

**Where are we in our discussion of error analysis?**

**Let's revisit:**

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Fundamentals of Chemical Engineering Laboratory

**Statistics Quick Start:  
Random Error and Replicates**

Professor Faith Morrison  
Department of Chemical Engineering  
Michigan Technological University

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Fundamentals of Chemical Engineering Laboratory

**Statistics Lecture 2:  
Reading Error**

Professor Faith Morrison  
Department of Chemical Engineering  
Michigan Technological University

- Quick Start—Replicates error
- Reading Error
- Calibration Error
- Error Propagation

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**Statistics Lecture 3:  
Calibration Error**

Professor Faith Morrison  
Department of Chemical Engineering  
Michigan Technological University

- Quick Start—Replicates error
- Reading Error
- Calibration Error
- Error Propagation

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## 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  $\pm 1$
- 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.**

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## Obtaining a Good Estimate of a Quantity

Replicate error  
Reading error  
Calibration error

But what do we do when we  
obtain a quantity from a  
*calculation?*

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

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

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

etc.

**Answer:**  
Propagate the error  
through the  
calculation

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## Statistics Lecture 4: Error Propagation

**Professor Faith Morrison**

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

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## 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?



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Image source:  
[//en.wikipedia.org/wiki/Relative\\_density](https://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?



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

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

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[www.coleparmer.com](http://www.coleparmer.com)

Image source:  
[//en.wikipedia.org/wiki/Relative\\_density](http://en.wikipedia.org/wiki/Relative_density)

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### Example 1:

$e_s \equiv$  Standard Error

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

Three 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

$$e_s = (\text{as determined})$$

Standard error due to Calibration Error

**For each variable, determine the three  $e_s$ , then pick the largest**  
(or average if they are close and you want to be less conservative)

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**Replicate Error Worksheet**  
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Prof. Faith Morrison

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 $Y_1, Y_2, \dots, Y_n$	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)	
$Y_1$					$n = 1$	$n/s$ (include units)
$Y_2$					$n = 2$	$\pm 12.7e_s$ ±
$Y_3$					$n = 3$	$\pm 4.30e_s$
$Y_4$					$n = 4$	$\pm 3.18e_s$
$Y_5$					$n = 5$	$\pm 2.78e_s$
$Y_6$					$n = 6$	$\pm 2.57e_s$
$Y_7$					$n \geq 7$	$\pm 2e_s$
					$\infty$	$\pm 1.96e_s$

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

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

11-Sep-14

Handy worksheet for replicate error

[www.chem.mtu.edu/~fmorriso/cm3215/ReplicateErrorWorksheet.pdf](http://www.chem.mtu.edu/~fmorriso/cm3215/ReplicateErrorWorksheet.pdf)

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**Reading Error Worksheet**  
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Prof. Faith Morrison


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  $e_r$  may subsequently be used in propagation of error calculations of derived quantities.

Reading error			
Measured Quantity: (give symbol)	(include units)		Quantity or Not Applicable
Representative value:	Issue	contribution to error	
Reading error, $e_r$ :	Resolution	How much signal does it take to cause the reading to change?	1
	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:	$e_s = e_r/\sqrt{3}$	$e_s =$	
	95% Confidence Interval on the reading: $\pm 1.96e_s$		

Handy worksheet for reading error

[www.chem.mtu.edu/~fmorriso/cm3215/ReadingErrorWorksheet.pdf](http://www.chem.mtu.edu/~fmorriso/cm3215/ReadingErrorWorksheet.pdf)

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**Calibration Error Worksheet**  
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The error  $e_x$  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  $\pm 2e_x$ . Alternatively, a value of a constant (the viscometer constant  $\alpha$ , for example) may be provided by the manufacturer with no specific uncertainty. In this case, the method of "least significant digit" is appropriate 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.

Quantity:	Symbol:	Representative value: (include units)	
			<i>Estimate of <math>e_x</math></i> (or Not Applicable)
Method 1: Manufacturer maximum error allowable	$2e_x \approx$		
Method 2: Least significant digit on provided value	Least significant digit varies by at least $\pm 1$		
Method 3: User calibration	$2e_x \approx$		
	Maximum of Methods 1 - 3	$e_x =$ $2e_x =$	95% C.I.: quantity $\pm 2e_x$  (units)

Handy worksheet for calibration error

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[www.chem.mtu.edu/~fmorriso/cm3215/CalibrationErrorWorksheet.pdf](http://www.chem.mtu.edu/~fmorriso/cm3215/CalibrationErrorWorksheet.pdf)

**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](http://www.coleparmer.com)

Image source:  
[//en.wikipedia.org/wiki/Relative\\_density](http://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?

**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

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**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	}	[Redacted Box]	(reading)
$M_{empty}$ :	= 13.410 g			
$V_{pycnometer}$	= 10.00 ml			

**Now, how to combine?**  
**Propagation of Errors**

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## Error Propagation

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We seek to combine the errors associated with the various quantities in a calculation

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

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

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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 the function  $f(x_1, x_2, x_3)$  from uncertain values of  $x_1, x_2, x_3$  is a random variable of mean  $\bar{f}$  and variance  $\sigma_f^2$ :

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

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## 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 the function  $f(x_1, x_2, x_3)$  from uncertain values of  $x_1, x_2, x_3$  is a random variable of mean  $\bar{f}$  and variance  $\sigma_f^2$ :

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

neglect

Covariance terms, if  $x_i$  are correlated

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

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## Error Propagation

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

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

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

$$\begin{matrix} e_{S_{M_{full}}} \\ e_{S_{M_{empty}}} \\ e_{S_{V_{pycnometer}}} \end{matrix}$$

We estimate these standard errors with our 3 worksheets

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## Error Propagation

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

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

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

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

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## Error Propagation

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

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

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

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

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

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## Error Propagation

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

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

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

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

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

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### Error Propagation Worksheet

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This worksheet guides the user through the determination of the standard error  $e_{sf}$  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  $e_{sf}$ , using the relationship given below.

$f(x_1, x_2, x_3, x_4, x_5)$ :			Formula for $f$ :	Representative value of $f$ : (include units)	95% C.I. of $f$ : ( $f \pm 2e_{sf}$ ) (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			
$x_1$					
$x_2$					
$x_3$					
$x_4$					
$x_5$					
$e_{sf}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2 + \left(\frac{\partial f}{\partial x_4}\right)^2 e_{x_4}^2 + \left(\frac{\partial f}{\partial x_5}\right)^2 e_{x_5}^2$					$e_{sf}^2 =$ $e_{sf} =$ units Standard error of calculated quantity, $f$

Handy worksheet for error propagation

[www.chem.mtu.edu/~fmorriso/cm3215/ErrorPropagationWorksheet.pdf](http://www.chem.mtu.edu/~fmorriso/cm3215/ErrorPropagationWorksheet.pdf)

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### Example 1:

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



Data:

$$M_F = 30.800 \text{ g}$$

$$M_E = 13.410 \text{ g}$$

$$V_{pyc} = 10.00 \text{ ml}$$

Formula:

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

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,  $f$

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

You try.

Standard error of calculated quantity,  $f$

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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) 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			
$x_2$	$M_E$	13.410 g			
$x_3$	$V_{pyc}$	10.00 ml			
$x_4$					
$x_5$					
$e_{s_f}^2 = \left(\frac{\partial f}{\partial x_1}\right)^2 e_{x_1}^2 + \left(\frac{\partial f}{\partial x_2}\right)^2 e_{x_2}^2 + \left(\frac{\partial f}{\partial x_3}\right)^2 e_{x_3}^2 + \left(\frac{\partial f}{\partial x_4}\right)^2 e_{x_4}^2 + \left(\frac{\partial f}{\partial x_5}\right)^2 e_{x_5}^2$					$e_{s_f}^2 =$ $e_{s_f} =$ units



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**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									
$f(x_1, x_2, x_3)$			$f$	$\rho_{BF}$	1.739	g/ml	$2e_s$		g/ml
	$x_i$	value		df/dx <sub>i</sub>	(df/dx <sub>i</sub> ) <sup>2</sup>	$e_{xi}$	$e_{xi}^2$	(df/dx <sub>i</sub> ) <sup>2</sup> $e_{xi}^2$	
	$x_1$	$M_F$ 30.800	g						g <sup>2</sup> /ml <sup>2</sup>
	$x_2$	$M_E$ 13.410	g						g <sup>2</sup> /ml <sup>2</sup>
	$x_3$	$V_{pvc}$ 10.000	ml						g <sup>2</sup> /ml <sup>2</sup>
							$e_s^2$		g <sup>2</sup> /ml <sup>2</sup>
							$e_s$		g/ml

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**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									
[Redacted content]									
							$e_s^2$	1.21E-05	g <sup>2</sup> /ml <sup>2</sup>
							$e_s$	0.0035	g/ml

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### Example 1:

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

**Answer from error propagation:**

$$1.739 \pm 0.007 \text{ g/ml}$$



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### Summary: Error Analysis with Real Numbers

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

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

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 largest of:
  - $e_s$  determined by replicates  $e_s = s/\sqrt{n}$  or
  - $e_s$  by estimate of reading error  $e_s = e_R/\sqrt{3}$  or
  - $e_s$  by estimate of calibration error  $e_s = \text{max error}/2$
- 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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## Example 2: Replicates revisited

In Example 1, we calculated a value of  $\rho_{BF}$  along with its uncertainty from a single determination of density using error propagation. In lab, we have replicates of density measurements. How does the result from the **single** value compare to the result determined from **replicates**?

$i$	$\rho_{BFi}$ 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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## Example 2: Replicates revisited

In Example 1, we calculated a value of  $\rho_{BF}$  along with its uncertainty from a single determination of density using error propagation. In lab, we have replicates of density measurements. How does the result from the **single** value compare to the result determined from **replicates**?

Replicate Worksheet			
$i$	$\rho_{BFi}$	$n =$	9
	g/cm	<b>mean <math>\rho =</math></b>	1.718 g/ml <sup>2</sup>
1	1.7162	$s^2 =$	0.00015 g <sup>2</sup> /ml <sup>2</sup>
2	1.7162	$s =$	0.0121 g/cm
3	1.69942	<b><math>s/\sqrt{n} =</math></b>	0.0040 g/cm
4	1.7110	<b><math>2e_s =</math></b>	0.008 g/cm
5	1.7152	<b><math>te_s =</math></b>	0.009 g/cm
6	1.70616		
7	1.73097		
8	1.73746		
9	1.727		



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## Example 2: Replicates revisited

In Example 1, we calculated a value of  $\rho_{BF}$  along with its uncertainty from a single determination of density using error propagation. In lab, we have replicates of density measurements. How does the result from the **single** value compare to the result determined from **replicates**?

### Solution:

Single measurement:

$$1.739 \pm 0.007 \text{ g/ml}$$

9 replicates:

$$1.718 \pm 0.009 \text{ g/ml}$$

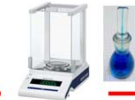


Do they agree?

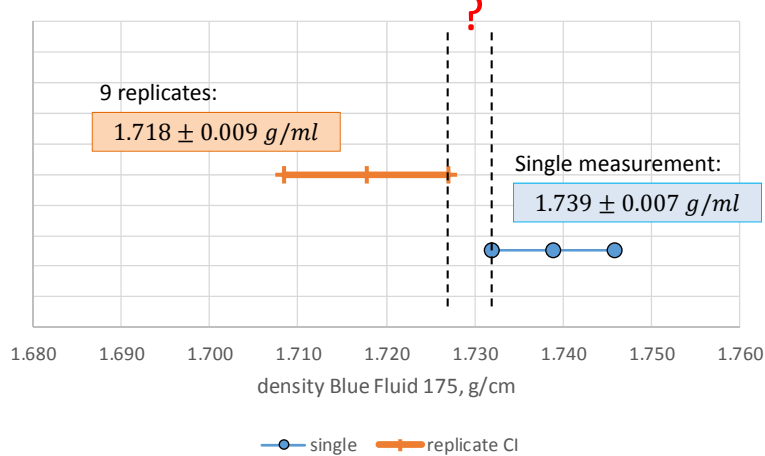
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## Example 2: Replicates revisited

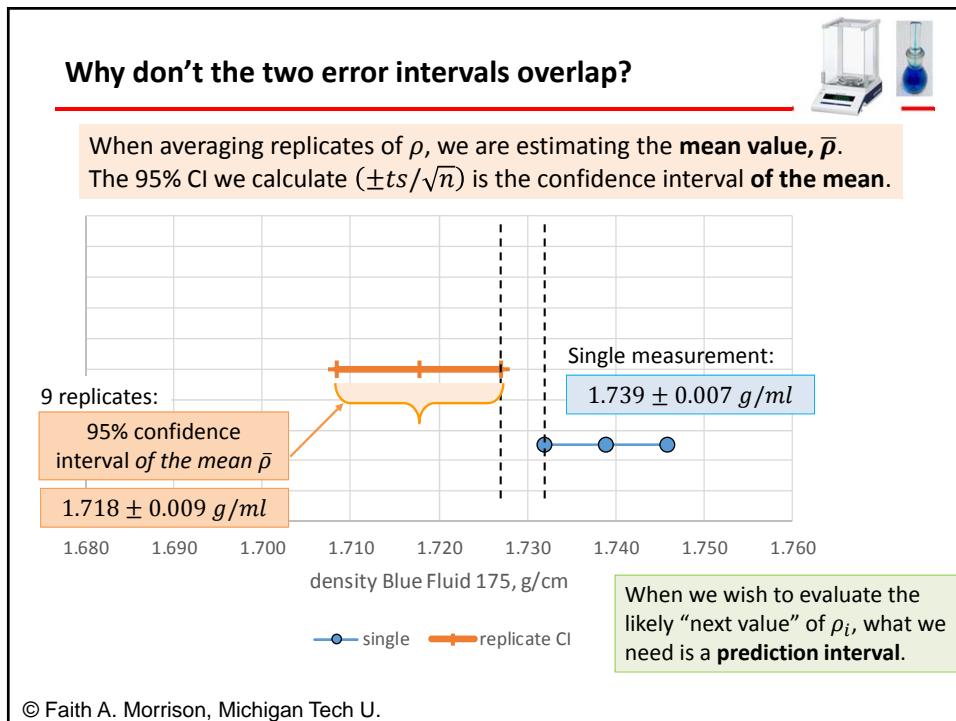
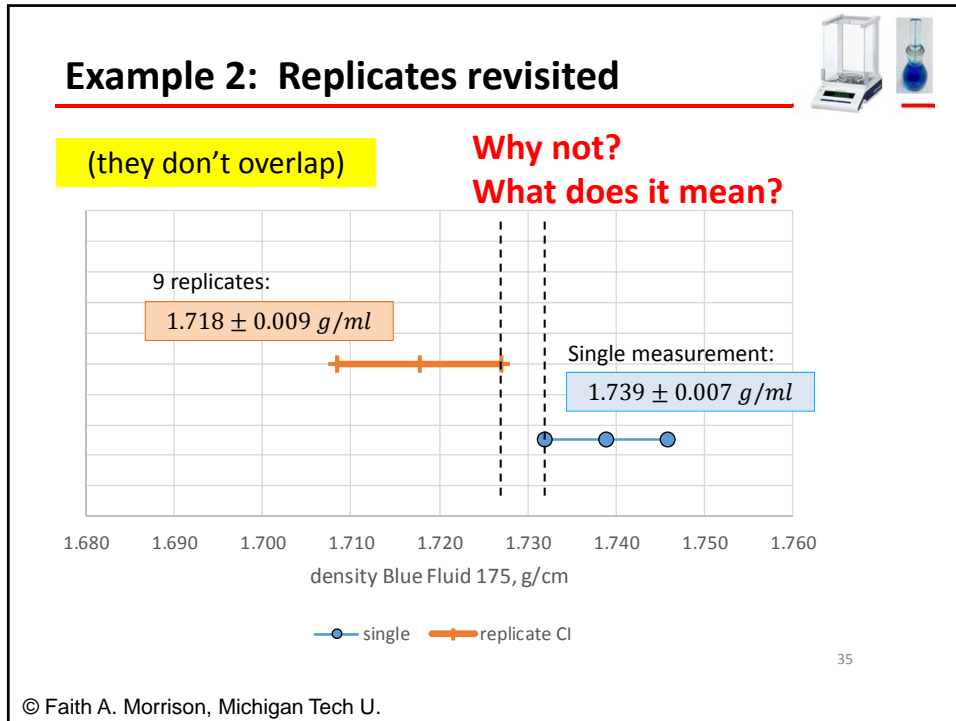


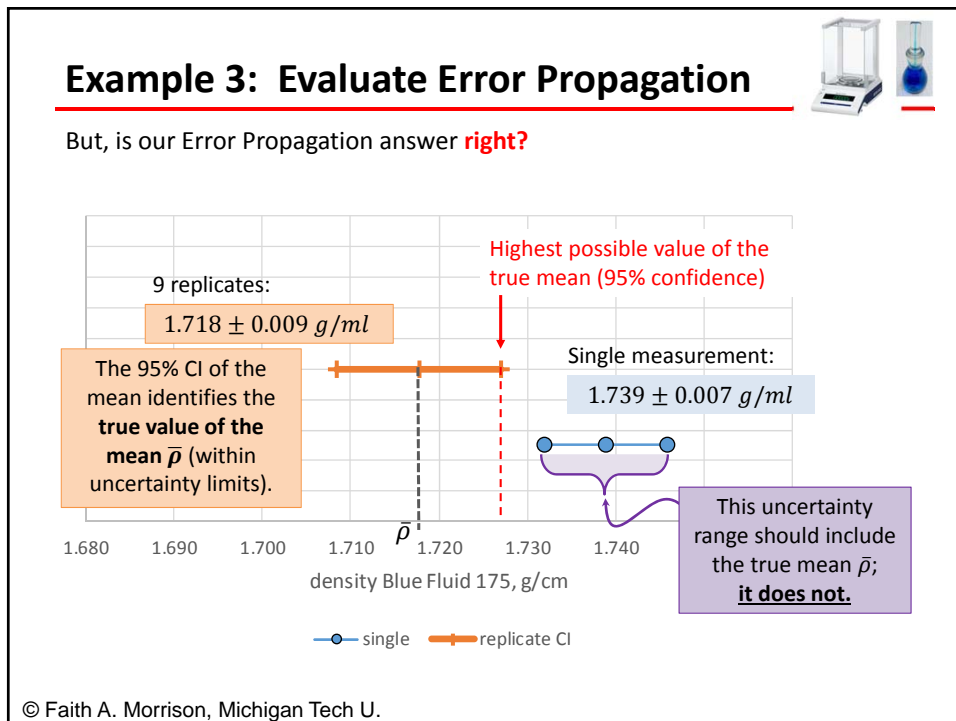
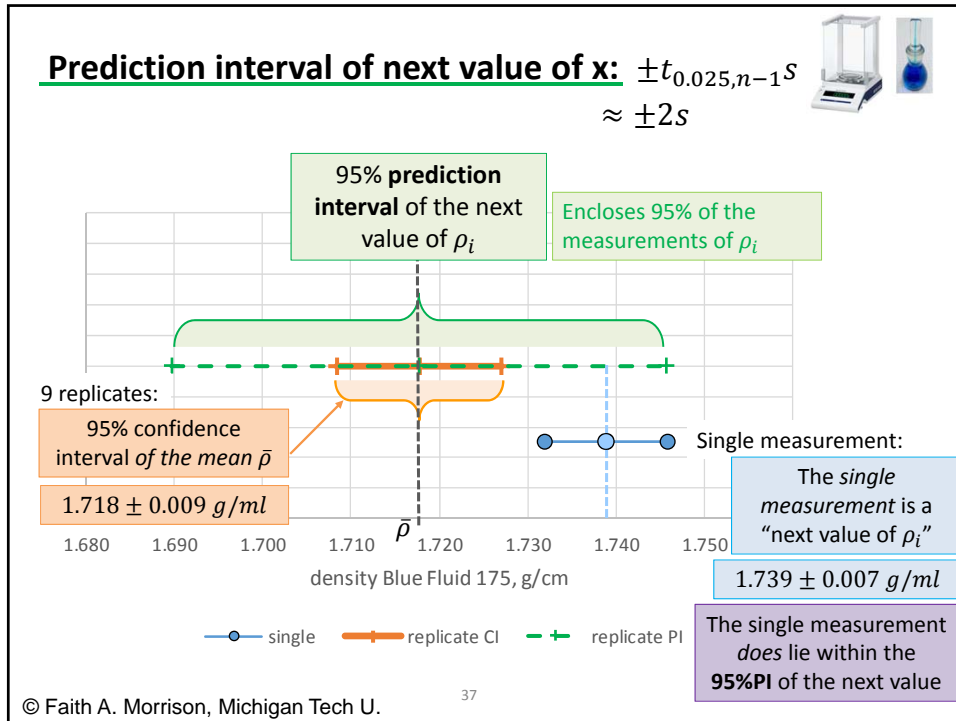
(they don't overlap)



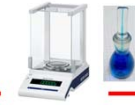
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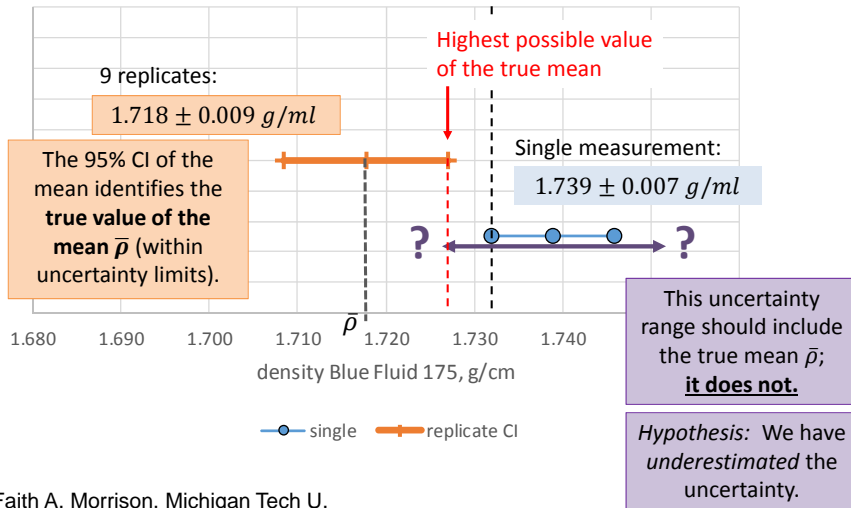




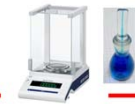
### Example 3: Evaluate Error Propagation



But, is our Error Propagation answer **right**?



### Example 2: Replicates revisited

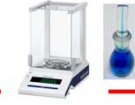


Could it be we underestimated the **reading error on mass**?

						new reading error on mass:		0.01 g		
<b>Error propagation Worksheet</b>										
$f(x_1, x_2, x_3)$		$f$	$\rho_{BF}$	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	$\text{g}^2/\text{ml}^2$
	$x_2$	$M_E$	13.410	g	-0.10	0.010	5.8E-03	3.3E-05	3.33E-07	$\text{g}^2/\text{ml}^2$
	$x_3$	$V_{DVC}$	10.000	ml	-0.174	0.0302	0.02	4.0E-04	1.210E-05	$\text{g}^2/\text{ml}^2$
							$e_s^2$	1.28E-05	$\text{g}^2/\text{ml}^2$	
							$e_s$	0.0036	g/ml	

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## Example 2: Replicates revisited

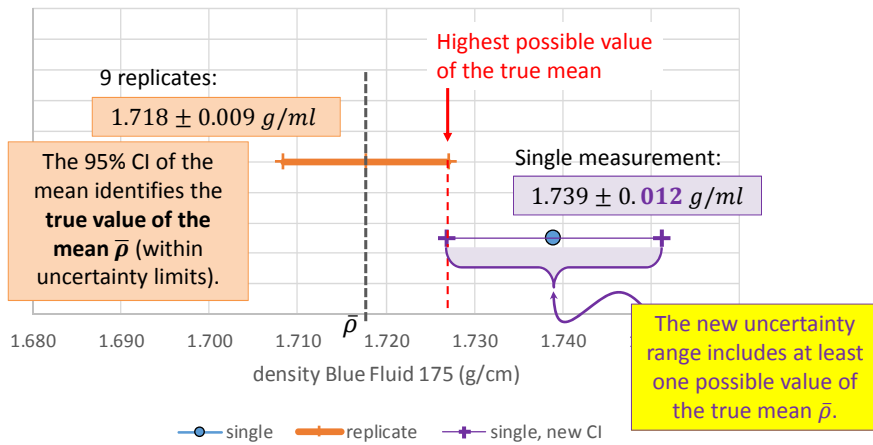
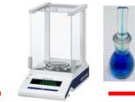


Could it be we underestimated the **calibration error on volume**?

				reading error on mass:		1.00E-04 g	
				new reading error on vol:		0.035 ml	
<b>Error propagation Worksheet</b>							
$f(x_1, x_2, x_3)$		$f$	$\rho_{BF}$	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 <sup>2</sup> /ml <sup>2</sup>
	$x_2$	$M_E$ 13.410 g	-0.10	0.010	5.8E-05	3.3E-09	3.33E-11 g <sup>2</sup> /ml <sup>2</sup>
	$x_3$	$V_{DVC}$ 10.000 ml	-0.174	0.0302	0.035	1.2E-03	3.705E-05 g <sup>2</sup> /ml <sup>2</sup>
						$e_s^2$	3.70E-05 g <sup>2</sup> /ml <sup>2</sup>
						$e_s$	0.0061 g/ml

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## Example 2: Replicates revisited



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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 largest of:  
 $e_s$  determined by replicates  $e_s = s/\sqrt{n}$  or  
 $e_s$  by estimate of reading error  $e_s = e_R/\sqrt{3}$  or  
 $e_s$  by estimate of calibration error  $e_s = \text{max error}/2$
- Standard error  $e_f$  for derived quantities (arrived at from equations), is obtained through **error propagation**, which is a combination of *variances*.
- Replication always improves the **estimation of the mean**.      The answer from replicates is more reliable than single values.
- 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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### 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.

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Next:  
Least Squares  
(an application of error  
propagation)

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Uncertainty in Least Squares  
Curve Fitting: Excel's LINEST

**Professor Faith Morrison**  
Department of Chemical Engineering  
Michigan Technological University

Reference:  
▪ [www.chem.mtu.edu/~fmorrison/cm3215/uncertaintySlopeInterceptOfLeastSquaresFit.pdf](http://www.chem.mtu.edu/~fmorrison/cm3215/uncertaintySlopeInterceptOfLeastSquaresFit.pdf)

