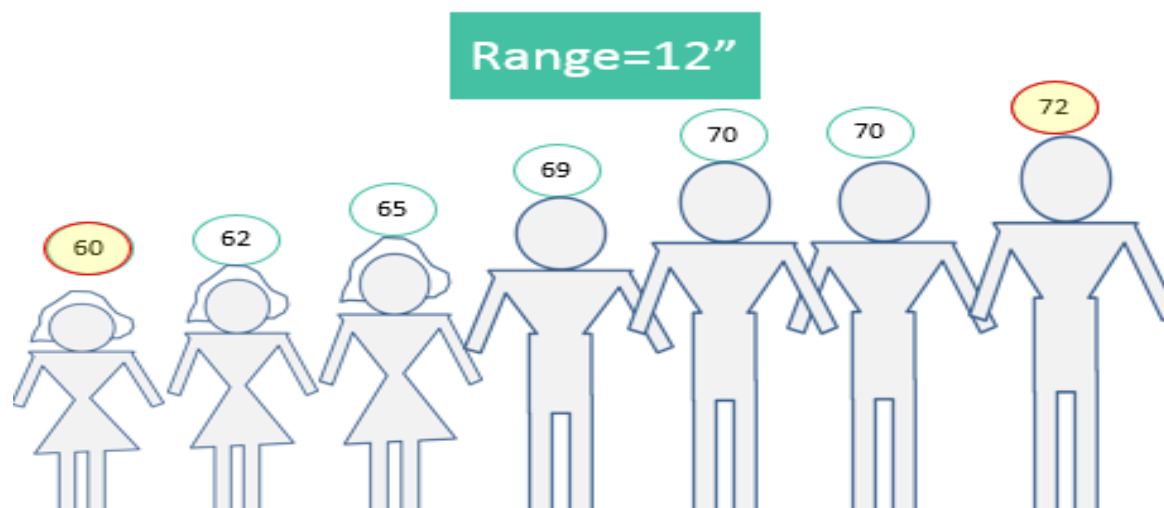
# Uncertainty Type A

## Some Statistical Methods You can Use:



- Calculate the standard deviation (SD) of the mean (most commonly used),
- Using the method of least squares to fit a curve to data to estimate parameters of the curve & their standard deviations,
- Analysis of Variation (ANOVA), or
- Correlation coefficients.



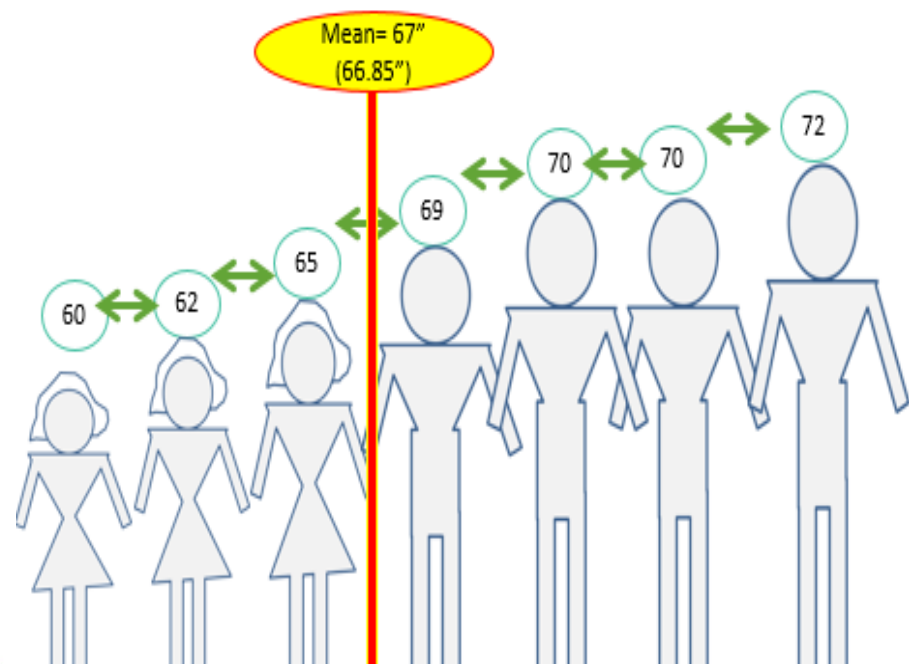


- The SD is not the same as the range. Range tells us the distance between the smallest and highest value in a set of numbers.
- Let's say we measure the height of all seven students on the tennis team at Ridgeville High.
  - The range of heights in inches is the difference between the lowest value, 60, and the highest value, 72.
  - So the range of this set of values is 12 inches. In a moment, we'll calculate the standard deviation for this set of values and see if the value is also 12.

# Standard Deviation (SD)

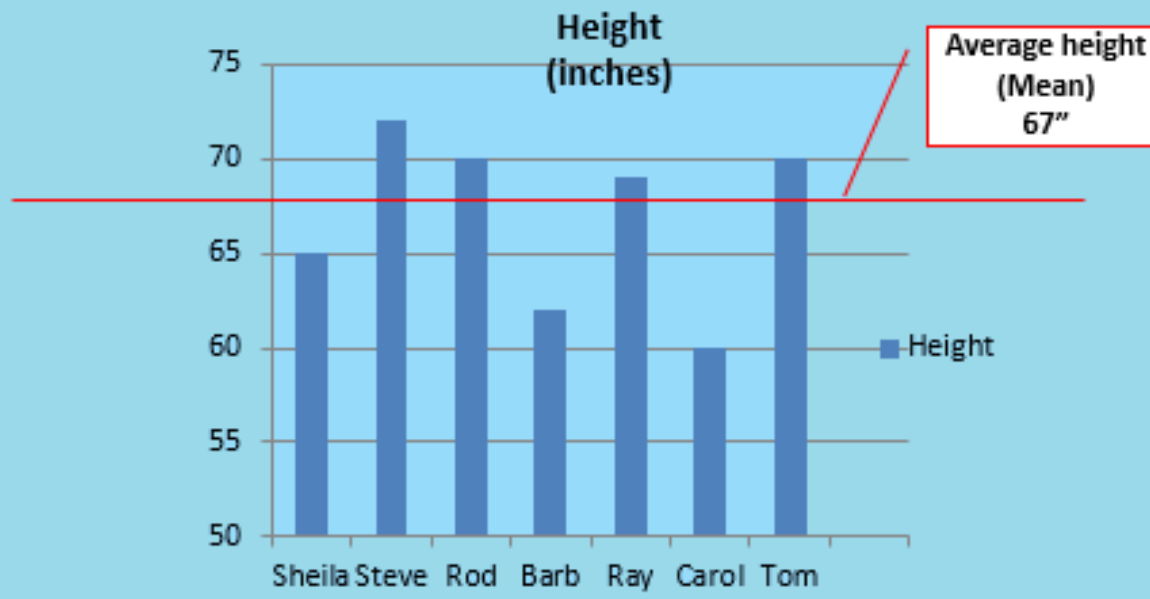
Standard deviation is a way of representing how spread out the values are within the set. The spread can help.

- Standard deviation also tells us how different each value is from the average, or mean, of the set.
- In our illustration, we have rounded off the mean to the nearest whole number.



$$65+72+70+62+69+60+70 = 468$$

$$468 \div 7 = \mathbf{67} \text{ (mean)}$$



To calculate the mean or average, we simply added all the values, which in our example, total 468. We then divide the total by the number of values in the set, 7, to find the mean. The mean of our seven values is 67.

# Mean = 67

| <u>Value</u> | <u>Deviation (Difference)<br/>from mean of 67:</u> |
|--------------|----------------------------------------------------|
|--------------|----------------------------------------------------|

|    |                |
|----|----------------|
| 65 | $65 - 67 = -2$ |
| 72 | $72 - 67 = 5$  |
| 70 | $70 - 67 = 3$  |
| 62 | $62 - 67 = -5$ |
| 69 | $69 - 67 = 2$  |
| 60 | $60 - 67 = -7$ |
| 70 | $70 - 67 = 3$  |

Next we calculate the deviations, that is, we subtract the mean of 67 from each value in the set to determine the amount each one differs, or deviates, from the mean.



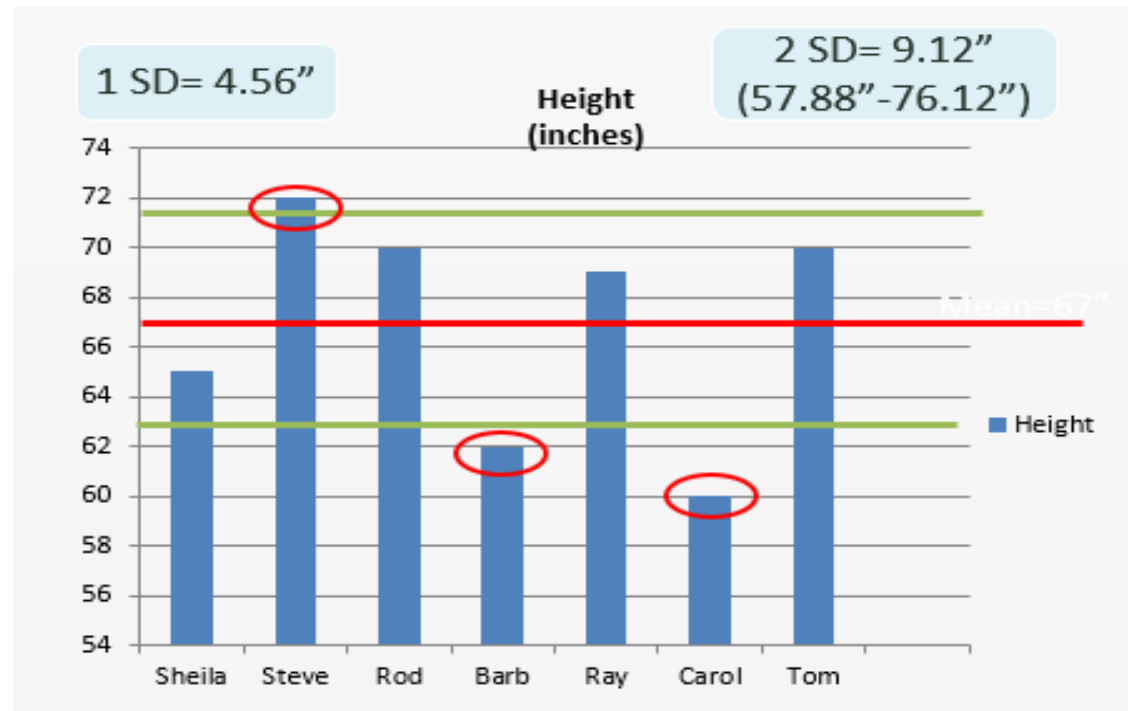
# Mean = 67

- The next step is to square each difference. Remember that when you square a negative number, the result is a positive number. Now we add the squares and get 125.
- Next we divide the sum of the squares by one less than the total number (n) of values in the set (n-1), or 6.
- This gives us 20.83 and we're almost there.

| Deviation | Squared             |                       |
|-----------|---------------------|-----------------------|
| -2        | $-2 \times -2 = 4$  | 20.83                 |
| 5         | $5 \times 5 = 25$   |                       |
| 3         | $3 \times 3 = 9$    |                       |
| -5        | $-5 \times -5 = 25$ |                       |
| 2         | $2 \times 2 = 4$    | 6 $\sqrt{125}$        |
| -7        | $-7 \times -7 = 49$ |                       |
| 3         | $3 \times 3 = 9 +$  | $\sqrt{20.83} = 4.56$ |
|           | <hr/> 125           |                       |

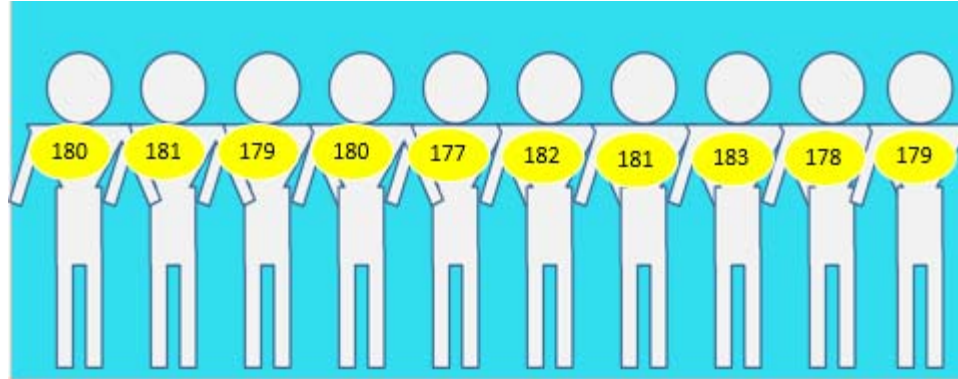
- The square root of this number is the estimated standard deviation for heights of the seven members of the tennis team. Remember the range of heights was 12 inches. The standard deviation, however, is 4.56.





- On the graph, the red line indicates the mean value of 67 inches and the two green lines show the area included in one standard deviation. In this case, 4.56 inches above or below the mean.
- The heights of three people, Steve, Barb and Carol, are outside of one standard deviation but they would all be well within two standard deviations of the mean.

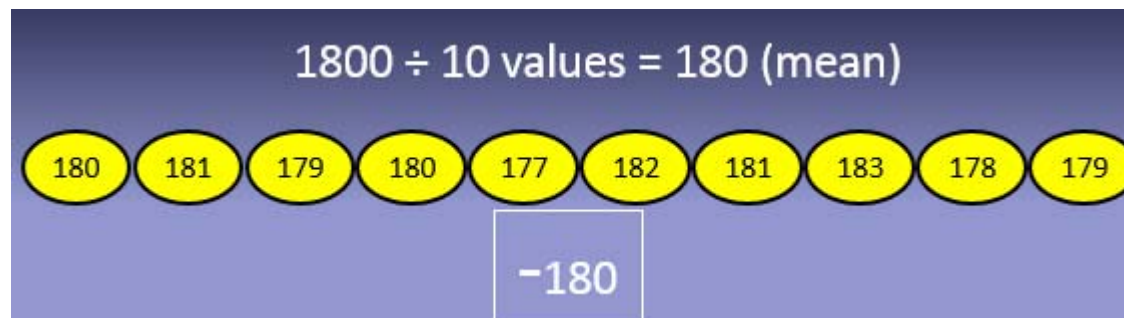
# Total of all values = 1800 lbs.



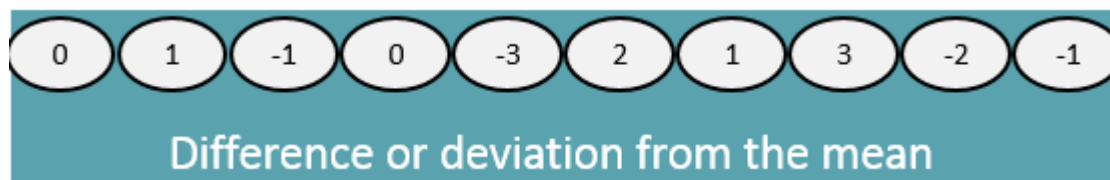
- Now let's look at something closer to what may interest a lab scientist: repeated measurements of the same sample.
- If we wanted to know the weight of just one of the tennis players, Ray, we could weigh him. Let's say we weighed Ray ten times, using the exact same method, instrument and operator.
- To see the spread of the weights, we want to calculate the standard deviation of the values. The more readings we use to estimate the standard deviation, the better the estimate of uncertainty will be.
- Ten is a good number for our purposes. The estimate of *uncertainty* improves with the number of readings. We have added the values to find the total.



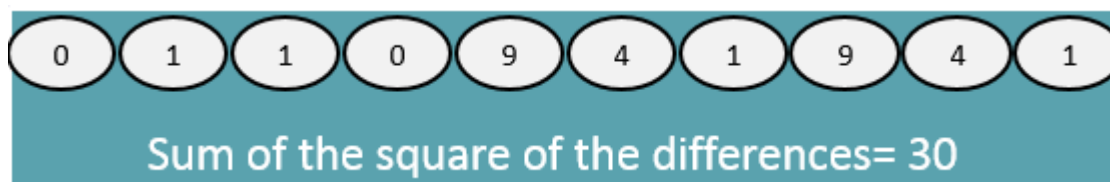
Next we find the average or mean:



Now we subtract the mean from each value:



Square the differences and add them together:





Sum of the square of the differences= 30

Now that we have the sum of the square of the differences, we divide the sum by one less than the number of values in our set

$$30 \div 9 = 3.33$$

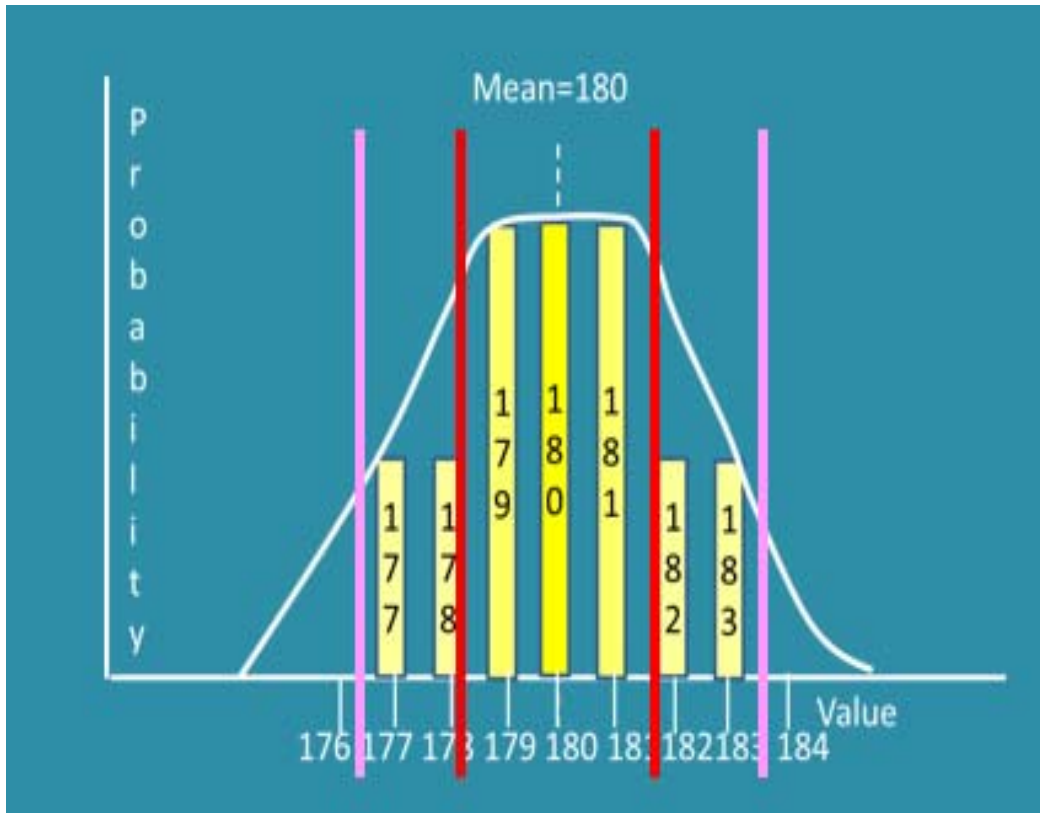
Take the square root of that number and we have a standard deviation of 1.82 pounds for this set of values

$$\sqrt{3.33} = 1.82 \text{ lb.}$$

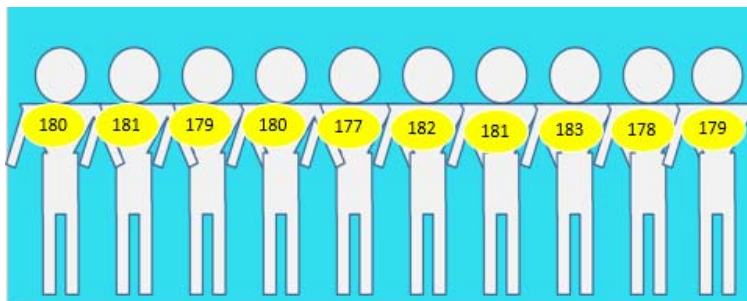
1 std deviation =  
178.18-181.82

2 std deviation =  
176.36-183.64





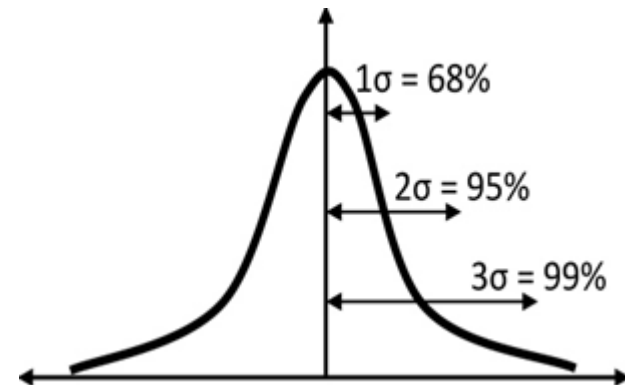
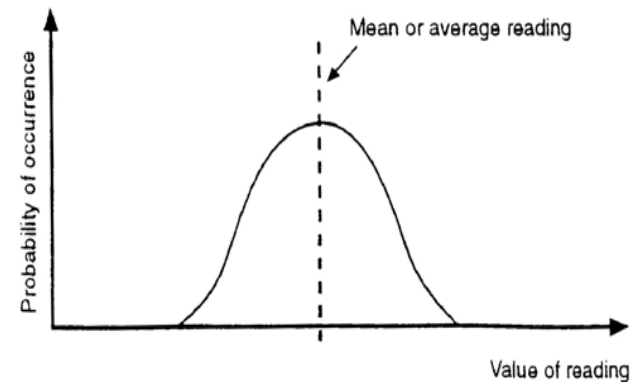
- This curve shows the distribution of the values we got for Ray's weight.
- The columns for 179, 180, and 181 represent results for when there were 2 counts of that value. The shorter columns show the values for when there was only one reading in the measurements.
- The values between the red lines are within one standard deviation and the values between the pink lines are within two standard deviations.



# Distribution-shape of errors

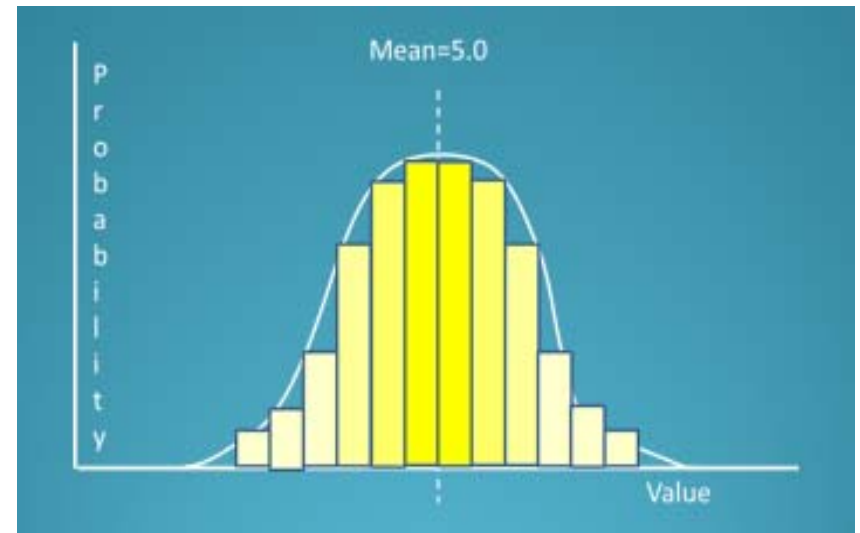
Normal (Gaussian) distribution; values are more likely to fall near the mean.

- The curve is symmetrical, indicating that deviations from the mean are comparable in either direction. When plotting the values of repetitive measurements, we would expect to see a normal distribution curve because all the values should be close to the mean.
- As a 'rule of thumb', in a normal distribution, roughly two thirds of all readings will fall between plus and minus one standard deviation of the average. Roughly 95% of all readings will fall within two standard deviations. This 'rule' applies widely although it is by no means universal.



# What the shape tells us

- The curve we made from Ray's weight measurements was a normal distribution, or Gaussian curve, named in honor of the mathematician Carl Gauss.
- A normal distribution curve, such as would be expected in the distribution of repeated test results on a sample, or calibration values for a single standard, is bell-shaped; most of the values fall closer to the mean than away from it.
- We can make some assumptions with data when all we know is the mean and standard deviation, which control the height and width of the curve.
- The values for this curve have a mean value of 5. The number of readings for each value in this graph is represented by the height of the yellow bars, the taller bars represent more readings of the value.

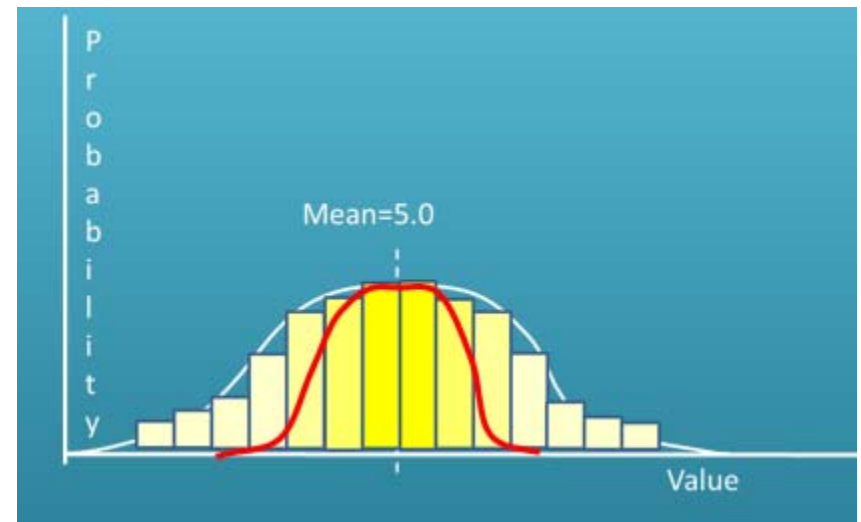


The appearance of this curve tells us that most readings are near the mean of 5.0 because the shape of the curve is tall and narrow.



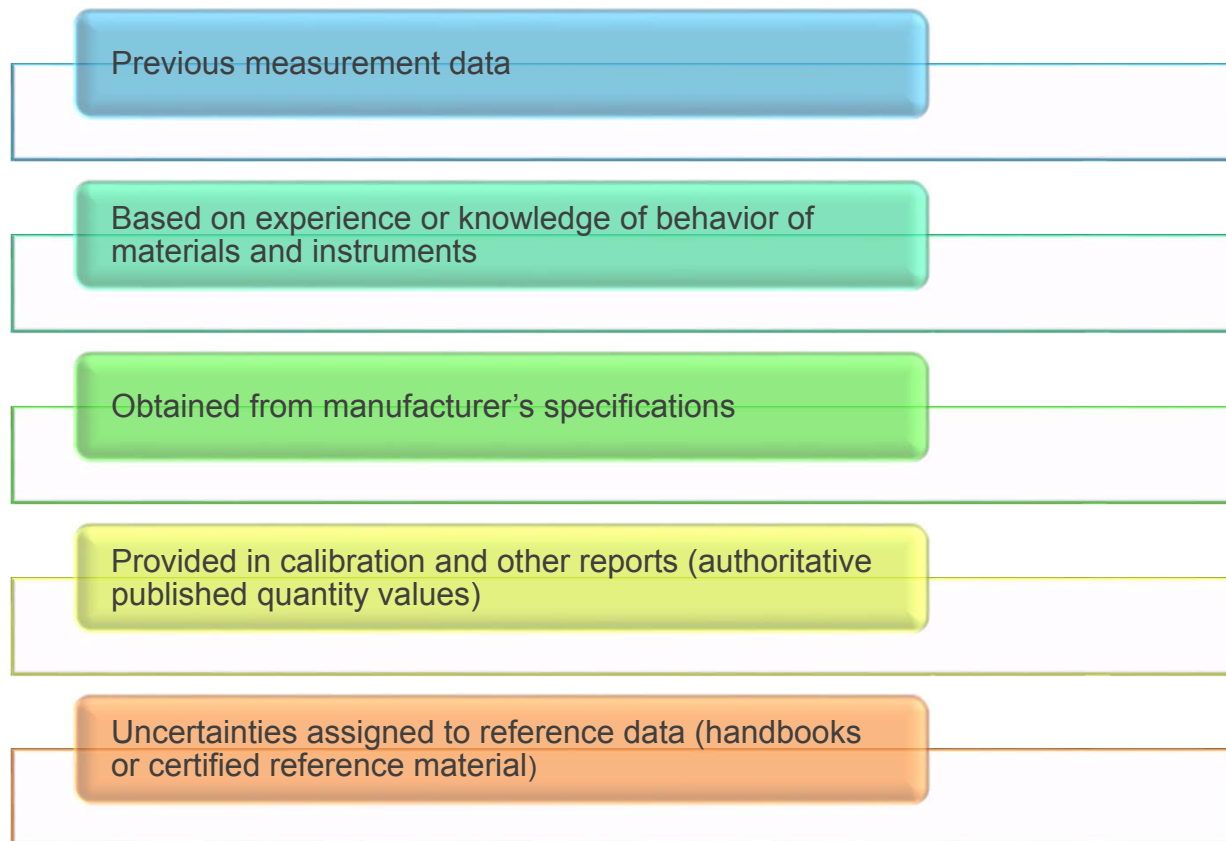
# What the shape tells us

- In contrast, the values here are spread farther from the mean of 5.0 and therefore the curve is flatter and more spread out.
- The standard deviation of the values in this curve is higher than the standard deviation of the values represented in the previous curve, where most values were close to the mean.



# Type B: Based on Scientific Judgment or Relevant Information

Uncertainty that is evaluated by ways other than statistical methods are type B and are based on scientific judgment or relevant information as listed here.

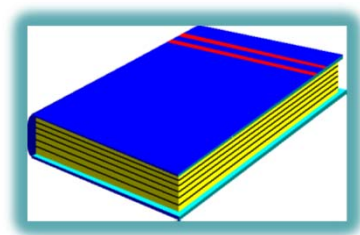


# What should I use to calculate Uncertainty?

Preferred Option (#1):

Use what is specified in your standard method.

- When a well-recognized test method (EPA, NIOSH, OSHA, ASTM, AOAC International, etc.), **specifies the limits of what can cause uncertainty** and **explains how to calculate results**, follow the SOP's instructions.
- Be able to show you follow it as written, and
- That the results are within the limits specified by the method.



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# What else can I use?



- Next Option (#2): Use Laboratory Control Samples (LCS) or Matrix Spikes
  - Use **standard deviation** of **long term data** collected from **routine** sample runs.
  - For new test methods, use the standard deviation of the LCS or matrix spike data collected in the method validation/verification studies.



# Method Specified Uncertainty when there is no Duplicate Sub-sampling

- Example: Industrial Hygiene (IH) lead (Pb) in air samples (units are mg/M<sup>3</sup>)
- For IH air samples and Pb Wipes or other samples where there is no duplicate sub-sampling, the uncertainty will be calculated using the SD of long term data collected from LCS and Laboratory Control Sample Duplicates (LCSD) specific to the analyte and matrix of the sample.
- Uncertainty will be reported in the same unit as the analytical result
- (Confidence level of 95% is referred to as 'k=2')



## Method Specified Uncertainty when there is no Duplicate Sub-sampling

- Example using a Test Result of:  $0.25 \text{ mg/M}^3$ 
  - SD of last 40 data points for the Pb LCS = 4.0
  - At 95% Confidence ( $k = 2$ ) [Confidence level: I can be 95% sure that my value is...]
  - Uncertainty of the system = SD times 2 ( $k$ ) =  $4.0 \times 2 = 8.0\%$  (.08)
  - Sample Uncertainty Calculation:  $(0.25) (.08) = 0.02$
- **Result for Pb is  $0.25 \text{ mg/M}^3$  with an analytical uncertainty  $\pm 0.02 \text{ mg/M}^3$  at 95% confidence level (where  $k=2$ ).**



# Method Specified Uncertainty when there is no Duplicate Sub-sampling, cont'd.

**Bias** is calculated using average percent recovery of the LCS.

Example: where the Mean Recovery of the LCS = 98.2%

- $100 - 98.2 = 1.8$ ; therefore there is a -1.8% bias to the system (negative because the recovery is  $< 100\%$ )

- Calculation: Result x the system bias = sample bias
- $0.25 \text{ mg/M}^3 \times (-0.018) = -0.0045 \text{ mg/M}^3$

- When requested by the client, the result will be reported with the uncertainty and bias associated with that result.

- For the above example when reporting a result of  $0.25 \text{ mg/M}^3$  Lead:

- **“ $0.25 \text{ mg/M}^3$  Lead with an analytical uncertainty of  $\pm 0.02 \text{ mg/M}^3$  at the 95% confidence level (where  $k=2$ ) with a probable bias of  $-0.0045 \text{ mg/M}^3$ ”**



# What else can I use?

- Option #3: Use Duplicate Data
  - Use **long term duplicate data** (should be over the reporting limit) collected from routine sample runs
  - For new test methods, use the duplicate data collected in the method validation/verification studies



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# When Sample Duplicates are Available

For samples where duplicate analysis data is available along with the LCS data, the calculation is expanded to include the SD of the % recovery of the LCS and the pooled relative standard deviation (RSD) of the duplicate (LCSD) analysis data. Use this formula:

$$\text{Combined Relative Standard Deviation (SDc)} = \sqrt{[\text{SD1}^2 + \text{SD2}^2]}$$



# Example Data - LCS and LCS true

| LCS    | LCS true | % Rec  |
|--------|----------|--------|
| 0.4190 | 0.4490   | 93.32  |
| 0.4700 | 0.4490   | 104.68 |
| 0.4430 | 0.4490   | 98.66  |
| 0.4670 | 0.4490   | 104.01 |
| 0.4670 | 0.4490   | 104.01 |
| 0.4330 | 0.4490   | 96.44  |
| 0.4580 | 0.4490   | 102.00 |
| 0.4440 | 0.4490   | 98.89  |
| 0.4520 | 0.4490   | 100.67 |
| 0.4780 | 0.4490   | 106.46 |
| 0.4540 | 0.4490   | 101.11 |
| 0.4680 | 0.4490   | 104.23 |
| 0.4440 | 0.4490   | 98.89  |
| 0.4550 | 0.4490   | 101.34 |
| 0.4260 | 0.4490   | 94.88  |
| 0.4740 | 0.4490   | 105.57 |
| 0.4450 | 0.4490   | 99.11  |
| 0.4710 | 0.4490   | 104.90 |
| 0.4510 | 0.4490   | 100.45 |
| 0.4440 | 0.4490   | 98.89  |
| 0.4710 | 0.4490   | 104.90 |

|        |        |        |
|--------|--------|--------|
| 0.4730 | 0.4490 | 105.35 |
| 0.4420 | 0.4490 | 98.44  |
| 0.4470 | 0.4490 | 99.55  |
| 0.4450 | 0.4490 | 99.11  |
| 0.4390 | 0.4490 | 97.77  |
| 0.4400 | 0.4490 | 98.00  |
| 0.4490 | 0.4490 | 100.00 |
| 0.4380 | 0.4490 | 97.55  |
| 0.4160 | 0.4490 | 92.65  |
| 0.4390 | 0.4490 | 97.77  |
| 0.4140 | 0.4490 | 92.20  |
| 0.4250 | 0.4490 | 94.65  |
| 0.4470 | 0.4490 | 99.55  |
| 0.4230 | 0.4490 | 94.21  |
| 0.4520 | 0.4490 | 100.67 |
| 0.4370 | 0.4490 | 97.33  |
| 0.4590 | 0.4490 | 102.23 |
| 0.4450 | 0.4490 | 99.11  |
| 0.4720 | 0.4490 | 105.12 |
|        | mean%  |        |
|        | rec    | 99.87  |
|        | SD     | 3.78   |
|        | %CV    | 3.79   |

- First, figure % recovery using the LCS value vs. true value (also written as):
  - (LCS divided by LCS true value times 100)
    - $(\text{LCS}/\text{LCS true}) \times 100$
  - Using the first value from the table to the left, you can figure % Recovery.
    - $(0.4190/0.4490) \times 100 = 93.32 \%$



# Calculate the SD1 using LCS and LCSD from laboratory data

|  |              |       |
|--|--------------|-------|
|  | mean%<br>rec | 99.87 |
|  | SD           | 3.78  |
|  | %CV          | 3.79  |

(See the previous slide-bottom right of table—and above)

Average the 30 point mean % recovery = 99.87

Calculate the SD of LCS % recoveries = 3.78

Calculate the %CV (also known in this example as SD1)

- $SD1 = [(SD \text{ of mean } \% \text{ recovery}) \text{ divided by (the mean } \% \text{ recovery)}] \text{ times } 100 = (3.78/99.87) \times 100 = 3.79$



**[Note: table has only partial amounts listed.]**



## Calculate SD2 using samples and sample duplicates

[illegible]

- S1 = sample result
- S2 = duplicate result
  - Average each duplicate (Col. 3: ave)
  - Find the SD of each duplicate (col. 4: SD)
  - Find the %CV (col. 5: %CV) [SD divided by the average] times 100
  - Col. 6:  $CV = SD/ave$
  - Col. 7: CV squared (square each CV)
  - Last column of CV squared is copied over without formula (value only)



# Calculate SD2, cont'd.

See previous slide for data  
(RSD = relative standard deviation)

|           |                                 |        |
|-----------|---------------------------------|--------|
|           | sum CV <sup>2</sup>             | 0.3142 |
|           | CV <sup>2</sup> /40             | 0.0079 |
| cv pooled | sq rt of<br>CV <sup>2</sup> /40 | 0.0886 |
|           | % RSD                           | 8.86   |

- Sum CV<sup>2</sup>
  - (add up all the CV<sup>s</sup> squared in the column) = 0.3142
- Sum CV<sup>2</sup>/40 (take the sum of the CV squared and divide by the number in column 1; n=40) = 0.0079
- CV pooled is the square root of CV<sup>2</sup>/40 = 0.0886
- % RSD is CV pooled times 100 = 8.86 = SD2
- 95% confidence (k=2)



# Combined Relative Standard Deviation

$$(SD_c) = \sqrt{[SD1^2 + SD2^2]}$$

- $SD_c = \sqrt{[(3.79)^2 + (8.86)^2]}$
- $SD_c = \sqrt{[14.36 + 78.49]}$
- $SD_c = \sqrt{[92.85]} = 9.64\%$

Expanded MU @ 95% Conf (k=2) =  $SD_c \times 2 = \% \text{ RSD}$

$$- 9.64 \times 2 = \underline{19.28\% \text{ RSD}}$$



# Example using a result of 10.57 %

- Figure Bias
  - Bias @ 99.87% recovery (LCS mean % recovery) =  $100 - 99.87 = -0.13$  (negative because recovery is <100%)
  - Bias = (Ex. result: 10.57%) x (-0.13) = -1.37%
- Example analytical uncertainty for 10.57% result (Pb in Paint units are %):
  - Using 10.57% result Pb in paint
  - With an analytical uncertainty of 0.192 (MU from previous slide)
    - $(10.57) \times (0.192) = 2.0\%$



## And the Result Is: drum roll, please



- Result is: 10.57% Pb in paint with an analytical uncertainty of  $\pm 2.0\%$  at the 95% confidence level ( $k=2$ ) and a probable bias of -1.37%
- Reference material used for calibration indicates concentration and expanded uncertainty of 0.011% at 95% confidence level. Expanded uncertainty divided by 2 to yield 0.0055 % Rel. SD. Insignificant compared to 8.86% and can be eliminated from calculation. No significant background in method blank.



# What else can I use?

- Least Preferred Option (#4): Proficiency Testing (PT) Sample Data.
  - In cases where the previous options are not available and where PT samples are analyzed with sufficient data above the reporting limit, use existing PT sample data to estimate uncertainty.



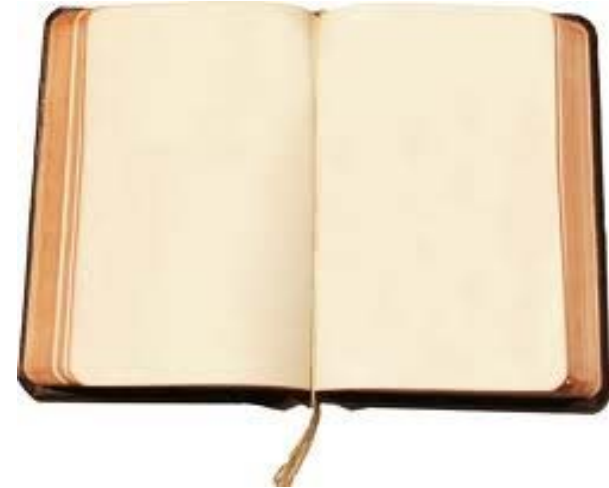
# What else should I do?

- **Update your procedure manuals** to indicate:
  - What you are measuring (the measurand)
- What variables contribute to uncertainty:
  - transportation, storage, holding time, sample preparation, reagent lots, temperature, instruments, operators, barometric pressure, etc.



# Update your procedure manuals:

- List the details of the approaches used (Type A and/or B).
- What calculations are you using? Do they make sense?
  - Standard deviations, formulas specified in methods, quality control measurements, etc.)
- Refer to any requirements by accrediting bodies.
- Make sure the procedures are implemented.
- How is it reported when required?
  - Your laboratory must have the ability to report uncertainty, even if the customer is currently not requesting it.



# AIHA Guidance on the Estimation of Uncertainty of Measurement

[http://www.aihaaccreditedlabs.org/Policies/2016%20Policies/8%202%202%20LAP%20Guidance%20on%20the%20Est%20of%20UoM\\_R3\\_FINAL.pdf](http://www.aihaaccreditedlabs.org/Policies/2016%20Policies/8%202%202%20LAP%20Guidance%20on%20the%20Est%20of%20UoM_R3_FINAL.pdf)



# AIHA-Examples of Analytical Measurement Uncertainty for Lead in Paint

<http://www.aihaaccreditedlabs.org/Policies/Resources/Example%20Chemistry%20Measurement%20Uncertainty%20Calculations%20V3%20corrected%20031312.xls>



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# References

- ISO/IEC 17025:2005
  - <https://www.iso.org/standard/39883.html>
- Learning Aid:
  - Introduction to Analytical Measurement of Uncertainty: Dictionary of Terms
  - Calculating Standard Deviation
  - Determining Measurement Uncertainty Using Combined and Expanded Uncertainty

