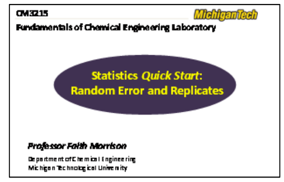
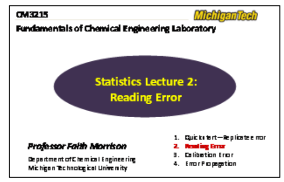
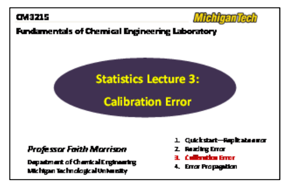
Where are we in our discussion of error analysis?

Let's revisit:







Obtaining a Good Estimate of a *Measured* Quantity

Summary:

Replicate error:

- Measure the quantity several times – replicates
- The average value is a good estimate of the quantity we are measuring if only random errors are present
- The 95% confidence interval comes from $\pm(**)e_s$
- $(**) = 2$ if the number of replicates is 7 or higher
- $(**)$ comes from the Student's t distribution if $N < 7$
- Report one sig fig on error (unless that digit is 1 or 2)

Reading error:

- Determine signal needed to change reading
- Determine half smallest division or decimal place
- Determine average of fluctuations
- Max of those $/\sqrt{3}$ =reading error
- use $\pm 2e_s$ for 95% confidence interval

Calibration error:

- Determine manufacturer maximum error allowable
- Assume least significant digit varies by ± 1
- Calibrate in-house
- Use largest uncertainty as determined above
- Replication cannot reduce calibration error

Measured quantities, e.g.: mass, temperature, DC current, time interval, etc.

Obtaining a Good Estimate of a Quantity

- **Replicate error**
- **Calibration error**
- **Reading error**

$$\rho = \frac{M_F - M_E}{V_{pyc}}$$

$$\mu = \rho\alpha\Delta t$$

$$Q = \dot{m}C_p(T_{out} - T_{in})$$

etc.

*<u>But</u> how do we **combine** the errors?*

*<u>And</u> what do we do when we obtain a quantity from a **calculation?***

Obtaining a Good Estimate of a Quantity

- **Replicate error**
- **Calibration error**
- **Reading error**

$$\rho = \frac{M_F - M_E}{V_{pyc}}$$

$$\mu = \rho\alpha\Delta t$$

$$Q = \dot{m}C_p(T_{out} - T_{in})$$

etc.

*<u>But</u> how do we **combine** the errors?*

*<u>And</u> what do we do when we obtain a quantity from a **calculation?***

<u>Answer for both:</u>
Propagate the **error** through the calculation

CM3215

Fundamentals of Chemical Engineering Laboratory

Statistics Lecture 4:

Error Propagation

Professor Faith Morrison

Department of Chemical Engineering
Michigan Technological University

1. Quick start—Replicate error
2. Reading Error
3. Calibration Error
4. **Error Propagation**
5. Least Squares Curve Fitting

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CM3215

Fundamentals of Chemical Engineering Laboratory

Statistics Lecture 4:

Error Propagation

Professor Faith Morrison

Department of Chemical Engineering
Michigan Technological University

References:

- *Dealing with Data,* Arthur J. Lyon (Pergamon Press, NY 1970)

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Example 1:

What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

Image source:
www.coleparmer.com

Image source:
//en.wikipedia.org/wiki/Relative_density

Example 1:

What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

$$\rho_{bluefluid} = \frac{M_{full} - M_{empty}}{V_{pycnometer}}$$

- The value of density obtained is a function of three measurements
- Each measurement has its own uncertainty

Image source:
www.coleparmer.com

Image source:
//en.wikipedia.org/wiki/Relative_density

Example 1:

$e_s \equiv$ Standard Error

What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

Three potential error sources on each measured quantity:

$$e_s = \frac{s}{\sqrt{n}}$$ Standard error of replicates

$$e_s = \frac{e_R}{\sqrt{3}}$$ Standard error due to Reading Error

$$e_s = \frac{\text{error limits}}{2}$$ Standard error due to Calibration Error

Replicate Error Worksheet
CM3215 Fundamentals of Chemical Engineering Lab
Prof. Faith Morrison

Michigan Tech
Michigan Technological University
Department of Chemical Engineering

Handy worksheet for replicate error

This worksheet guides the user through the calculation of the standard error and 95% confidence interval on a quantity that has been measured n times (replicated). The replicate-error-related standard error e_s may subsequently be used in propagation-of-error calculations of derived quantities.

Replicated Variable, Y:						Units:		
Measured values $Y_1, Y_2, \ldots, Y_n$		Sample Mean, $\bar{Y}$	Sample Variance, s^2	Sample Standard Deviation, s	Standard Error, $e_s = \frac{s}{\sqrt{n}}$	95% Confidence Interval based on n replicates (*Student's t* distribution)		
Y_1						$n = 1$	n/a	(include units) $\pm$
Y_2						$n = 2$	$\pm 12.7 e_s$	
Y_3						$n = 3$	$\pm 4.30 e_s$	
Y_4						$n = 4$	$\pm 3.18 e_s$	
Y_5						$n = 5$	$\pm 2.78 e_s$	
Y_6						$n = 6$	$\pm 2.57 e_s$	
Y_7						$n \geq 7$	$\pm 2 e_s$	
						∞	$\pm 1.96 e_s$	

$$\bar{Y} \equiv \frac{1}{n}\sum_{i=1}^{n} Y_i$$

$$s^2 \equiv \frac{1}{(n-1)^2}\sum_{i=1}^{n}(Y_i - \bar{Y})^2$$

11-Sep-14

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www.chem.mtu.edu/~fmorriso/cm3215/ReplicateErrorWorksheet.pdf

Reading Error Worksheet
CM3215 Fundamentals of Chemical Engineering Lab
Prof. Faith Morrison

Michigan Tech
Michigan Technological University
Department of Chemical Engineering

This worksheet guides the user through the calculation of the standard error and 95% confidence scale or off a digital readout (yielding value x and subject to reading error). The reading-error-related standard error e_s may subsequently be used in propagation of error calculations of derived quantities.

	Device name:			
	Measured Quantity: (give symbol)			
	Representative value:	(include units)		Quantity or **N**ot **A**pplicable
	issue	**contribution to error**		
Reading error, e_R:	Sensitivity (manufac. or estimated)	How much signal does it take to cause the reading to change?	1	
	Resolution: limitation on marked scale or digital readout	Half smallest division or decimal place	2	
	Fluctuations with time of observation	(max-min)/2	3	
		Maximum of 1, 2, & 3:	$e_R =$	
	Standard error based on reading error:	$e_s = e_R/\sqrt{3}$	$e_s =$	(units)
		95% Confidence Interval on the reading: $\pm 2e_s$		

Note: If a value is supplied by, for example, a manufacturer, with no indication of the uncertainty, we do not use this worksheet. Instead, see the Calibration Error worksheet.

13-Jan-16

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www.chem.mtu.edu/~fmorriso/cm3215/ReadingErrorWorksheet.pdf

Handy worksheet for reading error

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Calibration Error Worksheet
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Prof. Faith Morrison

The error e_s is defined as the "best-case" standard error for a quantity as determined for a brand-new unit by a manufacturer or for a particular device by someone with authority to certify the value. For example, the technical specifications of a device may indicate that it is accurate to a value $\pm 2e_s$. Alternatively, a value of a constant (the viscometer constant α, for example) may be provided by the manufacturer with no specific uncertainty. In this case, the rule of thumb method of "least significant digit" is acceptable for evaluating the uncertainty. Finally, a user may take steps to calibrate a meter on site; this determination of error (likely to be greater than the "best case" error) has the advantage of reflecting issues associated with the particular unit in question.

Device name:			
Measured quantity:	**Symbol:**	**Representative value: (include units)**	
		Estimate of e_s: (or **N**ot **A**pplicable)	
Rigorous Method: Manufacturer maximum error allowable	$2\,e_s \approx$		
Rule of Thumb Method: Least significant digit on provided value	Least significant digit varies by at least $\pm 1 = \pm 2e_s$		
Method 3: User calibration	$2e_s \approx$		
	Maximum of Methods 1 - 3	$e_s =$	**95% CI, Calibration error only: quantity$\pm 2e_s$**
		$2e_s =$	(units)

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www.chem.mtu.edu/~fmorriso/cm3215/CalibrationErrorWorksheet.pdf

Handy worksheet for calibration error

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

First:

What are the uncertainties e_{x_i} for M_{full}, M_{empty}, and V_{pyc}?

You try.

Image source: www.coleparmer.com

Image source: //en.wikipedia.org/wiki/Relative_density

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

First:

What are the uncertainties e_{x_i} for M_{full}, M_{empty}, and V_{pyc}?

Standard errors:

M_{full}:	$= 30.800\ g$
M_{empty}:	$= 13.410\ g$
$V_{pycnometer}$	$= 10.00\ ml$

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

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M_{full}:	$= 30.800\ g$	
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$V_{pycnometer}$	$= 10.00\ ml$	

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

First:

What are the uncertainties e_{x_i} for M_{full}, M_{empty}, and V_{pyc}?

Standard errors:

M_{full}:	$= 30.800\ g$	$\frac{0.0001}{\sqrt{3}} = 5.8 \times 10^{-5}\ g$	(reading dominates)
M_{empty}:	$= 13.410\ g$		
$V_{pycnometer}$	$= 10.00\ ml$	$\frac{max\ error\ allowable}{2} = 0.02\ ml$	(calibration dominates)

Now, can we determine $e_{s,\rho}$?
Yes ⇒ Propagation of Errors

Error Propagation

We seek to

- Combine the individual contributions to overall error: replicate, reading, calibration
- Combine the errors associated with the various quantities in a calculation.

$$\rho_{bluefluid} = \frac{M_{full} - M_{empty}}{\mathrm{V}_{pycnometer}}$$

For both of these tasks we use an analysis based on the calculation of variance. We use the Taylor series expansion of a nonlinear function.

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Error Propagation

We use an analysis based on the Taylor series expansion of a nonlinear function. (Derivation omitted)

Taylor series:

$$f(x_1, x_2, x_3) = f^0 + \frac{\partial f}{\partial x_1} x_1 + \frac{\partial f}{\partial x_2} x_2 + \frac{\partial f}{\partial x_3} x_3 + h.o.t.$$

(higher order terms)

A determination (measurement) of a value of the function $f(x_1, x_2, x_3)$ from uncertain values of x_1, x_2, x_3 is a stochastic variable of mean $\bar{f}$ and variance σ_f^2, given by:

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 \sigma_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \sigma_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 \sigma_{x_3}^2 + \text{Covariance terms, if } x_i \text{ are correlated}$$

where the variances $\sigma_{x_i}^2$ are the variances of the stochastic variables x_1, x_2, x_3.

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Error Propagation

We use an analysis based on the Taylor series expansion of a nonlinear function. (Derivation omitted)

Taylor series:

$$f(x_1, x_2, x_3) = f^0 + \frac{\partial f}{\partial x_1}x_1 + \frac{\partial f}{\partial x_2}x_2 + \frac{\partial f}{\partial x_3}x_3 + h.o.t.$$

(higher order terms)

A determination (measurement) of a value of the function $f(x_1, x_2, x_3)$ from uncertain values of x_1, x_2, x_3 is a stochastic variable of mean $\bar{f}$ and variance σ_f^2, given by:

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 \sigma_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \sigma_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 \sigma_{x_3}^2 + \text{Covariance terms, if } x_i \text{ are correlated}$$

often zero

where the variances $\sigma_{x_i}^2$ are the variances of the stochastic variables x_1, x_2, x_3.

Note: covariance terms are not always zero or small; but they often are. For now, this is fine.

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Let's now apply the **Error Propagation** equation to determine the error for experimental density.

Example 1:

What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

Error Propagation equation

Function:

$$f(x_1, x_2, x_3)$$

Error on Function:

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 \sigma_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \sigma_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 \sigma_{x_3}^2$$

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Error Propagation

(To avoid confusion with other variances, we use e_{x_i} nomenclature for errors)

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2$$

$$\rho_{bluefluid} = f\left(M_{full}, M_{empty}, V_{pycnometer}\right)$$

$e_{s_{M_{full}}}$

$e_{s_{M_{empty}}}$

$e_{s_{V_{pycnometer}}}$

We estimate these standard errors with our 3 worksheets

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Error Propagation

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2$$

$$\rho_{bluefluid} = f\left(M_{full}, M_{empty}, V_{pycnometer}\right)$$

These come from the formula for $\rho_{bluefluid}$

$$\rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$$

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Error Propagation

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2$$

$$f = \rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$$

$$\frac{\partial \rho_{BF}}{\partial M_F} =$$

$$\frac{\partial \rho_{BF}}{\partial M_E} =$$

$$\frac{\partial \rho_{BF}}{\partial V_{pyc}} =$$

You try.

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Error Propagation

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2$$

We seek this, the standard error of the calculated property, $f = \rho_{bluefluid}$

$$\rho_{bluefluid} = f\left(M_{full}, M_{empty}, V_{pycnometer}\right)$$

$$\rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$$

Think of the squared partial derivatives as the **weighting functions** for the individual *squared* standard errors.

It's good to look at these numbers.

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Error Propagation Worksheet
CM3215 Fundamentals of Chemical Engineering Lab
Prof. Faith Morrison

This worksheet guides the user through the determination of the standard error e_{s_f} of a quantity $f(x_1, x_2, x_3, x_4, x_5)$ that is calculated from measured quantities x_1, x_2, x_3, x_4 and x_5. The x_i are subject to random errors. The standard error e_{x_i} (replicate, reading, calibration; use the largest) for each variable x_i is determined first, and these uncertainties are propagated to determine e_{s_f} using the relationship given below.

Worksheet for error propagation

$f(x_1, x_2, x_3, x_4, x_5)$:	Formula for f:	Representative value of f: (include units)	95% C.I. of f: $(f \pm 2e_{s,f})$ (include units)

Measured quantities, x_i			$\frac{\partial f}{\partial x_i}$	$e_{x_i} = \frac{s_i}{\sqrt{N}}$ or $\frac{e_{R,i}}{\sqrt{3}}$ or e_{s_i}	$\left(\frac{\partial f}{\partial x_i}\right)^2 e_{x_i}^2$
x_i	Symbol	Representative value			
x_1					
x_2					
x_3					
x_4					
x_5					

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2 + \left(\frac{\partial f}{\partial x_4}\right)^2 e_{x_4}^2 + \left(\frac{\partial f}{\partial x_5}\right)^2 e_{x_5}^2$$

$e_{s_f}^2 =$

$e_{s_f} =$ units

Standard error of calculated quantity, f

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www.chem.mtu.edu/~fmorriso/cm3215/ErrorPropagationWorksheet.pdf

Example 1:

What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

Data:

$$M_F = 30.800\ g$$
$$M_E = 13.410\ g$$
$$V_{pyc} = 10.00\ ml$$

Density:

$$\rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$$

Image source: www.coleparmer.com

Image source: //en.wikipedia.org/wiki/Relative_density

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Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

$f(x_1, x_2, x_3, x_4, x_5)$:	Formula for f: $\rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$	Representative value of f: (include units)	95% C.I. of f: $(f \pm 2e_{sf})$ (include units)

Measured quantities, x_i			$\frac{\partial f}{\partial x_i}$	$e_{x_i} = \frac{s_i}{\sqrt{N}}$ or $\frac{e_{R_i}}{\sqrt{3}}$ or e_{s_i}	$\left(\frac{\partial f}{\partial x_i}\right)^2 e_{x_i}^2$
x_i	Symbol	Representative value			
x_1					
x_2					
x_3					
x_4					
x_5					

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2 + \left(\frac{\partial f}{\partial x_4}\right)^2 e_{x_4}^2 + \left(\frac{\partial f}{\partial x_5}\right)^2 e_{x_5}^2$$

$e_{s_f}^2 =$

$e_{s_f} =$ units

Standard error of calculated quantity, f

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

$f(x_1, x_2, x_3, x_4, x_5)$:	Formula for f: $\rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$	Representative value of f: (include units) $1.739\ g/ml$	95% C.I. of f: $(f \pm 2e_{sf})$ (include units)

Measured quantities, x_i			$\frac{\partial f}{\partial x_i}$	$e_{x_i} = \frac{s_i}{\sqrt{N}}$ or $\frac{e_{R_i}}{\sqrt{3}}$ or e_{s_i}	$\left(\frac{\partial f}{\partial x_i}\right)^2 e_{x_i}^2$
x_i	Symbol	Representative value			
x_1	M_F	$30.800\ g$			
x_2	M_E	$13.410\ g$			
x_3	V_{pyc}	$10.00\ ml$			
x_4					
x_5					

You try.

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2 + \left(\frac{\partial f}{\partial x_4}\right)^2 e_{x_4}^2 + \left(\frac{\partial f}{\partial x_5}\right)^2 e_{x_5}^2$$

$e_{s_f}^2 =$

$e_{s_f} =$ units

Standard error of calculated quantity, f

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

$f(x_1, x_2, x_3, x_4, x_5)$:	Formula for f: $\rho_{BF} = \dfrac{M_F - M_E}{V_{pyc}}$		Representative value of f: (include units)	95% C.I. of f: $(f \pm 2e_{sf})$ (include units)
Measured quantities, x_i				
x_i	Symbol	Representative value		
x_1	M_F	$30.800\ g$		
x_2	M_E	$13.410\ g$		
x_3	V_{pyc}	$10.00\ ml$		
x_4				
x_5				

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\ldots\right.$$

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

$f(x_1, x_2, x_3, x_4, x_5)$:	Formula for f: $\rho_{BF} = \dfrac{M_F - M_E}{V_{pyc}}$		Representative value of f: (include units) $1.739\ g/ml$		95% C.I. of f: $(f \pm 2e_{sf})$ (include units) $1.739 \pm 0.007\ g/ml$
Measured quantities, x_i			$\dfrac{\partial f}{\partial x_i}$	$e_{x_i} = \frac{s_i}{\sqrt{N}}$ or $\frac{e_{R_i}}{\sqrt{3}}$ or e_{s_i}	$\left(\dfrac{\partial f}{\partial x_i}\right)^2 e_{x_i}^2$
x_i	Symbol	Representative value			
x_1	M_F	$30.800\ g$	$1/V_{pyc}$	$5.8 \times 10^{-5} g$	$3.3 \times 10^{-11}\ g^2/ml^2$
x_2	M_E	$13.410\ g$	$-1/V_{pyc}$	$5.8 \times 10^{-5} g$	$3.3 \times 10^{-11}\ g^2/ml^2$
x_3	V_{pyc}	$10.00\ ml$	$-(M_F - M_E)/V_{pyc}^2$	$0.02\ ml$	$1.21 \times 10^{-5}\ g^2/ml^2$
x_4					
x_5					

$$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2 + \left(\frac{\partial f}{\partial x_4}\right)^2 e_{x_4}^2 + \left(\frac{\partial f}{\partial x_5}\right)^2 e_{x_5}^2$$

$e_{s_f}^2 = 1.21 \times 10^{-5}\ g^2/ml^2$

$e_{s_f} = 0.0035$ units g/ml — Standard error of calculated quantity, f

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Example 1: What is the uncertainty (95% confidence interval) in $\rho_{blue fluid}$ as determined in the lab?

$f(x_1, x_2, x_3, x_4, x_5)$:	Formula for f: $\rho_{BF} = \frac{M_F - M_E}{V_{pyc}}$		Representative value of f: (include units) $1.739\ g/ml$		95% C.I. of f: $(f \pm 2e_{sf})$ (include units) $1.739 \pm 0.007\ g/ml$
Measured quantities, x_i			$\frac{\partial f}{\partial x_i}$	$e_{x_i} = \frac{s_i}{\sqrt{N}}$ or $\frac{e_{R_i}}{\sqrt{3}}$ or e_{s_i}	$\left(\frac{\partial f}{\partial x_i}\right)^2 e_{x_i}^2$
x_i	Symbol	Representative value			
x_1	M_F	$30.800\ g$	$1/V_{pyc}$	$5.8 \times 10^{-5} g$	$3.3 \times 10^{-11}\ g^2/ml^2$
x_2	M_E	$13.410\ g$	$-1/V_{pyc}$	$5.8 \times 10^{-5} g$	$3.3 \times 10^{-11}\ g^2/ml^2$
x_3	V_{pyc}	$10.00\ ml$	$-(M_F - M_E)/V_{pyc}^2$	$0.02\ ml$	$1.21 \times 10^{-5}\ g^2/ml^2$
				$e_{x_5}^2$	$e_{s_f}^2 = 1.21 \times 10^{-5}\ g^2/ml^2$
					$e_{s_f} = 0.0035$ units g/ml

Standard error of calculated quantity, f

NOTE: The formula here must be dimensionally consistent (no ***implied*** unit **conversions— <u>include</u> them <u>explicitly</u>**)

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Example 1: What is the uncertainty (95% confidence interval) in $\rho_{blue fluid}$ as determined in the lab?

Excel **is an <u>excellent tool</u> for error propagation**

Error propagation Worksheet									
$f(x_1, x_2, x_3)$			f	ρ_{BF}	1.739	g/ml	$2e_s$		g/ml
	x_i	value		df/dx_i	$(df/dx_i)^2$	e_{xi}	e_{xi}^2	$(df/dx_i)^2 e_{xi}^2$	
x_1	M_F	30.800	g						g^2/ml^2
x_2	M_E	13.410	g						g^2/ml^2
x_3	V_{pyc}	10.000	ml						g^2/ml^2
							e_s^2		g^2/ml^2
							e_s		g/ml

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SolutionDensityBlueFluidLecture4PropagationLectureDemo.xlsx

Example 1: What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

Excel **is an** **excellent tool** **for error propagation**

Error propagation Worksheet									
$f(x_1,x_2,x_3)$			f						g/ml
	x_i	value							
x_1	M_F	30.800	g						g^2/ml^2
x_2	M_E	13.410	g						g^2/ml^2
x_3	V_{pyc}	10.000	ml						g^2/ml^2
									g^2/ml^2
									g/ml

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$f(x_1,x_2,x_3)$			f	ρ_{BF}	1.739	g/ml	$2e_s$	0.007	g/ml
	x_i	value		df/dx_i	$(df/dx_i)^2$	e_{xi}	e_{xi}^2	$(df/dx_i)^2 e_{xi}^2$	
x_1	M_F	30.800	g	0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
x_2	M_E	13.410	g	-0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
x_3	V_{pyc}	10.000	ml	-0.174	0.0302	0.02	4.0E-04	1.210E-05	g^2/ml^2
							e_s^2	1.21E-05	g^2/ml^2
							e_s	0.0035	g/ml

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x_1	M_F	30.800	g	0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
x_2	M_E	13.410	g	-0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
x_3	V_{pyc}	10.000	ml	-0.174	0.0302	0.02	4.0E-04	1.210E-05	g^2/ml^2
							e_s^2	1.21E-05	g^2/ml^2
							e_s	0.0035	g/ml

We can readily see that the error in pycnometer volume dominates the error in the calculation!

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Example 1:

What is the uncertainty (95% confidence interval) in $\rho_{bluefluid}$ as determined in the lab?

Answer:

$$\bar{\rho} \pm 2e_{s,\rho}$$

$$1.739 \pm 0.007\ g/ml$$

(from error propagation; single measurement)

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Summary: Error Analysis with Real Numbers

- To understand the accuracy of our numbers, we need to determine a ***confidence interval***.

$\bar{x} \pm 2e_s$ with 95.0% confidence

For replicate data with $n < 7$, replace "2" with $t_{0.025,n-1}$

- The **Standard error e_s** for a measured quantity is the sum *in quadrature* of:
  - e_s determined through *replicates* $e_s = s/\sqrt{n}$
  - e_s by estimate of *reading error* $e_s = e_R/\sqrt{3}$
  - e_s by estimate of *calibration error* $e_s = \text{error limits}/2$

- Standard error e_f for derived quantities (arrived at from equations), is obtained at through **error propagation,** which is a combination of *variances*.

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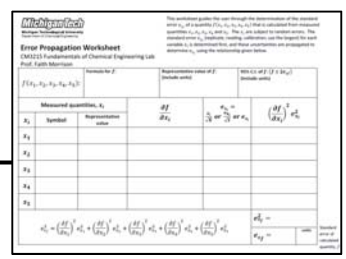
CM3215 (and U.O.) Error Analysis Expectations



- *From this point forward*, you are to include uncertainty limits (95% CI or PI intervals *as appropriate*) on your data.

- I will be working with you for the remainder of the semester to develop your ability to make your error analysis judgments.

- Please include error analysis worksheets in your report appendix (if there are many worksheets, include only selected, significant worksheets; please use your judgment)

- For error propagation, you may create tables for the appendix from your Excel calculations (recommendation: *Paste Special* as an *Enhanced Metafile* so that you can easily adjust the size of the graphic; put numbers in scientific notation).

Let's do some more work with the error calculations to see what it all means

Summary: Error Analysis with Real Numbers

- To understand the accuracy of our numbers, we need to determine a ***confidence interval***.

  $\bar{x} \pm 2e_s$ with 95.0% confidence

  For replicate data with $n < 7$, replace "2" with $t_{0.025,n-1}$

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- Standard error e_f for derived quantities (arrived at from equations), is obtained at through **error propagation,** which is a combination of *variances*.

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Example 2: Using CI/PI to Interpret Data

In Example 1, we used error propagation to calculate uncertainty a single determination of density.

In lab, we determined uncertainty from replicates of density measurements.

How does the result from the single value measurement compare to the result determined from replicates? Are they consistent?

i	ρ_{BFi}
	g/cm
1	1.7162
2	1.7162
3	1.69942
4	1.7110
5	1.7152
6	1.70616
7	1.73097
8	1.73746
9	1.727

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How does the result from the single value measurement compare to the result determined from replicates? Are they consistent?

Calculate the mean and the 95%CI of the mean using the replicates:

Replicate Worksheet

i	ρ_{BFi}				
	g/cm		**n=**	9	
1	1.7162		**mean ρ=**	1.718	g^2/ml^2
2	1.7162		**s^2=**	0.00015	g^2/ml^2
3	1.69942		**s=**	0.0121	g/cm
4	1.7110		**s/sqrt(n)=**	0.0040	g/cm
5	1.7152		**$2e_s$=**	0.008	g/cm
6	1.70616		**te_s=**	0.009	g/cm
7	1.73097				
8	1.73746				
9	1.727				

Side Question: What makes a replicate?

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Example 2: Using CI/PI to Interpret Data

In Example 1, we used error propagation to calculate uncertainty a single determination of density.

In lab, we determined uncertainty from replicates of density measurements.

How does the result from the single value measurement compare to the result determined from replicates? Are they consistent?

Results:

Mean of 9 replicates:

$$1.718 \pm 0.009\ g/ml$$

Single measurement:

$$1.739 \pm 0.007\ g/ml$$

(error propagation)

Are these two results consistent?

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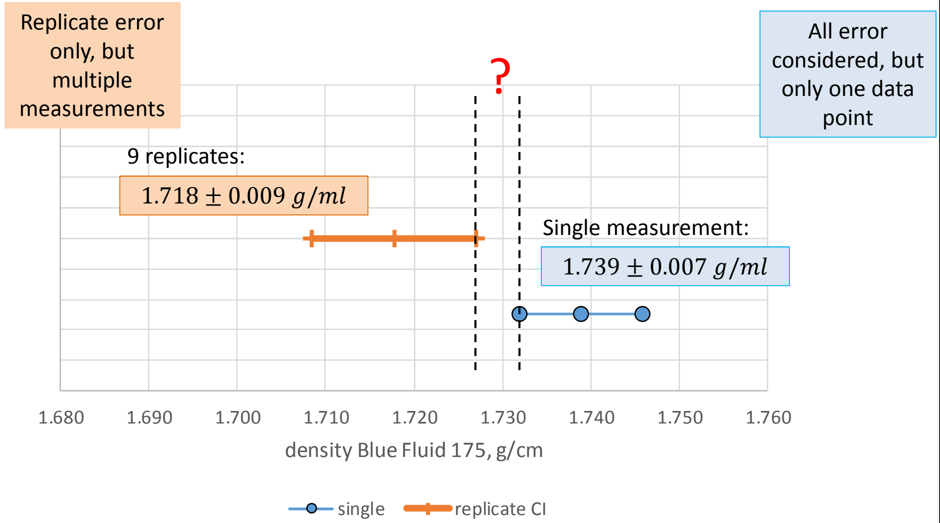
Example 2: Using CI/PI to Interpret Data



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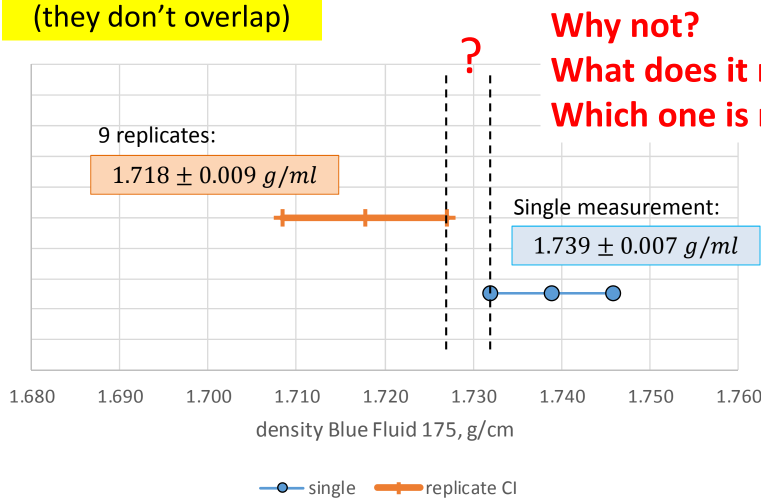
Example 2: Using CI/PI to Interpret Data

(they don't overlap)

Why not?
What does it mean?
Which one is right?



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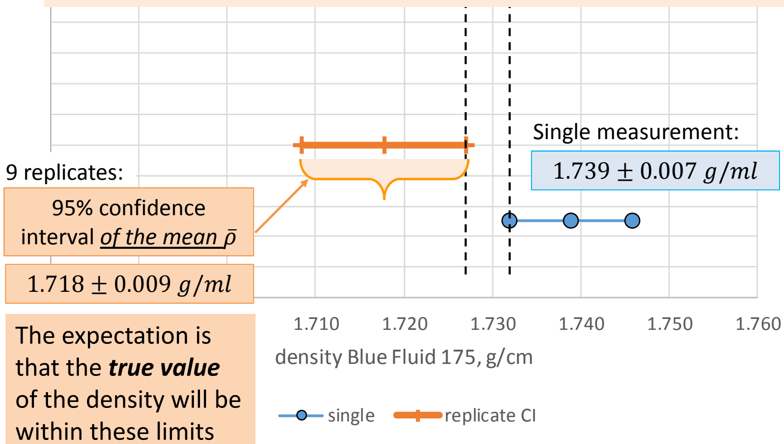
Why don't the two error intervals overlap?

When averaging replicates of ρ, we are estimating the **mean value, $\bar{\rho}$**. The 95% CI we calculate $(\pm ts/\sqrt{n})$ is the confidence interval **<u>of the mean</u>**. The error limits on the mean *<u>narrow</u>* as n increases.



The expectation is that the ***true value*** of the density will be within these limits

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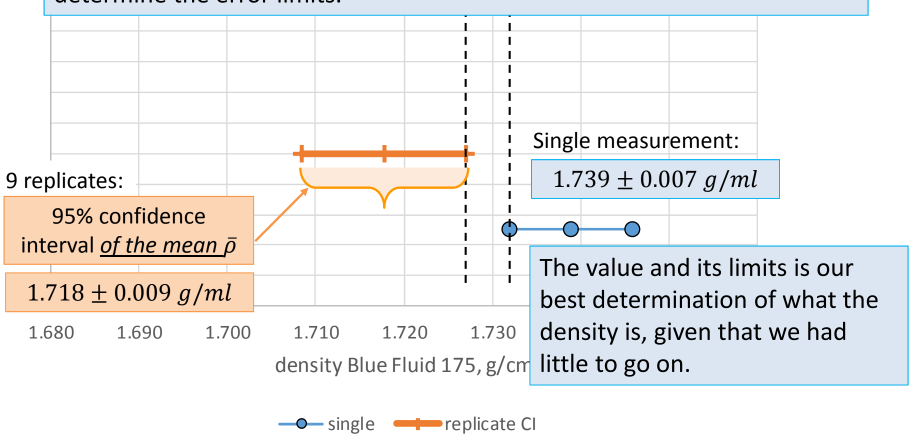
Why don't the two error intervals overlap?

The single measurement value is observation only. With so little to go on, we make what we believe are reasonable estimates of the uncertainty to determine the error limits.



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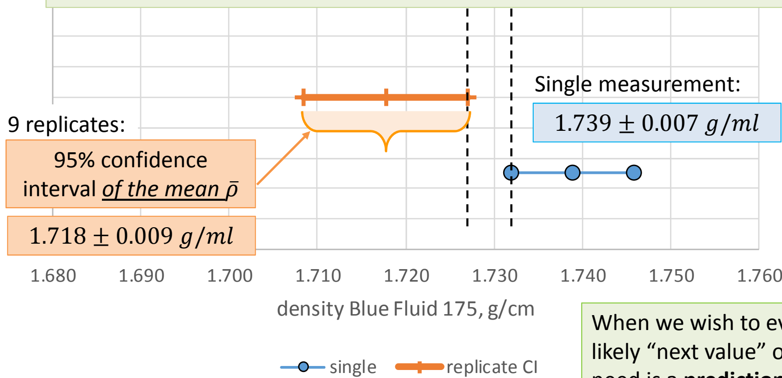
Why don't the two error intervals overlap?

Should these intervals overlap? **Yes they should**, since they are both estimates of the true value of the density. **We have a problem.**

To investigate the problem, we can first see if the *single measurement* might be an outlier (due to a blunder or mistake).

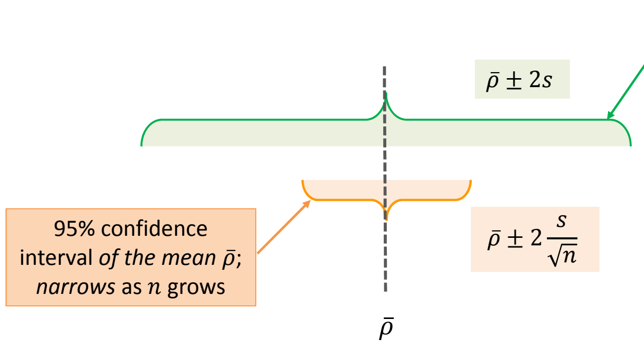


When we wish to evaluate the likely "next value" of ρ_i, what we need is a **prediction interval**.

Prediction interval of next value of x: $\pm t_{0.025,n-1}s$

$$\approx \pm 2s$$

- 95% of the time, the next value of x will be in the interval $\pm 2s$ $(\pm t_{0.025,n-1}s$ if $n < 7)$



- Encloses 95% of the measurements of ρ_i
- Does not narrow as n grows (for $n > 7$)

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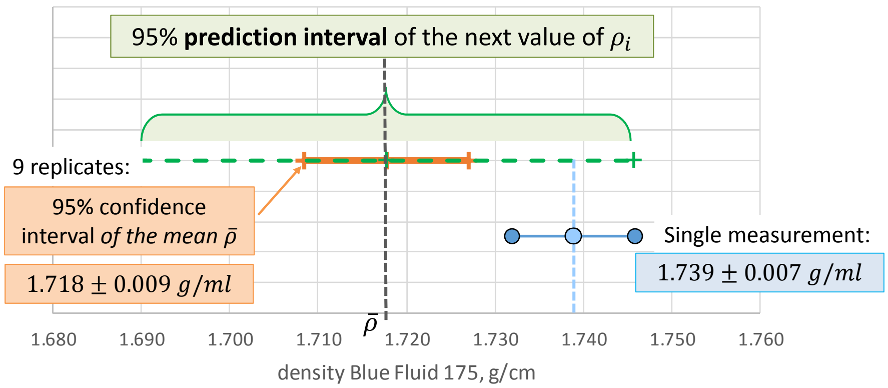
Prediction interval of next value of x: $\pm t_{0.025,n-1}s$
$\approx \pm 2s$



The single measurement ***does*** lie within the **95%PI** of the next value of ρ_i

The single value does not seem to be an outlier since it falls within expectations for a single value.

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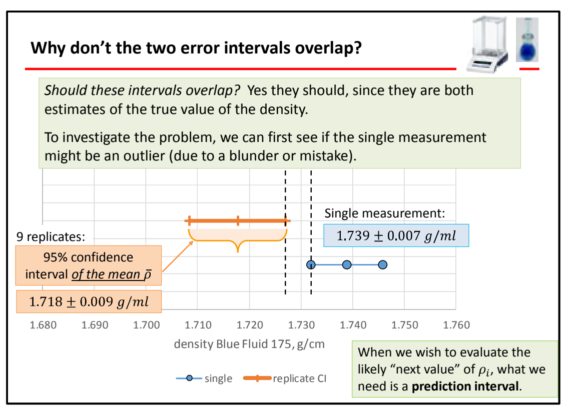
If the single measurement is not an outlier, then why don't the two intervals overlap?

They should.

We must look for another reason.



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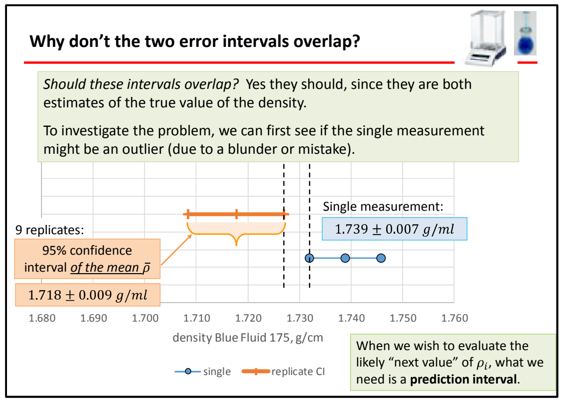

Hypothesis: The error limits determined for the single measurement are too narrow.

Example 3: Using CI/PI to Refine Error Estimates

Would making *reasonable* revisions to our error estimates in Example 2 ***improve the agreement*** between the replicate result and the single measurement result?

Single measurement:

$$1.739 \pm 0.007\ g/ml$$

9 replicates:

$$1.718 \pm 0.009\ g/ml$$

(error propagation)

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Single measurement:

$$1.739 \pm 0.007\ g/ml$$

9 replicates:

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(error propagation)

Let's plot these intervals

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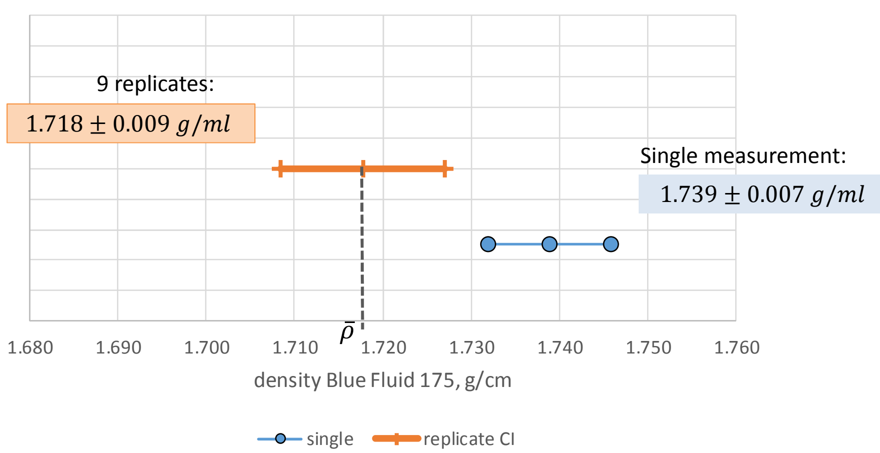
Example 3: Using CI/PI to Refine Error Estimates

Can the single-value result (with error limits) be made to agree with the *good* estimate from the mean of replicates?



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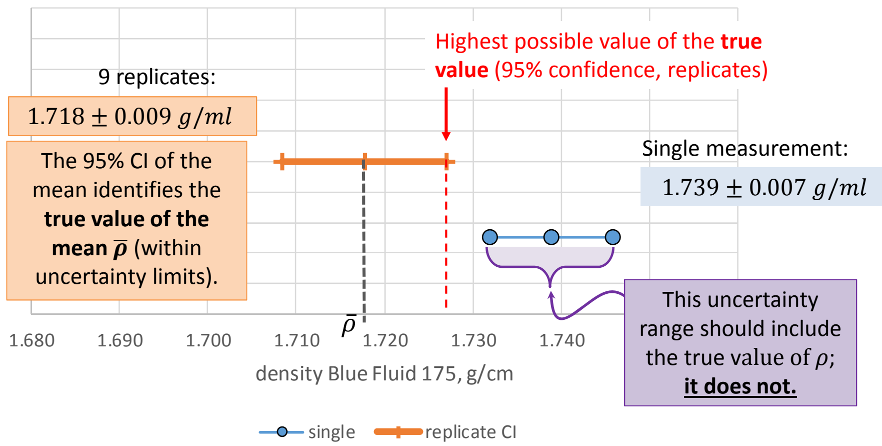

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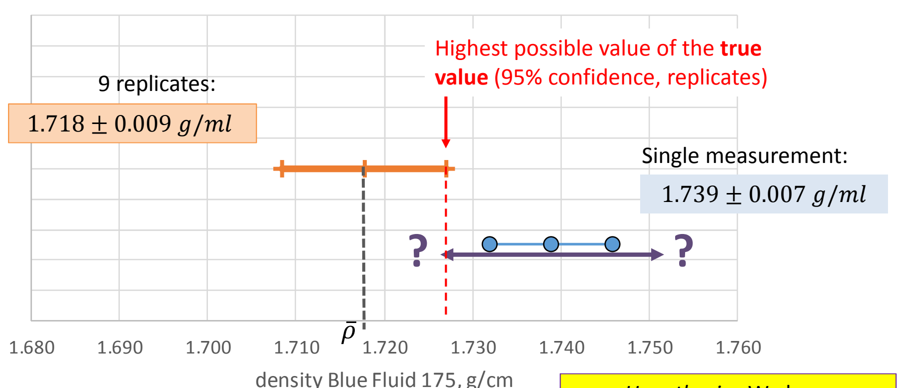

Why do they disagree?

Hypothesis: We have *underestimated* the uncertainty in the error propagation calculation.

Example 3: Using CI/PI to Refine Error Estimates

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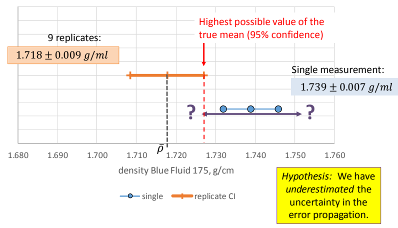

Single measurement:

$$1.739 \pm 0.007\ g/ml$$

- This uncertainty limit came from *error propagation*
- *We* chose the estimates of e_s that were used
- Perhaps we underestimated the error
- Error propagation calculations in Excel are very convenient for evaluating your e_s "guesses"

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Example 3: Using CI/PI to Refine Error Estimates

Could it be we underestimated the **reading error on mass**?

$$e_{R,old} = 10^{-4} g$$

$$e_{R,new} = 0.01g$$

$$e_{s,reading} = \frac{0.01g}{\sqrt{3}} = 5.8 \times 10^{-3}$$

					new reading error on mass:			0.01	g
Error propagation Worksheet									
f(x₁,x₂,x₃)			***f***	ρ_{BF}	**1.739**	**g/ml**	**$2e_s$**	**0.007**	**g/ml**
	x_i	**value**		**df/dx_i**	**$(df/dx_i)^2$**	**e_{xi}**	**e_{xi}^2**	**$(df/dx_i)^2 e_{xi}^2$**	
x_1	M_F	30.800	g	0.10	0.010	5.8E-03	3.3E-05	3.33E-07	g^2/ml^2
x_2	M_E	13.410	g	-0.10	0.010	5.8E-03	3.3E-05	3.33E-07	g^2/ml^2
x_3	V_{pyc}	10.000	ml	-0.174	0.0302	0.02	4.0E-04	1.210E-05	g^2/ml^2
							e_s^2	1.28E-05	g^2/ml^2
							e_s	0.0036	g/ml

Example 3: Using CI/PI to Refine Error Estimates


Could it be we underestimated the **reading error on mass**?

$e_{R,old} = 10^{-4} g$

$e_{R,new} = 0.01g$

$e_{s,reading} = \frac{0.01g}{\sqrt{3}} = 5.8 \times 10^{-3}$

new reading error on mass: 0.01 g

Error propagation Worksheet

$f(x_1,x_2,x_3)$			f	ρ_{BF}	1.739	g/ml	$2e_s$	0.007	g/ml

	x_i	value		df/dx_i	$(df/dx_i)^2$	e_{xi}	e_{xi}^2	$(df/dx_i)^2 e_{xi}^2$	
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x_2	M_E	13.410	g	-0.10	0.010	5.8E-03	3.3E-05	3.33E-07	g^2/ml^2
x_3	V_{pyc}	10.000	ml	-0.174	0.0302	0.02	4.0E-04	1.210E-05	g^2/ml^2

e_s^2	1.28E-05	g^2/ml^2
e_s	0.0036	g/ml

Error on density barely budges with this large change
Conclusion: final error on ρ is <u>not</u> sensitive to reading error on mass

Example 3: Using CI/PI to Refine Error Estimates


Could it be we underestimated the **calibration error on volume**?

$2e_{s,old} = 0.04ml$

$\pm 2e_{s,new} = \pm 0.07ml$

$e_{s,calibration} = \frac{0.07ml}{2} = 0.035ml$

~~reading error on mass: 1.00E-04 g~~
new calibration error on vol: 0.035 ml

Error propagation Worksheet

$f(x_1,x_2,x_3)$			f	ρ_{BF}	1.739	g/ml	$2e_s$	0.012	g/ml

	x_i	value		df/dx_i	$(df/dx_i)^2$	e_{xi}	e_{xi}^2	$(df/dx_i)^2 e_{xi}^2$	
x_1	M_F	30.800	g	0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
x_2	M_E	13.410	g	-0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
x_3	V_{pyc}	10.000	ml	-0.174	0.0302	0.035	1.2E-03	3.705E-05	g^2/ml^2

e_s^2	3.70E-05	g^2/ml^2
e_s	0.0061	g/ml

Example 3: Using CI/PI to Refine Error Estimates

Could it be we underestimated the **calibration error on volume**?

$2e_{s,old} = 0.04ml$

$\pm 2e_{s,new} = \pm 0.07ml$

$e_{s,calibration} = \frac{0.07ml}{2} = 0.035ml$

reading error on mass: 1.00E-04 g
new calibration error on vol: 0.035 ml

Error propagation Worksheet

$f(x_1,x_2,x_3)$			f	ρ_{BF}	1.739	g/ml	$2e_s$	0.012	g/ml
	x_i	value		df/dx_i	$(df/dx_i)^2$	e_{xi}	e_{xi}^2	$(df/dx_i)^2 e_{xi}^2$	
x_1	M_F	30.800	g	0.10	0.010	5.8E-05	3.3E-09	3.33E-11	g^2/ml^2
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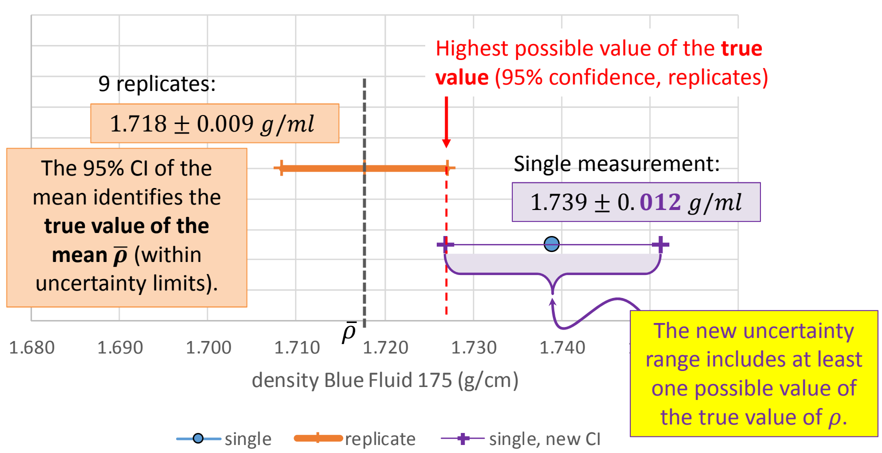
e_s^2	3.70E-05	g^2/ml^2
e_s	0.0061	g/ml

Error on density is quite sensitive to calibration error on the pycnometer volume.

Example 3: Using CI/PI to Refine Error Estimates

Hypothesis: we underestimated the **calibration error on volume**



Example 3: Using CI/PI to Refine Error Estimates

Can we *do* this? (Seems like fudging the data)

- The individual measured density values are very sensitive to pycnometer volume
- The manufacturer reports a calibration uncertainty of $\pm 0.04ml$
- We need to increase this to $\pm 0.07ml$ to get a final answer consistent with the "true" value determined from replicates
- *Hypothesis*: lab workers may over/under fill pycnometer leading to this increased uncertainty compared to the manufacturer's limits
- ***Conclusion*: good training and practice is needed in order to achieve the manufacturer's error tolerances**
- ***Conclusion*: It is preferable to have replicates rather than relying on a single measurement of a value.**

Yes, we can do this.

9 replicates: $1.718 \pm 0.009\ g/ml$

Single measurement: $1.739 \pm 0.\mathbf{012}\ g/ml$

//

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Summary: Error Analysis with Real Numbers

- To understand the accuracy of our numbers, we need to determine a ***confidence interval***.
  $\bar{x} \pm 2e_s$ with 95.0% confidence — For replicate data with $n < 7$, replace "2" with $t_{0.025,n-1}$
- The **Standard error e_s** for a measured quantity is the sum, in quadrature, of:
  e_s determined by *replicates* $e_s = s/\sqrt{n}$
  e_s by estimate of *reading error* $e_s = e_R/\sqrt{3}$
  e_s by estimate of *calibration error* $e_s =$ error limits$/2$
- Standard error e_f for derived quantities (arrived at from equations), is obtained through **error propagation,** which is a combination of *variances*.
- Replication improves the **estimation of the mean.** The answer from replicates is more reliable than single values (if no systematic errors).
- The **prediction interval of the next value of x** should encompass 95% of all measured values. 95% PI: $\bar{x} \pm 2s$ or $\bar{x} \pm t_{0.025,n-1}s$ if $n < 7$
- The weighting values $\left(\frac{\partial f}{\partial x_i}\right)^2 e_{x_i}^2$ indicate the **impact** of individual errors on the final value.
- **Estimates** for e_s (particularly those obtained through e_R) may need to be re-evaluated, if unreasonably narrow confidence intervals are identified.

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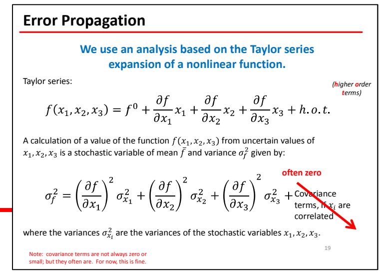
Note: We can use error propagation to justify the <u>quadrature</u> addition of independent errors.



Error Propagation

We use an analysis based on the Taylor series expansion of a nonlinear function.

Taylor series:

$$f(x_1,x_2,x_3) = f^0 + \frac{\partial f}{\partial x_1}x_1 + \frac{\partial f}{\partial x_2}x_2 + \frac{\partial f}{\partial x_3}x_3 + h.o.t.$$

(higher order terms)

A calculation of a value of the function $f(x_1,x_2,x_3)$ from uncertain values of x_1,x_2,x_3 is a stochastic variable of mean $\bar{f}$ and variance σ_f^2 given by:

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 \sigma_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 \sigma_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 \sigma_{x_3}^2 + \text{Covariance terms, if } x_i \text{ are correlated}$$

often zero

where the variances $\sigma_{x_i}^2$ are the variances of the stochastic variables x_1,x_2,x_3.

Note: covariance terms are not always zero or small; but they often are. For now, this is fine.

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Error in a Single Observation

<u>Function f</u>: An individual measurement of density, ρ_i

<u>Stochastic variables</u>:

$\delta_1 = \delta_{i,replicate}$ is a stochastic variable of variance $e_{s,replicate}^2$

$\delta_2 = \delta_{i,reading}$ is a stochastic variable of variance $e_{s,reading}^2$

$\delta_3 = \delta_{i,calibration}$ is a stochastic variable of variance $e_{s,calibration}^2$

$$f_i = f_{true} + \delta_{i,replicate} + \delta_{i,reading} + \delta_{i,calibration}$$

A constant

$$\frac{\partial f_i}{\partial \delta_{i,replicate}} = 1 \qquad \frac{\partial f_i}{\partial \delta_{i,reading}} = 1 \qquad \frac{\partial f_i}{\partial \delta_{i,calibration}} = 1$$

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Error in a Single Observation

$$f_i = f_{true} + \delta_{i,replicate} + \delta_{i,reading} + \delta_{i,calibration}$$

$$e_f^2 = \left(\frac{\partial \rho}{\partial \delta_1}\right)^2 e_s^2\Big|_{replicate} + \left(\frac{\partial \rho}{\partial \delta_2}\right)^2 e_s^2\Big|_{reading} + \left(\frac{\partial \rho}{\partial \delta_3}\right)^2 e_s^2\Big|_{calibration}$$

$$e_f^2 = e_s^2\Big|_{replicate} + e_s^2\Big|_{reading} + e_s^2\Big|_{calibration}$$

⇒ The correct way to add the three e_s's is to add them in **<u>quadrature</u>**.

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Recall from last lecture?

Summary of Errors of Temperature Indicator

Standard Errors, e_x:

- Replicate standard error is $\frac{s}{\sqrt{n}} = 0.3^oC$
- Reading standard error is $\frac{e_R}{\sqrt{3}} = 0.06^oC$
- Calibration error is $e_s = 0.55^oC$

Calibration error is the largest, followed by replicate error

The correct way to add the three e_s's is to add them in ***quadrature***.

$$e_{s,total}^2 = e_{s,replicate}^2 + e_{s,reading}^2 + e_{s,calibration}^2$$

$$e_{s,total}^2 = (0.3)^2 + (0.06)^2 + (0.55)^2$$

$$= 0.09 + 0.0036 + 0.3025 = 0.3961$$

$$e_{s,total} = 0.63^oC$$

Recall from previous lecture?

Summary of Errors of Temperature Indicator

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Calibration error is the largest, followed by replicate error

The correct way to add the three e_s's is to add them in ***quadrature***.

$$e_{s,total}^2 = e_{s,replicate}^2 + e_{s,reading}^2 + e_{s,calibration}^2$$

(This formula tells us that if one error dominates, that error will be $e_{s,total}$, which we guessed)

$$e_{s,total}^2 = (0.3)^2 + (0.06)^2 + (0.55)^2$$

$$= 0.09 + 0.0036 + 0.3025 = 0.3961$$

$$e_{s,total} = 0.63^oC$$

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Fundamentals of Chemical Engineering Laboratory

Error Analysis for Laboratory Data

1. Quick start—Replicate error
2. Reading Error
3. Calibration Error
4. Error Propagation

Professor Faith Morrison

Department of Chemical Engineering
Michigan Technological University

Final takeaway:

1. You must know the uncertainty in your numbers
2. The 3 worksheets help you assess: replicate, reading, and calibration error
3. Final worksheet helps you carry out error propagation
4. These are the tools you need to determine the uncertainty in your numbers.

Next:
Least Squares
(an application of error propagation)